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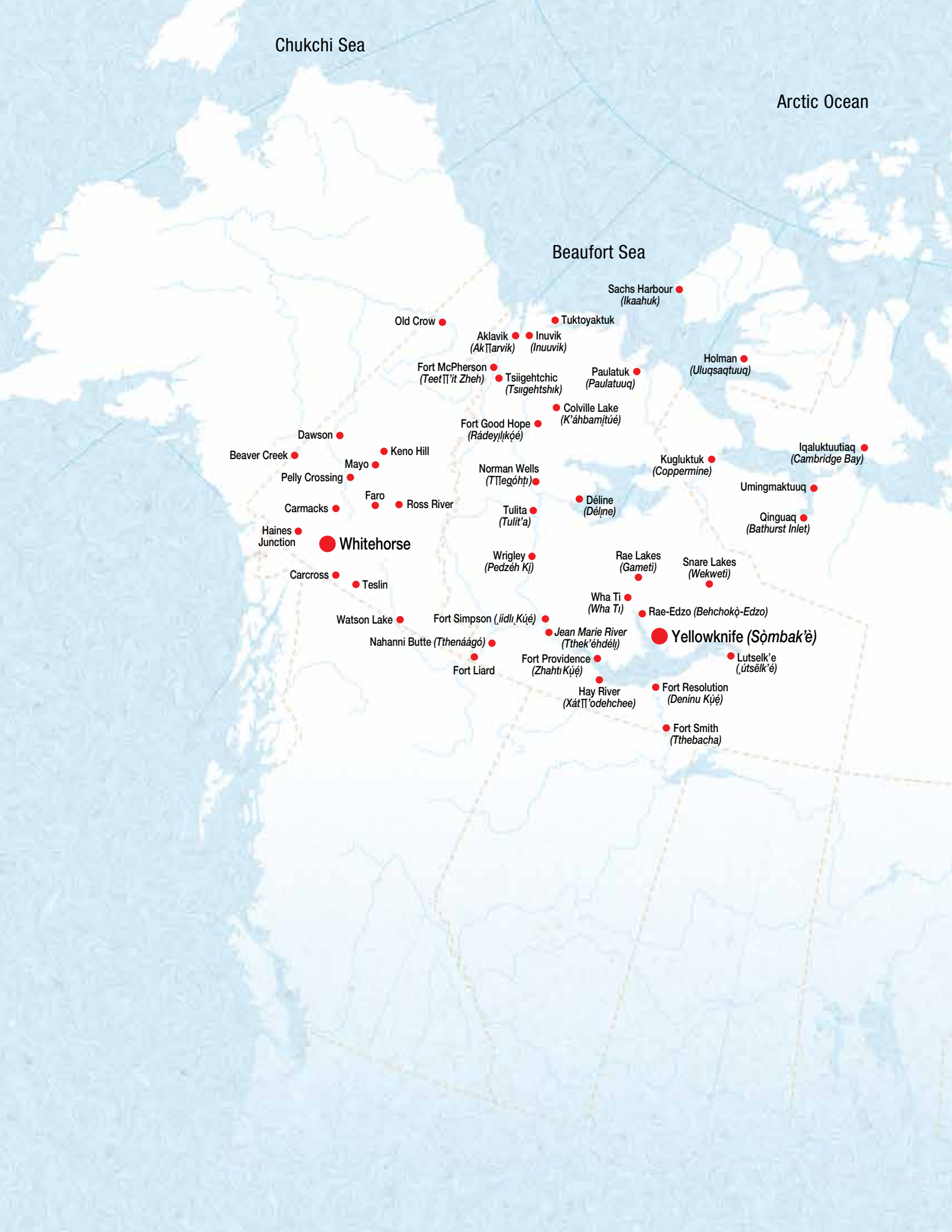
Northern Contaminants Program

Canadian Arctic Contaminants Assessment Report III 2013

Persistent Organic Pollutants in Canada's North

Canada


Chukchi Sea
Arctic Ocean
Beaufort Sea
Sachs Harbour
(Ikaahuk)
Old Crow
Tuktoyaktuk
Aklavik
(AkTarvik)
Inuvik
(Inuuvik)
Holman
(Uluqsaqtuuq)
Fort McPherson
(TeetTi'it Zheh)
Tsiigehtchic
(Tsiigehtshik)
Paulatuk
(Paulatuuq)
Colville Lake
(K'áhbamitúé)
Fort Good Hope
(Rádeyilikǫ́é)
Dawson
Beaver Creek
Keno Hill
Mayo
Pelly Crossing
Norman Wells
(TTegǫóhti)
Kugluktuk
(Coppermine)
Iqaluktuutiaq
(Cambridge Bay)
Umingmaktuuq
Faro
Carmacks
Ross River
Tulita
(Tulít'a)
Déline
(Délıne)
Qinguaq
(Bathurst Inlet)
Haines
Junction
Whitehorse
Wrigley
(Pedzéh Kí)
Rae Lakes
(Gameti)
Snare Lakes
(Wekweti)
Carcross
Teslin
Wha Ti
(Wha Ti)
Rae-Edzo (Behchokǫ̀-Edzo)
Watson Lake
Fort Simpson (ıídlıKúé)
Jean Marie River
(Tthek'éhdélı)
Yellowknife (Sǫ̀mbak'è)
Nahanni Butte (Tthenáágó)
Fort Liard
Fort Providence
(ZhahtıKǫ́ǫ́é)
Lutselk'e
(ıútsëlk'é)
Hay River
(XátTi'odehchee)
Fort Resolution
(Denínu Kǫ́ǫ́é)
Fort Smith
(Tthebacha)


Alert
Ausuittuq
(Grise Fiord)
Resolute
(Qausuittuq)
Ikpiarjuk/Tununirusiq
(Arctic Bay)
Mittimatalik
(Pond Inlet)
Kangiqtugaapik
(Clyde River)
Baffin Bay
Taloyoak
Igloolik
Qikiqtarjuaq
(Broughton Island)
Uqsuqtuuq
(Gjoa Haven)
Kugaaruk
(Pelly Bay)
Sanirajak
(Hall Beach)
Pangnirtung
Naujaat
(Repulse Bay)
Iqaluit
Kinngait
(Cape Dorset)
Qamanittuaq (Baker Lake)
Salliq
(Coral Harbour)
Kimmirut
(Lake Harbour)
Igluligaarjuk (Chesterfield Inlet)
Kangiqliniq (Rankin Inlet)
Tikirarjuaq (Whale Cove)
Ivujivik
Salluit
Kangiqsujuaq
Quaqtaq
Akulivik
Kangirsuk
Arviat
Puvirnituq
Aupaluk
Kangiqsualujjuaq
Tasiujaq
Nain
Kuujjuaq
Hudson Bay
Inukjuak
Hopedale
Makkovik
Postville
Rigolet
Umiujaq
Sanikiluaq
Happy Valley/Goose Bay
Kuujjuarapik

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Canadian Arctic Contaminants Assessment Report on Persistent Organic Pollutants

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Photo: Rodd Laing

Executive Summary

1. The Context of This Assessment

The Northern Contaminants Program (NCP) was established in 1991 in response to concerns about human exposure to elevated levels of contaminants in wildlife species that are important to the traditional diets of northern Aboriginal peoples. This is the third assessment of persistent organic pollutants (POPs) conducted by the NCP and the first that focusses solely on POPs. It is a companion document to the Mercury assessment, as well as an earlier Human Health assessment. Previous assessments in 1997 and 2003 summarized results of Phase 1 (1991-1996) and Phase II (1997-2002) of the NCP and included both heavy metals and POPs. Under Phase III of the program which began in 2003-04, environmental monitoring focussed on fewer sampling sites for both air and biological samples (Table 1). The biological sampling programs were redesigned with the goal of being able to detect a 10% annual change in contaminant concentration over a period of 10-15 years with a power of 80% and confidence level of 95%. This involved moving to annual sampling for key species (beluga, ringed seals, seabirds, arctic char) and, for beluga and ringed seals, a reduction in the number of locations sampled. Starting in 2009, analysis of high volume air sample extracts from Alert was reduced to one sample every month with the remaining sample extracts archived and temporal trends for ringed seals, arctic char and beluga were limited to two or three major sites per species.

In addition to the enhanced long-term monitoring program, the NCP continued to fund research into pathways, processes and biological effects of POPs in the Canadian Arctic. This included modeling of long range atmospheric and oceanic transport, assessment of bioaccumulation and biomagnification in arctic food-webs, studies on the potential impact of climate change on POPs in the Arctic, and a comprehensive study of biological effects in beluga whales.

This assessment covers results on POPs in the Canadian Arctic over the period of 2003 to 2011. It draws on results from Phase III of the NCP (2003-2011) as well as on any other published or unpublished studies up to early 2013. This 8 to 9 year reporting period has seen much new knowledge developed on temporal trends of POPs in air and biota, new POPs in many environmental compartments, and on ocean transport to the Arctic. The possible influence of climate warming on trends of POPs has also been investigated.

TABLE 1. Overview of NCP POPs monitoring program media 2003–2011

Media	Locations	Sampling years[1]	Frequency
Air – hi volume	Alert	1992–2010	7 day continuous
Air – passives	Up to 7 arctic/sub-arctic locations	2005–2011	Quarterly
Arctic char (searun)	Cambridge Bay, Pond Inlet , Nain	2004–2011	Annual
Arctic char (landlocked)	Lakes Resolute, Char, Amituk and Hazen	2004–2011	Annual
Burbot	Fort Good Hope, Great Slave Lake West Basin and East Arm	2004–2011	Annual
Lake trout	Lake Laberge, Kusawa Lake, Great Slave Lake West Basin and East Arm	2004–2011	Annual
Caribou	Northern Yukon and Southwestern Nunavut (Porcupine, Qamanirjuaq herds)	2006, 2008	Single study
Ringed seals	Arviat, Resolute, Sachs Harbour and other locations to 2009	2004–2011	Annual
Beluga	South Beaufort, Cumberland Sound	2004–2011	Annual
Polar bears	West Hudson Bay and other locations	2004–2011	Annual
Seabirds (thickbilled murre, northern fulmar)	Prince Leopold Island, Coats Island	2004–2011	Annual

[1]All programs include data from earlier years based on existing data or reanalysis of archived samples

2. NCP Science to Policy Actions

The period of scientific developments covered by this assessment was also highly significant for global regulatory action on POPs. Most notably, the Stockholm Convention on POPs entered into force in 2004 introducing global regulations aimed at eliminating, or severely curtailing, emissions of the so-called "dirty dozen" POPs. The development of the Stockholm Convention is regarded as a major achievement for the NCP which, along with Arctic Council's Arctic Monitoring and Assessment Programme (AMAP), provided much of the foundational science upon which the Convention is based. This assessment documents declining levels of many of the dirty dozen POPs, also referred to as legacy POPs, and also presents data on many of the so-called new POPs, 11 of which have been added to the Stockholm Convention since 2004. Data and information from the NCP contributed to the addition of these new POPs and will continue to play a critical role in the assessment of future new POPs. The NCP will also be providing updated information from this assessment to the 2015 second report of the Global Monitoring Plan established under Article 16 of the Stockholm Convention. The ongoing active participation of the NCP on national and international initiatives related to the assessment and regulation of POPs will ensure that NCP science continues to have a significant influence on policies to protect ecosystem and human health in Canada's North. The following scientific recommendations have been developed based on NCP's continuing role to provide scientific input to domestic and international regulatory initiatives, and to better inform policy development at national and international levels.

Recommendation:

- There is a need for continued monitoring of POPs in the Arctic in order to ensure that the Stockholm Convention is effective at reducing levels of these pollutants in the environment. There is also a need for ongoing surveillance of emerging chemical contaminants, whose detection in the Arctic environment provides strong evidence for having them added to the Stockholm Convention as new POPs.
- In order to improve the regulation of POPs, domestic and international regulatory agencies require a better understanding of how POPs behave in the environment and the effects that they have on ecosystems and human health. As recommended by this assessment and echoed by international organizations such as UNEP and AMAP, a better understanding of how climate change will influence POPs is also needed. Predicting the impacts climate change will have on POPs will be critical to future development of POPs regulations and evaluating the effectiveness of these regulations.

3. Information on the Chemicals of Interest Has Expanded

The list of individual compounds analysed was expanded in Phase III particularly for perfluorinated and polyfluorinated alkyl substances (PFASs), brominated flame retardants (BFRs) and current use pesticides (CUPs). About 35 chemicals or chemical groups that were not previously reported, or for which only very limited measurements were available in the previous assessment, have been detected particularly in arctic air, snow and biota (Table 2). See the Glossary for more details on the chemical names and abbreviations.

Among the chlorinated organics, PCNs are now more widely measured (air, seals, beluga, seabirds). Only limited new data were available for chlorinated paraffins over the period 2003-2011 due to analytical difficulties for the labs involved with measurement. Both the PCNs and short chain chlorinated paraffins SCCPs) are currently being evaluated for inclusion in the Stockholm Convention.

New groups of chemicals measured in the past 10 years included CUPs such as dacthal, PCNB, trifluralin and chlorthalonil which became routinely reported for air and seawater. Limited measurements of CUPs were also made in marine and terrestrial food webs which indicated that these CUPs do not biomagnify. About 20 brominated and chlorinated flame retardant chemicals also were included in analytical suites. Many were also being assessed under Canada's Chemicals Management Plan. For HBCDD, the most widely detected non-PBDE flame retardant, the data for HBCDD in Canadian arctic biota formed an important part of the risk profile adopted by the Stockholm Convention in 2010. However most of the other non-PBDE BFRs have been below detection limits in air and biological samples.

The discovery of oly- and perfluorinated alkyl substances (PFASs) in arctic wildlife, and subsequently in all environmental compartments, is perhaps the most surprising result of the past 10 years of arctic contaminants monitoring. Unlike chlorinated and brominated POPs, these chemicals are relatively water soluble and "oleophobic",

TABLE 2. Major groups of POPs and other persistent organics in environmental compartments of the Canadian Arctic determined under the NCP core monitoring and research programs

	NCP I (1991-1996)	NCP II (1997-2002)	NCP III (2003-2011)
PCBs[1]	Air, snow, sediment, seawater, biota	Air, seawater, sediment, biota	Air, snow, seawater, biota
OC pesticides[2]	Air, snow, sediment, seawater, biota	Air, seawater, sediment, biota	Air, snow, biota
Chlorobenzenes	Air, snow, sediment, seawater, biota	Air, seawater, sediment, biota	Air, snow, biota
Chlorinated dioxins/furans	Biota	Air, sediment, biota	Biota
Chlorinated naphthalenes (PCNs)		Air, biota	Air, biota
Chlorinated paraffins		Air, sediment, biota	Biota
Endosulfan		Air, seawater, biota	Air, seawater, biota
Polybrominated diphenyl ethers (PBDEs)		Sediment, biota	Air, snow, seawater, sediment, biota
Hexabromocyclododecane (HBCDD)			Air, snow, seawater, biota
Other Brominated and chlorinated flame retardants			Air, snow, seawater, biota
Penta and hexabromobiphenyls			Air, biota
Current use pesticides[3]			Air, snow, seawater, lake water, biota
Perfluorooctane sulfonate (PFOS) and other perfluoro-alkyl acids and alcohols			Air, snow, seawater, lake water, sediment, biota
Siloxanes			Air

[1]various congeners depending on the study; [2]DDTs, hexachlorocyclohexanes (HCHs), chlordanes, toxaphene; [3]Current use pesticides including dacthal, chlorothalonil, chlorpyrifos, pentachloronitrobenzene (PCNB), trifluralin.

accumulating in protein rich tissues such as liver and blood. The precursors of PFOS and other PFASs are highly volatile and best measured in the atmosphere. However they can be degraded in the atmosphere to persistent and bioaccumulative substances. The presence of high levels of PFOS and long chain perfluorocarboxylates (PFCAs) in arctic marine mammals and polar bears also illustrated the need to examine a broader array of chemicals for their ability to be transported to the Arctic, to be transformed to persistent substances, and to accumulate in arctic food webs.

The use of passive air samplers began under Phase III and results for Arctic locations from this program, which was part of the Global Atmospheric Passive Sampling (GAPS) network were comparable with the active high volume sampling at Alert. Passive air samplers are advantageous because of their low cost, simple construction and electricity-free operation. Modification of the absorbent in the samplers enabled sampling of volatile precursors of PFOS and PFCAs as well as volatile methyl siloxanes in Arctic air and comparisons with rural and urban areas around the globe. However, low air concentrations in the Arctic often result in detectability issues. A newly developed flow-through passive sampler, which has shown comparable results at a much lower cost and maintenance than high-volume air sampling at Alert may resolve this issue.

The importance of particle transport of non-volatile contaminants such as the widely used flame retardant decaBDE has been demonstrated by the detection of elevated concentrations in the Devon Island ice cap. This transport pathway was previously recognized mainly for inorganic chemicals such as lead or sulfate. Other “new” flame retardant chemicals in air samples taken at Alert are also mainly on particles. BFRs such as bis(tribromophenoxy) ethane, ethyl-hexyl-tetrabromobenzoate and bis(ethylhexyl) tetrabromophthalte were generally detected with concentrations similar to those of the dominant PBDE congeners.

Several independent studies that have screened chemicals in commerce have demonstrated there are hundreds of substances with properties similar to those of known persistent organic chemicals detected in the Arctic. These may be future candidates for monitoring in Arctic air and wildlife. To model the transport of these candidate chemicals to the Arctic requires information on quantities of chemicals used and emitted in source regions. This information is generally not available except for CUPs. However, modeling of long range atmospheric transport of POPs has advanced to the point that it is possible to use a global model to suggest a cap on the annual emissions in various parts of the world, depending on the efficiency of transport to a vulnerable area.

The detection of perfluorinated alkyl acids such as PFOS and PFOA in arctic seawater, along with global modeling, has demonstrated the importance of ocean transport of contaminants. The slow movement and large mass of seawater also underlines the very long term nature of the exposure of arctic marine food chains to contaminants. The discovery of the PFASs in seawater has led to a tremendous expansion of modelling of long range ocean transport (LROT) transport of PFASs and other POPs to the Arctic. Environmental measurements of two major PFASs, PFOS and PFOA are in reasonable agreement with currently available data for ocean waters suggesting that available emission estimates for these two compounds are plausible. Modelling results suggest that redistribution of these contaminants from lower latitudes to the Arctic Ocean is ongoing and the total mass (and average concentration) of PFOA and PFOS in the marine environment is expected to increase for the next 10 to 20 years. A major conclusion from LROT modelling is that exposure of marine food webs to more water soluble POPs in the eastern Arctic waters, may be substantially different than exposure elsewhere e.g. in the western Canadian arctic waters. This pattern of distribution is distinct from LRAT, which tends to result in more uniform deposition fluxes and therefore of concentrations/exposure in the water column. This is borne out by observations of different concentrations and rates of change of POPs in beluga and ringed seals from the southern Beaufort Sea compared to Hudson Bay and Cumberland Sound regions.

Recommendations:

- Much further work is needed to assess whether climate change, particularly warming trends, is affecting POPs transport to the Arctic.
- Urgent need for more research on other particle bound organic chemicals that may be entering the arctic environment.
- More data are required on the quantities of chemicals used and emitted in source regions.
- Monitoring programs need to consider including a broader range of chemicals, including both parents and transformation products, which may have POP-like properties to assess their potential for long-range transport as well as to assess changes by developing time trends in different media. Chemicals with potential for arctic contamination can first be identified using fate and transport models.
- More focus is needed on new candidate chemicals on current Stockholm Convention and UNECE LRTAP Convention lists (PCNs, pentachlorophenol, hexachlorobutadiene) as well as on SCCPs, chlordecone and hexabromobiphenyl in order to fully assess their importance as contaminants in the biological environment.

4. Knowledge of Time Trends of POPs Has Greatly Improved

Temporal trends of POPs listed in the Stockholm Convention and on other persistent organic chemicals are summarized in Table 3 by colour-coding (Green for declines; red for increases). Results for air monitoring indicate that many legacy POPs, including organochlorine (OC) pesticides and PCBs, are declining. Results for air sampled at Alert, on Northern Ellesmere Island, indicate that the rates of decline for the legacy POPs were generally more rapid in the period 1993 to 2001 compared to 2002 to 2009 (the most recent year reported). While overall trends (1993-2009) for PCBs show a decline, the rates have slowed and some more highly chlorinated congeners have increased slightly in recent years. These increases may be associated with the increase in boreal forest fires that release previously deposited organic chemicals, such as PCBs. Changes associated with sea-ice cover and the cryosphere in general could also be a factor. Chlorinated pesticides such as hexachlorocyclohexanes (HCHs, particularly γ-HCH or lindane), DDT- and chlordane-related compounds (CHL) show more consistent declines over the period 1993 to 2009. Lindane was de-registered in Canada for use on canola seeds in July 2001 and a ban was introduced in 2004; air concentrations declined steadily as of 2001. Another widely used pesticide, endosulfan, showed steady concentrations in the period 1993 to 2001 but declining concentrations from 2006 to 2009 possibly reflecting reduced use in Canada, the USA, and Europe as this insecticide came under greater regulatory scrutiny.

Despite recent measurements of PFASs, time-series data for other POPs in seawater remain a major knowledge gap for Arctic contaminants. This information is crucial for understanding the fate and trends of contaminants and would be particularly useful for less bioaccumulative, more water soluble chemicals, such as current use pesticides. There is a need to clarify the relative importance of atmospheric and oceanic inputs as well as the relative importance of direct and precursor emissions to different remote ecosystems. Given the challenges for obtaining POPs

data by large volume water sampling due to ship board contamination and infrequent cruises, consideration needs to be given to deploying passive samplers.

The statistical power of the temporal trend datasets for POPs in fish, seabirds and marine mammals has improved since the publication of CACAR II in 2003 and some datasets are capable of detecting a 5% change in concentration at a power of 80%. The main reason for the increased power is the introduction of annual sampling of key monitoring species beginning in 2004 which has increased the number of sampling years.

The declining trend in concentrations in biota is most apparent for OC pesticides and less evident for PCBs and chlorobenzenes (ΣCBz) (Table 3). In marine species, percent annual declines of ΣDDT ranged from 2.5%/year in thick-billed murre eggs (Lancaster Sound) to 11%/year in polar bear fat (western Hudson Bay, WHB). Declines of chlordane-related compounds (ΣCHL) ranged from 1.2%/year in murre eggs to 7.4%/year in blubber of ringed seals in Hudson Bay, while polar bears (WHB) showed no decline. Total HCHs (ΣHCH) declined in seals, beluga and polar bears due to rapid decline of the major isomer α-HCH (e.g. 12%/year in bears). However, β-HCH, the more bioaccumulative isomer, increased in the same species. This increase in β-HCH in seals varied regionally, with large increases in South Beaufort Sea seals (16% at Ulukhaktok) and a decline in Hudson Bay (2.5%/year). The case of β-HCH highlights the importance of ocean water moving through the Arctic archipelago from the Pacific Ocean via the Bering Sea and possibly Russian freshwater inputs. No other POPs shows this trend although declines of PCBs, ΣDDT, ΣCHL were lower or non-existent in beluga, ringed seals and polar bears in the South Beaufort compared to Hudson Bay and East Baffin regions.

Declines of legacy POPs have generally been more rapid in freshwater fish than in marine animals. For example, PCBs in landlocked arctic char declined by 6.4% and 7.6%/year in Amituk Lake and Lake Hazen, respectively, versus 3.8% and 4.0%/year in thick-billed murres and northern fulmars, respectively. Declines of ≥ 5%/year were also seen for ΣHCH, ΣCHL, ΣDDT and toxaphene in lake trout from Lakes Laberge, Kusawa Lake and western basin of Great Slave Lake as well as in landlocked char in Lake Hazen, Char Lake and Amituk Lake. Declines for these OC pesticides were generally <5%/year in seabird eggs and marine mammals. A notable exception was the increase in concentrations of PCBs, ΣCHL, ΣDDTs, and toxaphene were over the period 2001 to 2009 in burbot liver sampled at Fort Good Hope on the Mackenzie River. However, as of 2010 concentrations of all four POPs had returned to levels found in the 1990s and early 2000s. PCBs and ΣCBz also increased in burbot and lake trout in Great Slave Lake in the period 2001–2005. These increases were not seen in lake trout in the Yukon (Lake Laberge and Kusawa Lake) or in landlocked char. Annual sampling made it possible to observe these changes. These temporary increases suggests some process that is influencing the availability of POPs in the Mackenzie basin. Climate warming has been suggested, however a general warming trend would not explain the increase followed by a decrease in concentrations. Nevertheless, shifts in the burbot and lake trout diet and feeding areas, which could also be induced by climate change, might change contaminant availability. Other possibilities include mobilization of legacy sources due to warming, e.g., increased erosion of river sediments.

New POPs such as PBDEs and PFOS generally increased in seals, seabirds, beluga, and polar bear samples from the 1990s until the early 2000s and are now declining. Retrospective analysis of collections from specimen banks enabled measurements of the PBDEs, PFASs and other contaminants in samples from the 1970s, '80s and '90s, and annual sampling as of early 2000s enabled relatively rapid declines to be observed. For example, ΣPBDEs achieved maximum concentrations in northern fulmar and thick-billed murre eggs in 2005 and 2006, respectively and declined to levels similar to those in the early 1990s within 3 years. Polar bears, ringed seals and beluga appear to have achieved maximum ΣPBDEs in the period 2000-2004 in most locations. Similarly PFOS concentrations reached maxima in ringed seal livers in 1999-2003 in Hudson Bay, Lancaster Sound and East Baffin samples although in the southern Beaufort Sea animals concentrations continued to increase slowly (3.6%/year) to 2011.

A decline in PBDEs was also observed in air samples at Alert. PFOS precursors, MeFOSE and EtFOSE also declined while fluorotelomer alcohols (FTOHs) with 8 and 10-fluorinated carbon chains, increased over the period 2006-2010. The declines in PBDEs and PFOS in air and biota appear to be related to bans and voluntary phase outs of these substances in North America and Europe over the period 2001-2004. On the other hand some replacement chemicals such as HBCDD appear to be increasing. HBCDD

TABLE 3. Overview of time trends of selected POPs and persistent organics in Canadian arctic air and biota . Estimated for all results from early 1990s to 2011

	Air	Burbot[1]		Lake trout[2]			Landlocked char[3]		Sea-birds[4]	seals[5]			Beluga[6]		Polar bears[7]
		FGH	GSL	KW	LL	GSL	H	A	PLI	SBS	LS	HB	SBS	CS	HB
PCBs															
ΣCBz															
ΣHCH															
ΣCHL															
ΣDDT															
toxaphene															
endosulfan															
SCCPs															
PCNs															
PCDD/Fs															
ΣPBDEs															
HBCDD															
PFOS and precursors															
PFCAs and precursors															

	Limited or no results to assess trends
	No statistically significant change (typically < 3%/yr)
	Significant declining trend (typically > -5%/yr)
	Significant increasing trend (typically > +5%/yr)
	Significant increase in the early 2000s, currently stable or declining

[1]FGH = Fort Good Hope, GSL = Great Slave Lake - East Arm and West Basin

[2]LL & KW = Lake Laberge and Kusawa; GSL = Great Slave Lake - East Arm and West Basin

[3]H = Lake Hazen. A= Amituk Lake

[4]PLI = Prince Leopold Island, Lancaster Sound

[5]SBS = Southern Beaufort Sea (Ulukhaktok, Sachs Harbour), LS = Lancaster Sound (Resolute, Arctic Bay and Grise Fiord), HB = Hudson Bay (Arviat and Inukjuaq)

[6]SBS = Southern Beaufort Sea (Hendrickson Is); CS= Cumberland Sound (Pangnirtung)

[7]HB = Hudson Bay – for all compounds except PFOS and PFCAs where results for N. Baffin Island and Baffin Bay were used

was undetectable in biological samples from the 1990s and early 2000s but increased well above detection limits during 2005-2011 for burbot, lake trout, landlocked arctic char, and ringed seals. Maximum HBCDD was observed somewhat earlier (2003) in polar bears in WHB and beluga from southern Beaufort Sea. Data are too limited and levels too close to detection limits to assess whether other BFRs are increasing in air or biota.

Recommendations:

- Continued annual sampling is essential for detecting temporal trends of chemicals in commerce in biota. Annual sampling has been instrumental in demonstrating the rise and fall of new POPs, improving the statistical power of trends of legacy POPs, as well as in allowing investigations of the effect of climate change.
- There are limited measurements and a lack of time trends of atmospheric POPs in the western and eastern Canadian Arctic. This data gap needs to be addressed either by use of hi-vol samplers or passive air samplers or some combination. Air monitoring seems particularly critical for the western Arctic given the known rise of organic chemical production and uses in Asia in the past decade.
- Time-series data for POPs and new contaminants in seawater are needed for understanding the fate and trends of contaminants and would be particularly useful for the less bioaccumulative chemicals such as current use pesticides.

- While annual sample collection has boosted the statistical power of the biological program and therefore must be continued, consideration should be given to de-emphasizing annual measurements of some legacy POPs, where statistical analysis shows that the datasets meet monitoring goals, and placing more emphasis on new candidate or emerging chemicals which may have limited datasets.
- It must be recognized that a major strength of the temporal trend programs conducted under the NCP is the availability of archived samples from specimen banks. These must be maintained to continue to have a strong program for POPs monitoring.

5. Local Sources May Be Important for New POPs

While the focus of this assessment is mainly on POPs entering the Canadian arctic via LRAT and LROT local sources of new POPs, as well as trends of legacy contaminants at contaminated sites, continued to be of interest. Measurements during the period 2003-2011 showed that PBDEs, PFOS and SCCPs were sources of local contamination in or near communities in the Canadian arctic. For example, a study of dumpsites in Iqaluit, Cambridge Bay and Yellowknife showed significantly higher ΣPBDE concentrations compared to corresponding background sites in these locations suggesting that PBDEs leach from the landfill. Short-chain and medium-chain chlorinated paraffins (MCCPs) levels were shown to be higher in sediments, water and fish samples collected in and around Iqaluit compared to a remote reference site. PFOS and related chemicals used in aqueous film forming foams (used to suppress fuel fires) were elevated in water and landlocked char from Merretta and Resolute Lakes, which are downstream of the Resolute Bay airport.

Monitoring in the marine and terrestrial environment at Saglek Bay (Nunatsiavut/Labrador) has shown that PCB concentrations in the surrounding environment (sediments, plants, deer mice, sculpin, and black guillemots) have decreased since the source of PCBs has been removed, and companion studies have shown that the decline in the PCB concentrations are associated with a decline in biological effects

The continued study of PCBs at Saglek Bay has improved the knowledge of the fate of sediment associated contaminants in nearshore Arctic marine environments and particularly on their transport to offshore depositional areas.

Recommendations:

- Better knowledge of local contamination sources is needed for the interpretation of spatial and temporal trends particularly of new POPs which are in consumer products and therefore found in homes and dumpsites in all arctic communities.

6. Knowledge of Factors Influencing Levels and Trends of POPs Has Improved

Over the period 2003-2011, significant progress was made in bioaccumulation modelling of POPs in both terrestrial and marine food webs. These modelling studies provided insights into understanding of pathways and processes influencing the accumulation of POPs in wildlife and humans and also the properties of chemicals that would likely biomagnify. Studies of the lichen-caribou-wolf food web showed that a wider range of chlorinated organics may biomagnify in terrestrial compared to marine food webs. This was explained by the presence of two air-breathing species in the food web and the fact that some chemicals with high octanol-air partition coefficients are eliminated less efficiently in air via the lungs than in water over the gill, resulting in their higher net uptake and retention in terrestrial top predators. Biomagnification of PFOS and PFCAs in this food web was shown to occur to a similar extent as in marine food webs. In caribou and moose, PFASs were the major POPs with concentrations in liver ranking ahead of PCBs and PBDEs (ΣPFCAs> PFOS> ΣPCBs> ΣPBDEs). However, concentrations of new POPs and CUPs in caribou, moose, and other terrestrial animal samples were much lower compared with marine mammals, as observed for PCBs and OC pesticides in previous assessments.

The potential for climate warming to influence levels and trends of POPs in the arctic has emerged as a major line of investigation in the past 5 years. The relatively long time series for POPs now available e.g. ~18 years continuous measurement for air, 15 to 18 years of sampling over the past 35-50 years for lake trout, burbot, arctic char, seabirds, seals, polar bears, and beluga are beginning to be examined for possible linkages to climate variables (temperature, ice free times), as well as to parameters associated with dietary and species shifts (carbon and nitrogen stable isotope ratios, fatty acid signatures). For example, dietary tracers (carbon stable isotope ratios, fatty acid patterns) were found to explain trends of ΣPCB and ΣCHL in WHB polar bears. This result suggested that a dietary shift of polar bears to harbor seals, harp and bearded seals might lead to higher

actual contaminant concentrations. Adjusting concentrations of ΣPCB and ΣDDT in murre eggs for trophic position resulted in little change in the calculated rate of decline of these legacy POPs at Prince Leopold Island in Lancaster Sound but reduced the rates of decline at Coats Island, in Hudson Strait, suggesting that the shift in diet which occurred in the murres at Coats Island has affected the temporal trends of contaminants for that colony.

POPs monitoring programs, both abiotic and biotic, in the Arctic can provide valuable data to fingerprint the impact of arctic warming (Arctic amplification) on the environmental fate of POPs. However, there are still large uncertainties in understanding the influence of rapid climate change on the fate and mobilization of both legacy and new POPs in the Arctic. Although recent studies have revealed revolatilization of POPs from arctic repositories, such as arctic waters, soils, snow/ice and permafrost, the actual net amounts released to atmosphere are not known, and whether a sink to source reversal in the Arctic is taking place also still remain unknown.

Recommendations:

- Better data is required on key modeling parameters in food webs including efficiencies of uptake from water, air and food, and especially on the biotransformation rates that play a key role in biomagnification.
- The measurements in biological samples could be better synchronized with atmospheric measurements, where a greater number of chemicals are being analyzed in air e.g., novel BFRs and other flame retardants, siloxanes, and CUPs, both in the Canadian Arctic and in other air measurement programs.

7. Assessment of Biological Effects Remains a Challenge

Assessing the effects of POPs on the health of Canadian arctic biota is very challenging due to factors such as low contaminant exposures, limited access to fresh samples, difficulties in processing samples in a way that suits the needs of health endpoints in the field, and a limited knowledge of life history and feeding ecology of many species. While toxicological studies of arctic wildlife remain challenging, recent investment in research under the NCP has increased the understanding of the effects of persistent contaminants on high trophic level biota and helped to develop new biochemical tools to assess effects.

There remains minimal evidence that POPs have widespread effects on the health of Canadian arctic animals. The best evidence for effects in top predators are from studies of East Greenland and Svalbard polar bears, as well as Svalbard glaucous gulls, which have much higher exposures to most POPs than in the Canadian Arctic. However, studies at the PCB contaminated site at Saglek Bay have demonstrated declines in the concentrations of PCBs in sediment, in biota, and in biological effects in the marine environment over time, illustrating that the tools and knowledge are available to assess effects where relatively high exposures are documented. PCB concentrations in shorthorn sculpin and black guillemot nestlings at Saglek Bay are below concentrations (1,000 ng g^{-1} ww) previously associated with risks of impaired reproduction and survival.

ΣPCB concentrations in beluga and polar bears exceed the toxicity reference value for immunotoxicity and endocrine disruption of 1.3 μg g^{-1} lw in harbor seals. Mean ΣPCB concentrations in Canadian arctic seabird eggs are well below reported thresholds for egg mortality and hatching success in fish-eating birds (except for glaucous gulls). Concentrations of PFOS in polar bear livers exceed the estimated no-effects values but PFOS levels in liver of birds and seals were an order of magnitude below no effects values.

Recommendations

- The development, validation and application of new genomics methods provides a powerful means of examining the relationship between physiological endpoints and persistent contaminants and should be applied to examine subtle effects on higher trophic level arctic animals.
- For studies of biological effects as well as effects of climate change on exposure to POPs, emphasis should be placed on the multiple ecological, biological, and physical (natural and anthropogenic) variables that need to be considered when analyzing contamination in species and when comparing data between studies.

Résumé

1. Contexte de la présente évaluation

Le Programme de lutte contre les contaminants dans le Nord (PLCN) a été établi en 1991 pour répondre aux préoccupations relatives à l'exposition des gens à des concentrations élevées de contaminants chez les espèces sauvages qui constituent un élément important du régime alimentaire traditionnel des Autochtones du Nord. Il s'agit de la troisième évaluation des polluants organiques persistants (POP) réalisée dans le cadre du PLCN, et de la première se concentrant uniquement sur les POP. Le présent document accompagne une évaluation sur le mercure, et une évaluation réalisée antérieurement sur la santé humaine. Les évaluations antérieures de 1997 et de 2003 faisaient la synthèse des résultats de la phase I (de 1991 à 1996) et de la phase II (de 1997 à 2002) du PLCN, et traitaient à la fois des métaux lourds et des POP. Dans le cadre de la phase III, laquelle a commencé en 2003-2004, la surveillance environnementale visait un moins grand nombre de sites d'échantillonnage, tant pour les échantillons atmosphériques que pour les échantillons biologiques (tableau 1). Les programmes d'échantillonnage biologique ont été repensés de manière à ce qu'on puisse déceler une variation annuelle de 10 % de la concentration d'un contaminant sur une période de 10 à 15 ans, avec une puissance statistique de 80 % et un niveau de confiance de 95 %. Il a donc fallu passer à un échantillonnage annuel pour certaines espèces clés (béluga, phoque annelé, oiseaux marins, omble chevalier); pour le béluga et le phoque annelé, on a réduit le nombre de sites d'échantillonnage. Depuis 2009, l'analyse des extraits d'échantillons de grands volumes d'air à Alert a été réduite à un échantillon par mois; les autres extraits d'échantillons sont archivés. Les tendances temporelles concernant le phoque annelé, l'omble chevalier et le béluga ne sont maintenant étudiées que dans deux à trois sites importants par espèce.

En plus de son programme amélioré de surveillance à long terme, le PLCN finance toujours la recherche relative aux voies de transport, aux processus et aux effets biologiques des POP dans l'Arctique canadien. La recherche comprend la modélisation du transport atmosphérique et océanique à grande distance, l'évaluation et la bioamplification dans les réseaux trophiques de l'Arctique, des études sur les effets potentiels du changement climatique sur les POP dans l'Arctique, et une étude exhaustive sur les effets biologiques des POP chez les bélugas.

La présente évaluation fait état des résultats obtenus concernant les POP dans l'Arctique canadien de 2003 à 2011. Elle s'appuie sur les résultats de la phase III du PLCN (de 2003 à 2011), de même que sur toutes les études publiées ou non publiées réalisées jusqu'au début de 2013. Cette période de référence de huit à

TABLEAU 1. Aperçu des éléments échantillonnés dans le cadre du programme de surveillance des POP du PLCN de 2003 à 2011

Élément	Emplacements	Années d'échantillonnage[1]	Frequency
Air – grand débit	Alert	1992–2010	7 jours consécutifs
Air – échantillonnage passif	Jusqu'à 7 emplacements (zones arctiques et subarctiques)	2005–2011	Trimestriellement
Omble chevalier (anadrome)	Cambridge Bay, Pond Inlet , Nain	2004–2011	Annuellement
Omble chevalier (confiné aux eaux intérieures)	Lacs Resolute, Char, Amituk et Hazen	2004–2011	Annuellement
Lotte	Fort Good Hope, bassin ouest et bras est du Grand lac des Esclaves	2004–2011	Annuellement
Touladi	Lac Laberge, lac Kusawa, bassin ouest et bras est du Grand lac des Esclaves	2004–2011	Annuellement
Caribou	Nord du Yukon et sud-ouest du Nunavut (hardes de Porcupine et de Qamanirjuaq)	2006, 2008	Une seule étude
Phoque annelé	Arviat, Resolute, Sachs Harbour et autres emplacements (jusqu'en 2009)	2004–2011	Annuellement
Béluga	Sud de la mer de Beaufort, baie Cumberland	2004–2011	Annuellement
Ours blanc	Ouest de la baie d'Hudson et autres emplacements	2004–2011	Annuellement
Oiseaux marins (Guillemot de Brünnich, Fulmar boréal)	Île Prince Leopold et île Coats	2004–2011	Annuellement

[1]Tous les programmes incluent des données des années antérieures (données existantes ou nouvelle analyse des échantillons archivés)

neuf ans a permis d'en apprendre beaucoup sur les tendances temporelles des POP dans l'air et dans le biote, sur les nouveaux POP dans de nombreux compartiments de l'environnement, et sur le transport océanique vers l'Arctique. L'influence possible du réchauffement climatique sur les tendances des POP a également été étudiée.

2. De la science aux mesures stratégiques

La période de percées scientifique que couvre la présente évaluation était également très importante sur le plan des mesures réglementaires mondiales prises à l'égard des POP. La Convention de Stockholm sur les POP est notamment entrée en vigueur en 2004, introduisant une réglementation mondiale visant à éliminer ou à limiter sérieusement les émissions des POP qui font partie de ce qu'on appelle la « sale douzaine ». L'élaboration de la Convention de Stockholm est vue comme une réalisation majeure pour le PLCN, qui, de concert avec le Programme de surveillance et d'évaluation de l'Arctique (PSEA) du Conseil de l'Arctique, a fourni une grande partie des données scientifiques sur lesquelles s'appuie la Convention. La présente évaluation documente les déclins des concentrations de beaucoup de POP appartenant au groupe de la « sale douzaine » (ces polluants sont également appelés POP hérités du passé), et contient aussi des données sur un grand nombre de nouveaux POP, dont 11 ont été ajoutés à la Convention de Stockholm depuis 2004. Les données et les renseignements tirés du PLCN ont contribué à l'inclusion de ces nouveaux POP à la Convention, et continueront de jouer un rôle essentiel dans l'évaluation des nouveaux POP dans le futur. Le PLCN fournira aussi des renseignements à jour tirés de son évaluation pour l'élaboration du deuxième rapport du Plan mondial de surveillance, en 2015, établi aux termes de l'article 16 de la Convention de Stockholm. La participation active et continue du PLCN à des initiatives nationales et internationales liées à l'évaluation et à la réglementation des POP fera en sorte que les données scientifiques du PLCN continueront d'influer de façon notable sur les politiques visant à protéger les écosystèmes et la santé humaine dans la Nord canadien. Les recommandations scientifiques qui suivent ont été élaborées en fonction du rôle continu du PLCN en matière de formulation d'avis scientifiques dans le cadre d'initiatives de réglementation nationales et internationales, et visent à étayer les nouvelles politiques nationales et internationales.

Recommandations

- La surveillance continue des POP dans l'Arctique est nécessaire pour garantir que la Convention de Stockholm est efficace en matière de réduction des concentrations de ces polluants dans l'environnement. On doit également assurer la surveillance continue des contaminants chimiques émergents, dont la détection dans les milieux arctiques appuie solidement leur inclusion à la Convention de Stockholm en tant que nouveaux POP.
- Afin d'améliorer la réglementation des POP, les organismes de réglementation nationaux et internationaux doivent mieux comprendre la façon dont les POP se comportent dans l'environnement, de même que leurs effets sur les écosystèmes et la santé humaine. Comme le soulignent la présente évaluation ainsi que des organisations internationales telles que le Programme des Nations Unies pour l'environnement (PNUE) et le PSEA, il est également nécessaire de mieux comprendre la façon dont le changement climatique influe sur les POP. La prédiction des effets du changement climatique sur les POP sera essentielle pour élaborer des règlements visant les POP et pour évaluer l'efficacité de ces règlements dans le futur.

3. Les connaissances sur les substances chimiques d'intérêt se sont étendues

La liste des composés analysés s'est allongée au cours de la phase III, en particulier en ce qui concerne les substances perfluoroalkylées et polyfluoroalkylées (SPFA), les produits ignifuges bromés et les pesticides d'usage courant (PUC). Environ 35 substances chimiques ou groupes de substances chimiques qui n'avaient pas été signalés avant, ou pour lesquels on ne disposait que de mesures très limitées lors de l'évaluation précédente, ont été décelés, en particulier dans l'air, dans la neige et dans le biote arctiques (tableau 2). Voir le glossaire pour de plus amples détails sur les noms des substances chimiques et leurs acronymes.

Parmi les substances organiques chlorées, les polychloronaphtalènes (PCN) sont aujourd'hui décelées dans un plus grand nombre d'éléments (air, phoques, bélugas, oiseaux marins). Les nouvelles données étaient limitées en ce qui concerne les paraffines chlorées pour la période 2003-2011 en raison des difficultés d'analyse des laboratoires où les mesures ont été faites. Les PCN et les paraffines chlorées à chaîne courte (PCCC) sont actuellement

TABLEAU 2. Principaux groupes de POP et autres substances organiques persistantes présentes dans différents compartiments environnementaux de l'Arctique canadien déterminés dans le cadre des programmes de surveillance et de recherche du PLCN.

	PLCN I (1991–1996)	PLCN II (1997–2002)	PLCN III (2003–2011)
Polychlorobiphényles (PCB)[1]	Air, neige, sédiments, eau de mer, biote	Air, eau de mer, sédiments, biote	Air, neige, eau de mer, biote
Pesticides organochlorés (OC)[2]	Air, neige, sédiments, eau de mer, biote	Air, eau de mer, sédiments, biote	Air, neige, biote
Cholorobenzènes	Air, neige, sédiments, eau de mer, biote	Air, eau de mer, sédiments, biote	Air, neige, biote
Dioxines/furanes chlorés	Biote	Air, sédiments, biote	Biote
Polychloronaphtalènes (PCN)		Air, biote	Air, biote
Paraffines chlorées		Air, sédiments, biote	Biote
Endosulfan		Air, eau de mer, biote	Air, eau de mer, biote
Polybromodiphényléthers (PBDE)		Sédiments, biote	Air, neige, eau de mer, sédiments, biote
Hexabromocyclododécane (HBCDD)			Air, neige, eau de mer, biote
Autres produits ignifuges bromés et chlorés			Air, neige, eau de mer, biote
Penta- et hexabromodiphényles			Air, biote
Persticides d'usage courant (PUC)			Air, neige, eau de mer, eau lacustre, biote
Perfluorooctanesulfonate (PFOS) et autres acides et alcools perfluoroalkylés (SPFA)			Air, neige, eau de mer, eau lacustre, sédiments, biote
Siloxanes			Air

[1]Divers congénères selon l'étude; 2 DDT, hexachlorocyclohexanes (HCH), chlordanes, toxaphène; 3 PUC, notamment les suivants : Dacthal, chlorothalonil, chlorpyrifos, pentachloronitrobenzène (PCNB), trifluraline.

évaluées en vue de leur inclusion à la Convention de Stockholm.

Les nouveaux groupes de substances chimiques mesurées au cours des 10 dernières années comprennent des PUC, notamment le Dacthal, le pentachloronitrobenzène (PCNB), la trifluraline et le chlorothalonil, qui sont maintenant régulièrement décelés dans l'air et dans l'eau de mer. Des mesures limitées de PUC ont également été faites dans des réseaux trophiques marins et terrestres, et les résultats indiquent que ces PUC ne se bioamplifient pas. Environ 20 produits ignifuges bromés et chlorés ont aussi été inclus dans les séries d'analyses. De nombreux autres sont également évalués dans le cadre du Plan de gestion des produits chimiques du gouvernement du Canada. En ce qui concerne le HBCDD, le produit ignifuge n'appartenant pas au groupe des PBDE le plus largement décelé, les données dans le biote de l'Arctique canadien ont servi de fondement à une grande partie du profil de risque adopté par la Convention de Stockholm en 2010. Toutefois, la plupart des autres produits ignifuges bromés n'appartenant pas au groupe des PBDE se trouvaient en deçà des limites de détection dans les échantillons atmosphériques et biologiques.

La découverte de SPFA chez certaines espèces sauvages de l'Arctique, puis dans tous les compartiments environnementaux, est peut-être le résultat le plus surprenant obtenu au cours des 10 dernières années de surveillance des contaminants dans l'Arctique. Contrairement aux POP chlorés et bromés, ces substances chimiques sont relativement solubles dans l'eau, sont oléophobes, et s'accumulent dans les tissus riches en protéines, comme le foie et le sang. Les précurseurs du PFOS et d'autres SPFA sont hautement volatils, et c'est dans l'atmosphère qu'on les mesure le mieux. Toutefois, ces substances peuvent être dégradées dans l'atmosphère en substances persistantes et bioaccumulables. La présence de fortes concentrations de PFOS et de perfluorocarboxylates (PFCA) à chaîne longue chez certains mammifères et chez l'ours blanc, dans l'Arctique, met également en évidence la nécessité d'examiner un large éventail de substances chimiques relativement à leur capacité d'être transportés vers l'Arctique, d'être transformés en substances persistantes, et de s'accumuler dans les réseaux trophiques de l'Arctique.

On a commencé à utiliser des échantillonneurs d'air passifs au cours de la phase III, et les résultats pour les emplacements dans l'Arctique pour ce programme, qui faisait partie du Programme d'échantillonnage atmosphérique passif mondial (GAPS), étaient comparables à ceux obtenus au moyen d'échantillonneurs d'air à grand débit, à Alert. Les échantillonneurs atmosphériques passifs sont avantageux, car ils sont peu coûteux, sont simples à construire et ne nécessitent pas d'énergie électrique.

La modification de la matière absorbante dans les échantillonneurs a permis d'échantillonner des précurseurs volatils du PFOS et de PFCA, de même que des siloxanes méthylés volatils dans l'atmosphère de l'Arctique, et de faire des comparaisons entre des régions rurales et urbaines un peu partout sur la planète. Toutefois, les faibles concentrations atmosphériques dans l'Arctique entraînaient souvent des problèmes de détectabilité. Un échantillonneur passif à circulation d'air récemment mis au point ayant donné des résultats comparables à bien moindre coût et nécessitant moins d'entretien que les échantillonneurs à fort débit utilisés à Alert pourrait bien régler ce problème.

L'importance du transport particulaire des contaminants non volatils comme les décabromodiphényléthers (déca-BDE), qui sont des produits ignifuges largement utilisés, a été prouvée par la détection de fortes concentrations sur la calotte glaciaire de l'île Devon. Cette voie de transport a déjà été reconnue, principalement pour les substances chimiques inorganiques, comme le plomb et les sulfates. D'autres « nouveaux » produits ignifuges observés dans les échantillons atmosphériques prélevés à Alert sont aussi en grande partie fixés à des particules. Les produits ignifuges bromés, comme le bis(tribromophénoxy)éthane, l'éthylhexyltétrabromobenzoate et le bis(éthylhexyl)tétrabromophtalate ont été généralement décelés à des concentrations similaires à celles des PBDE congénères dominants.

Plusieurs études indépendantes ayant réalisé un examen préalable de substances chimiques utilisées dans le commerce ont montré qu'il existe des centaines de substances dont les propriétés sont similaires à celles de substances chimiques organiques persistantes connues décelées dans l'Arctique. Ces substances pourraient être de futures candidates à la surveillance dans l'atmosphère et chez les espèces sauvages de l'Arctique. Pour modéliser le transport de ces substances candidates vers l'Atctique, on doit disposer de renseignements sur les quantités utilisées et émises dans les régions sources. Ces renseignements ne sont généralement pas disponibles, sauf en ce qui concerne les PUC. Toutefois, la modélisation du transport atmosphérique à grande distance (TAGD) des POP a évolué au point où il est maintenant possible d'utiliser un modèle planétaire pour suggérer un plafond relatif aux émissions annuelles dans différentes parties du monde, en fonction de l'efficacité du transport vers un endroit vulnérable.

La détection d'acides perfluoroalkylés, tels que le PFOS et l'acide perfluorooctanoïque (APFO) dans l'eau de mer de l'Arctique, conjuguée à la modélisation à l'échelle planétaire, ont prouvé l'importance du transport océanique des contaminants. Le lent déplacement et la grande étendue des masses d'eau de mer mettent également en évidence l'exposition à très long terme des réseaux trophiques de l'Arctique aux contaminants. La découverte de SPFA dans l'eau de mer a mené à une expansion colossale de la modélisation du transport océanique à grande distance (TOGD), et du transport des SPFA ainsi que d'autres POP vers l'Arctique. Les mesures environnementales de deux SPFA majeures, le PFOS et l'APFO, concordent raisonnablement avec les données actuellement disponibles pour les eaux océaniques, ce qui laisse croire que les estimations disponibles relatives aux émissions de ces deux composés sont plausibles. Les résultats de la modélisation donnent à penser que la redistribution de ces contaminants à partir de basses latitudes vers l'océan Arctique est continue et que la masse totale (et la concentration moyenne) de l'APFO et du PFOS dans le milieu marin devrait augmenter au cours des 10 à 20 prochaines années. La principale conclusion tirée à partir de la modélisation du TOGD veut que l'exposition des réseaux trophiques marins à des POP davantage solubles dans l'eau dans les eaux de l'est de l'Arctique soit substantiellement différente de l'exposition à d'autres endroits, par exemple dans les eaux de l'ouest de l'Arctique canadien. Ce schéma de distribution est distinct de celui du TAGD, qui tend à rendre les flux de dépôt (et par conséquent les concentrations/l'exposition dans la colonne d'eau) plus uniformes. Ces observations sont corroborées par des différences en termes de concentrations et de taux de variation des concentrations des POP entre, d'une part, les bélugas et les phoques annelés du sud de la mer de Beaufort et, d'autre part, ceux des régions de la baie d'Hudson et de la baie Cumberland.

Recommandations

- Beaucoup de travaux sont encore nécessaires pour déterminer si le changement climatique, en particulier les tendances du réchauffement, influe sur le transport des POP vers l'Arctique.
- Il est urgent de réaliser de nouvelles recherches sur d'autres substances chimiques se fixant à des particules susceptibles de pénétrer dans le milieu arctique.

- Davantage de données sont nécessaires sur les quantités de substances chimiques utilisées et émises dans les régions sources.
- Les programmes de surveillance doivent envisager l'inclusion d'une plus vaste gamme de substances chimiques, notamment de produits parents et de transformation, qui pourraient posséder des propriétés semblables à celles des POP, pour étudier leur potentiel de transport sur de grandes distances de même que pour évaluer les changements en élaborant des tendances temporelles dans différents milieux. Les substances chimiques susceptibles de contaminer l'environnement arctique pourraient être décelées à l'aide de modèles sur leur devenir dans l'environnement et leur mode de transport.
- On devrait mettre davantage l'accent sur les nouvelles substances chimiques candidates figurant sur les listes actuelles de la Convention de Stockholm et de la Convention sur la pollution atmosphérique transfrontière à longue distance de la Commission économique pour l'Europe des Nations Unies (CEE-ONU) (PCN, pentachlorophénol, hexachlorobutadiène), de même que sur les PCCC, le chlordécone et l'hexabromodiphényle afin d'évaluer pleinement leur importance en tant que contaminants de l'environnement biologique.

4. La connaissance des tendances temporelles des POP s'est grandement améliorée

Les tendances temporelles de POP inscrits sur la liste de la Convention de Stockholm et d'autres substances chimiques organiques persistantes sont présentées au tableau 3 par code de couleurs (vert pour les déclins; rouge pour les augmentations). Les résultats de la surveillance atmosphérique indiquent que de nombreux POP hérités du passé, notamment les pesticides organochlorés (OC) et les PCB, sont en déclin. Les résultats obtenus grâce à l'échantillonnage réalisé à Alert, dans le nord de l'île Ellesmere, indiquent que le déclin des POP hérités du passé était généralement plus rapide durant la période 1993-2001, par rapport à la période 2002-2009 (la dernière année où des rapports ont été produits). Bien que les tendances globales (de 1993 à 2009) pour les PCB montrent un déclin, ce dernier a ralenti, et les concentrations de certains congénères plus fortement chlorés ont augmenté légèrement au cours des dernières années. Ces augmentations pourraient être associées à l'augmentation du nombre de feux de forêt dans la forêt boréale, qui rejettent les substances organiques qui s'y étaient déposées, notamment des PCB. Les changements associés à la couverture de glace de mer et à la cryosphère en général pourraient aussi être en cause. Les pesticides chlorés comme les hexachlorocyclohexanes (HCH, en particulier le γ-HCH, ou lindane), le DDT et les composés apparentés au chlordane (CHL) montrent des déclins plus stables au cours de la période 1993-2009. Le lindane a été radié de la liste des produits homologués au Canada pour l'utilisation sur les semences de canola en juillet 2001, et son utilisation est interdite depuis 2004. Les concentrations atmosphériques de lindane ont diminué de façon constante depuis 2001. L'endosulfan, un autre pesticide largement utilisé, était présent à des concentrations constantes de 1993 à 2001, et le déclin des concentrations de 2006 à 2009 reflète peut-être son utilisation réduite au Canada, aux États-Unis et en Europe depuis qu'il fait l'objet d'une surveillance réglementaire plus rigoureuse.

Malgré les détections récentes de SPFA, les séries chronologiques de données concernant d'autres POP présents dans l'eau de mer demeurent une lacune majeure sur le plan des connaissances sur les contaminants présents dans l'Arctique. Ces données sont essentielles pour comprendre le devenir dans l'environnement et les tendances des contaminants, et seraient particulièrement utiles en ce qui concerne les substances moins bioaccumulables et plus solubles dans l'eau, comme c'est le cas des PUC. Il est nécessaire de clarifier l'importance relative des apports atmosphériques et océaniques, de même que l'importance relative des émissions directes et de précurseurs vers différents écosystèmes éloignés. Compte tenu de la difficulté d'obtenir des données sur les POP en prélevant de grandes quantités d'eau en raison de la contamination à bord des navires et de la navigation peu fréquente, on doit envisager le déploiement d'échantillonneurs passifs.

La puissance statistique des ensembles de données sur les tendances temporelles des POP chez les poissons, les oiseaux marins et les mammifères marins s'est améliorée depuis la publication du Rapport de l'évaluation des contaminants dans l'Arctique canadien (phase II), en 2003, et certains ensembles de données sont en mesure de déceler un changement de l'ordre de 5 % sur le plan des concentrations (puissance statistique de 80 %). La principale raison pour laquelle la puissance statistique s'est accrue est l'introduction de l'échantillonnage annuel d'espèces clés depuis 2004, ce qui a fait en sorte d'accroître le nombre d'années ayant fait l'objet d'échantillonnage.

Les tendances à la baisse des concentrations dans le biote sont le plus évidentes pour les pesticides OC, et le moins évidentes pour les PCB et les chlorobenzènes (ΣCBz) (tableau 3). Chez les espèces marines, les taux annuels de déclin de ΣDDT étaient de 2,5 %/an dans les œufs de Guillemots de Brünnich (détroit de Lancaster) à 11 %/an dans la graisse d'ours blancs (ouest de la baie d'Hudson). Les déclins des concentrations des composés apparentés au chlordane (ΣCHL) étaient de 1,2 %/an dans les œufs de guillemots à 7,4 %/an dans le pannicule adipeux de phoques annelés dans la baie d'Hudson, alors que les concentrations chez les ours blancs ne montraient aucun déclin (ouest de la baie d'Hudson). Les concentrations totales de HCH (ΣHCH) ont diminué chez les phoques, les bélugas et les ours blancs en raison du déclin rapide de la concentration de l'isomère majeur α-HCH (p. ex. 12 %/an chez les ours). Toutefois, les concentrations de β-HCH, l'isomère le plus bioaccumulable, ont augmenté chez la même espèce. Cette augmentation des concentrations de β-HCH chez les phoques variait de région en région, avec de fortes augmentations chez les phoques du sud de la mer de Beaufort (16 % à Ulukhaktok), et un déclin dans la baie d'Hudson (2,5 %/an). Le cas du β-HCH met en évidence l'importance du déplacement de l'eau de mer dans l'archipel Arctique, de l'océan Pacifique en passant par la mer de Béring, et possiblement des apports des eaux douces de la Russie. Aucun autre POP ne montre cette tendance, bien que les déclins des concentrations de PCB, de ΣDDT et de ΣCHL chez les bélugas, les phoques annelés et les ours blancs aient été plus faibles (ou inexistants) dans le sud de la mer de Beaufort que chez ceux des régions de la baie d'Hudson et de l'est de la baie de Baffin.

Les déclins des concentrations des POP hérités du passé ont généralement été plus rapides chez les poissons d'eau douce que chez les mammifères marins. Par exemple, les concentrations de PCB chez les ombles chevaliers confinés aux eaux intérieures ont respectivement diminué de 6,4 % et de 7,6 %/an dans les lacs Amituk et Hazen, par rapport à 3,8 % et 4,0 %/an chez les Guillemots de Brünnich et les Fulmars boréaux. Des déclins ≥ 5 %/an ont aussi été observés pour le ΣHCH, le ΣCHL, le ΣDDT et le toxaphène chez les touladis des lacs Laberge et Kusawa, et dans le bassin ouest du Grand lac des Esclaves, de même que chez les ombles confinés aux eaux intérieures dans les lacs Hazen, Char et Amituk. Les déclins des concentrations de ces pesticides OC étaient généralement < 5 %/an dans les œufs d'oiseaux marins et chez les mammifères marins. L'augmentation des concentrations de PCB, de ΣCHL, de ΣDDT et de toxaphène de 2001 à 2009 dans le foie de lottes échantillonnées à Fort Good Hope, dans le fleuve Mackenzie, constitue une exception notable. Toutefois, depuis 2010, les concentrations de ces quatre POP sont revenues aux niveaux observés dans les années 1990 et au début des années 2000. Les concentrations de PCB et de ΣCBz ont également augmenté chez les lottes et les touladis du Grand lac des Esclaves au cours de la période 2001-2005. Ces augmentations n'ont pas été observées chez les touladis du Yukon (lacs Laberge et Kusawa) ou chez les ombles confinés aux eaux intérieures. L'échantillonnage annuel a permis d'observer ces changements. Ces augmentations temporaires suggèrent qu'il existe un processus qui influe sur la disponibilité des POP dans le bassin du fleuve Mackenzie. Le réchauffement climatique a été évoqué, mais une tendance générale de réchauffement n'expliquerait pas l'augmentation suivie d'une diminution des concentrations. Néanmoins, les changements sur le plan de l'alimentation et des aires d'alimentation des lottes et des touladis, qui pourrait aussi être induits par le changement climatique, pourraient faire en sorte de modifier la disponibilité des contaminants. Les autres possibilités comprennent la mobilisation de sources héritées du pasée en raison du réchauffement, par exemple par l'érosion accrue des sédiments des cours d'eau.

Les concentrations de nouveaux POP, notamment de PBDE et de PFOS ont augmenté de manière générale chez les phoques, les oiseaux marins, les bélugas et les ours blancs dans les années 1990 jusqu'au début des années 2000, et sont maintenant en déclin. Une analyse rétrospective des collections des banques de spécimens a permis de mesurer les concentrations de PBDE, de SPFA et d'autres contaminants à partir d'échantillons prélevés dans les années 1970, 1980 et 1990; l'échantillonnage annuel réalisé à partir du début des années 2000 a quant à lui permis d'observer les déclins relativement rapides. Par exemple, les concentrations de ΣPBDE ont atteint respectivement leur maximum dans les œufs de Fulmars boréaux et de Guillemots de Brünnich en 2005 et 2006, puis ont décliné, en trois ans, jusqu'à des niveaux similaires à ceux observés au début des années 1990. Les concentrations maximales de PBDE chez les ours blancs, les phoques annelés et les bélugas semblent avoir été atteintes durant la période 2000-2004 dans la plupart des emplacements. De manière similaire, les concentrations de PFOS ont atteint un maximum dans le foie des phoques annelés de 1999 à 2003 dans la baie d'Hudson, dans le détroit de Lancaster et dans l'est de la baie de Baffin,

TABLEAU 3. Aperçu des tendances temporelles de certains POP et autres composés organiques persistants dans l'air et le biote de l'Arctique canadien. Tendances estimées pour tous les résultats de la période commençant au début des années 1990 et se terminant en 2011.

	Air	Lotte[1]		Touladi[2]			Omble chevalier confiné aux eaux intérieures[3]		Oiseaux de mer[4]	Phoque[5]			Béluga[6]		Ours blanc[7]
		FGH	GLE	KW	LL	GLE	H	A	IPL	SMB	DL	BH	SMB	BC	BH
PCB															
ΣCBz															
ΣHCH															
ΣCHL															
ΣDDT															
Toxaphène															
Endosulfan															
PCCC															
PCN															
PCDD/F															
ΣPBDE															
HBCDD															
PFOS et précurseurs															
PFCA et précurseurs															

	Résultats limités ou aucun résultat pour permettre d'évaluer les tendances
	Aucun changement statistiquement significatif (généralement < 3 %/an)
	Tendance à la baisse significative (généralement > –5 %/an)
	Tendance à la hausse significative (généralement > +5 %/an)
	Hausse significative au début des années 2000, tendance actuelle stable ou à la baisse

[1]FGH = Fort Good Hope, GLE = Grand lac des Esclaves – bras est et bassin ouest

[2]LL et KW = lacs Laberge et Kusawa; GLE = Grand lac des Esclaves – bras est et bassin ouest

[3]H = lac Hazen; A = lac Amituk

[4]IPL = île Prince Leopold, détroit de Lancaster

[5]SMB = sud de la mer de Beaufort (Ulukhaktok, Sachs Harbour); DL = détroit de Lancaster (Resolute, baie de l'Arctique et fjord Grise), BH = baie d'Hudson (Arviat et Inukjuaq)

[6]SMB = sud de la mer de Beaufort (île Hendrickson); BC= baie Cumberland (Pangnirtung)

[7]BH = baie d'Hudson – pour tous les composés, sauf le PFOS et les PFCA; dans leur cas, on a utilisé les résultats du nord de l'île de Baffin et de l'île de Baffin.

mais, dans le sud de la mer de Beaufort, les concentrations chez les animaux ont continué d'augmenter lentement (3,6 %/an) jusqu'en 2011.

Un déclin des concentrations de PBDE a aussi été observé dans les échantillons atmosphériques prélevés à Alert. Les concentrations des précurseurs du PFOS, le MeFOSE et l'EtFOSE ont aussi connu un déclin, alors que les concentrations des alcools fluorotélomères qui comptent 8 et 10 chaînes de carbone fluoré, ont augmenté au cours de la période 2006-2010. Le déclin des concentrations de PBDE et de PFOS dans l'air et dans le biote semble être lié aux interdictions et à l'élimination progressive volontaire de ces substances en Amérique du Nord et en Europe au cours de la période 2001-2004. D'un autre côté, les concentrations de certaines substances chimiques de rechange, comme le HBCDD, semblent augmenter. Le HBCDD n'était pas décelable dans les échantillons biologiques prélevés des années 1990 au début des années 2000, mais les concentrations ont augmenté et ont largement dépassé les limites de détection de 2005 à 2011 chez la lotte, le touladi, l'omble chevalier confiné aux eaux intérieures et le phoque annelé. Les concentrations maximales de HBCDD ont été observées un peu plus tôt (en 2003) chez l'ours blanc, dans l'ouest de la baie d'Hudson, et chez le béluga, dans le sud de la mer de Beaufort. Les données sont trop limitées et les concentrations sont trop près des limites de détection pour déterminer si les concentrations d'autres produits ignifuges bromés augmentent dans l'air ou dans le biote.

Recommandation

- L'échantillonnage annuel continu est essentiel à la détection, dans le biote, des tendances temporelles des produits chimiques commercialisés. Il permet de démontrer la hausse et la baisse des nouveaux POP, d'améliorer la puissance statistique des tendances des POP hérités du passé et d'étudier les effets du changement climatique.
- Les POP atmosphériques font l'objet de peu de mesures et d'un manque de tendances temporelles dans l'ouest et l'est de l'Arctique canadien. Cette lacune dans les données doit être comblée par l'utilisation soit d'échantillonneurs d'air à grand débit, soit d'échantillonneurs d'air passifs, ou encore d'une combinaison des deux. La surveillance atmosphérique semble particulièrement critique dans l'ouest de l'Arctique compte tenu de l'augmentation de la production et de l'utilisation de substances chimiques organiques en Asie cette dernière décennie.
- Il faut des données chronologiques concernant les POP et les nouveaux contaminants présents dans l'eau de mer pour comprendre le devenir et les tendances de ces produits. De plus, de telles données seraient particulièrement utiles dans le cas des substances chimiques moins bioaccumulables, comme les PUC.
- Le prélèvement annuel d'échantillons a amélioré la puissance statistique du programme biologique et doit donc être poursuivi. Néanmoins, il faut aussi envisager de mettre de côté les mesures annuelles de certains POP hérités du passé, pour lesquels les analyses statistiques montrent que les ensembles de données répondent aux objectifs de surveillance, et mettre plutôt l'accent sur les nouvelles substances chimiques candidates ou émergentes, qui ne font peut-être pas l'objet d'un grand nombre de données.
- Il faut reconnaître qu'une force importante des programmes axés sur les tendances temporelles menés dans le cadre du PLCN réside dans la disponibilité d'échantillons archivés à partir de banques de spécimens. Ces dernières doivent être maintenues pour assurer la solidité continue du programme de surveillance des POP.

5. Les sources locales peuvent être importantes pour les nouveaux POP

Bien que l'accent de la présente évaluation soit principalement mis sur les POP qui pénètrent dans l'Arctique canadien par TAGD et TOGD, les sources locales des nouveaux POP, de même que les tendances des contaminants hérités du passé, sont encore pertinentes. Les mesures prises au cours de la période 2003-2011 ont montré que les PBDE, le PFOS et les PCCC étaient des sources de contamination locale au sein ou à proximité des collectivités dans l'Arctique canadien. Par exemple, dans une étude, on a constaté que les décharges d'Iqaluit, de Cambridge Bay et de Yellowknife présentaient des concentrations de ΣPBDE significativement plus élevées que les sites témoins dans ces localités, ce qui donne à penser que des PBDE sont lixiviés à partir des décharges. Les teneurs en PCCC et en paraffines chlorées à moyenne chaîne (PCMC) étaient plus élevées dans les échantillons de sédiments, d'eau et de poissons prélevés dans la ville d'Iqaluit et autour que dans un site témoin éloigné. Les concentrations de PFOS et de substances chimiques apparentées utilisées dans des mousses à formation de pellicule aqueuse (pour éteindre les incendies de carburant) étaient élevées dans l'eau et les ombles chevaliers confinés aux eaux intérieures des lacs Merretta et Resolute, lesquels se trouvent en aval de l'aéroport de Resolute Bay.

La surveillance dans les milieux marins et terrestres de la baie de Saglek (Nunatsiavut/Labrador) montre que les concentrations de PCB dans les environs (sédiments, végétaux, souris sylvestre, chaboisseaux et Guillemot à miroir) ont baissé depuis l'élimination de la source de PCB, et des études parallèles indiquent que le déclin des teneurs en PCB est associé à un déclin des effets biologiques.

L'étude continue des PCB dans la baie de Saglek a amélioré les connaissances sur le devenir des sédiments associés aux contaminants dans les milieux marins littoraux de l'Arctique et, plus particulièrement, sur leur transport vers des sites de dépôt extracôtiers.

Recommandations

- De meilleures connaissances sur les sources locales de contamination sont nécessaires pour interpréter les tendances spatiales et temporelles des contaminants, notamment des nouveaux POP qui se trouvent dans les produits de consommation et, par conséquent, dans les maisons et les décharges de toutes les collectivités arctiques.

6. Les connaissances sur les facteurs influant sur les concentrations et les tendances des POP se sont améliorées

Durant la période 2003-2011, d'importants progrès ont été réalisés au chapitre de la modélisation de la bioaccumulation des POP, et ce, dans les réseaux trophiques tant terrestres que marins. Ces études de modélisation éclairent les connaissances sur les voies et les processus qui influent sur l'accumulation des POP chez les espèces sauvages et les humains ainsi que sur les propriétés des substances chimiques susceptibles de se bioamplifier. Les études sur le réseau trophique lichen-caribou-loup ont montré qu'un plus grand éventail de composés organiques chlorés peuvent se bioamplifier dans les réseaux trophiques terrestres que dans les réseaux trophiques marins. Cela s'explique par la présence de deux espèces respirant à l'air libre dans le réseau trophique et par le fait que certaines substances chimiques à coefficients de partage octanol-air élevés sont moins efficacement éliminées dans l'air par les poumons que dans l'eau par les branchies, ce qui entraîne une absorption et une rétention nettes plus fortes chez les prédateurs terrestres supérieurs. La bioamplification du PFOS et des PFCA dans ce réseau trophique se produisait à un degré semblable à celui observé dans les réseaux trophiques marins. Chez les caribous et les orignaux, les SPFA constituaient les principaux POP dont les concentrations dans le foie dépassaient celles des PCB et des PBDE (ΣPFCA > PFOS > ΣPCB > ΣPBDE). Toutefois, les teneurs en nouveaux POP et PUC dans les échantillons de caribous, d'orignaux et d'autres animaux terrestres étaient bien inférieures à celles des mammifères marins, comme cela avait été observé pour les PCB et les pesticides OC dans des évaluations antérieures.

La probabilité que le réchauffement climatique influe sur les concentrations et les tendances des POP dans l'Arctique est devenue un axe de recherche important ces cinq dernières années. La série chronologique relativement longue portant sur les POP (par exemple : environ 18 années de prise de mesures continue dans l'air, 15 à 18 années d'échantillonnage et les 35 à 50 dernières années d'échantillonnage visant le touladi, la lotte, l'omble chevalier, les oiseaux de mer, l'ours blanc et le béluga) est maintenant disponible, et l'on commence à l'examiner afin d'y repérer des liens possibles avec les variables du climat (température, périodes libres de glace) ainsi qu'avec les paramètres liés aux changements de régime alimentaire et aux changements chez les espèces (rapports des isotopes stables du carbone et de l'azote, signatures des acides gras). Par exemple, on a constaté que les traceurs alimentaires (rapports des isotopes stables du carbone, profils des acides gras) expliquaient les tendances des ΣPCB et des ΣCHL chez les ours blancs de l'ouest de la baie d'Hudson, ce qui laisse croire qu'un changement dans le régime alimentaire des ours favorisant plutôt le phoque commun, le phoque du Groenland et le phoque barbu pourrait entraîner des concentrations de contaminants réelles plus élevées. L'ajustement des concentrations de ΣPCB et de ΣDDT dans les œufs des guillemots en fonction du niveau trophique n'a eu qu'une faible incidence sur le taux de déclin calculé de ces POP hérités du passé à l'île Prince Leopold, dans le détroit de Lancaster, mais a abaissé les taux de déclin à l'île Coats, dans le détroit d'Hudson, ce qui porte à croire que le changement de régime alimentaire des guillemots de l'île Coats a influé sur les tendances temporelles des contaminants dans cette colonie.

Le programme de surveillance des POP dans l'Arctique, en milieu tant abiotique que biotique, peut fournir des données précieuses permettant de définir l'empreinte de l'impact du réchauffement arctique (amplification arctique) sur le devenir environnemental des POP. Toutefois, il reste encore de grandes incertitudes concernant l'influence du changement climatique rapide sur le devenir et la mobilisation des POP, tant hérités du passé que nouveaux, dans l'Arctique. Bien que de récentes études aient révélé la revolatilisation des POP à partir des sites de stockage dans l'Arctique, par exemple les eaux arctiques, les sols, la neige/glace et le pergélisol, on ne connaît pas les quantités réelles nettes rejetées dans l'atmosphère. On ne sait pas non plus si l'on est en train d'assister à un renversement des puits et des sources dans l'Arctique.

Recommandations

- Il faut acquérir de meilleures données sur les paramètres clés de modélisation dans les réseaux trophiques, notamment l'efficacité de l'absorption à partir de l'eau, de l'air et des aliments, et, surtout, sur les taux de biotransformation qui jouent un rôle primordial dans la bioamplification.
- Les mesures dans les échantillons biologiques pourraient être mieux synchronisées avec les mesures dans l'atmosphère, où un plus grand nombre de substances chimiques sont analysées dans l'air (produits ignifuges bromés et autres nouveaux, siloxanes, PUC, etc.), à la fois dans l'Arctique canadien et dans le cadre d'autres programmes de mesure atmosphérique.

7. L'évaluation des effets biologiques demeure un défi

L'évaluation des effets des POP sur la santé du biote dans l'Arctique canadien pose beaucoup de défis en raison de facteurs tels que la faible exposition aux contaminants, l'accès limité à des échantillons frais, les difficultés de traiter les échantillons d'une manière adaptée aux besoins des paramètres sanitaires sur le terrain, et les connaissances limitées du cycle vital et de l'écologie de l'alimentation de nombreuses espèces. La réalisation d'études toxicologiques sur les espèces sauvages de l'Arctique reste difficile, mais de récents investissements dans la recherche dans le cadre du PLCN ont amélioré les connaissances sur les effets des contaminants persistants sur le biote de niveau trophique supérieur et aidé à élaborer de nouveaux outils biochimiques visant à évaluer ces effets.

Il existe peu de preuves selon lesquelles les POP ont des effets étendus sur la santé des animaux arctiques du Canada. Les meilleures preuves de tels effets chez les prédateurs supérieurs sont tirées d'études réalisées sur des ours blancs de l'est du Groenland et du Svalbard, de même que sur des Goélands bourgmestres du Svalbard, animaux qui sont beaucoup plus exposés à la plupart des POP que ceux de l'Arctique canadien. Toutefois, des études menées dans des sites contaminés par les PCB dans la baie de Saglek révèlent des déclins des concentrations de PCB dans les sédiments et le biote, et des effets biologiques du milieu marin au fil du temps, illustrant ainsi que les connaissances et les outils existants permettent d'évaluer les effets là où des taux d'exposition relativement élevés sont documentés. Les concentrations de PCB chez des petits de deux espèces, soit le chaboisseau à épines courtes et le Guillemot à miroir, dans la baie de Saglek, sont inférieures aux concentrations (1 000 ng g^{-1} poids humide) précédemment associées aux risques de perturbation de la reproduction et de la survie.

Les concentrations de ΣPCB chez le béluga et l'ours blanc dépassent la valeur toxicologique de référence à l'égard de l'immunotoxicité et de la perturbation endocrinienne (1,3 µg g^{-1} lipides) pour le phoque commun. Les concentrations moyennes de ΣPCB dans les œufs d'oiseaux de mer de l'Arctique canadien sont bien en deçà des seuils rapportés pour la mortalité des œufs et le succès d'éclosion des oiseaux piscivores (sauf le Goéland bourgmestre). Les concentrations hépatiques de PFOS chez les ours blancs dépassent les valeurs estimées sans effet observé, mais celles détectées chez les oiseaux et les phoques sont inférieures aux valeurs estimées sans effet observé par un ordre de grandeur.

Recommandations

- La mise au point, la validation et l'application de nouvelles méthodes de génomique fournissent un moyen puissant d'examiner la relation entre les paramètres physiologiques et les contaminants persistants. Ces méthodes devraient donc être appliquées à l'examen des effets subtils sur les animaux arctiques de niveau trophique supérieur.
- Pour les études sur les effets biologiques et les effets du changement climatique sur l'exposition aux POP, l'accent devrait être mis sur les multiples variables écologiques, biologiques et physiques (naturelles et anthropiques) à considérer lors de l'analyse de la contamination chez les espèces et de la comparaison des données entre les études.

***Langues officielles** – Le contenu suivant peut être fourni en français, sur demande. Veuillez communiquer avec le Secrétariat du PLCN à PLCN-NCP@aadnc-aandc.gc.ca.*

Acronyms and Abbreviations

Acronyms	Full name
ABL	Atmospheric Boundary Layer
AC-BAP	Arctic contamination and bioaccumulation potentials
ACP	Arctic Contamination Potential
AMAP	Arctic Monitoring and Assessment Programme
AMBBM	Arctic Mass Balance Box Model
AO	Arctic Oscillation
AOPWIN	A computer model for estimating atmospheric oxidation half-lives. Available in EPI Suite from the US EPA
BAP	Bioaccumulation potential
BCF	Bioconcentration factor
BCFWIN	A computer model for estimating bioconcentration factors in fish. Available in EPI Suite from the US EPA
BDL	Below detection limit
BETR-World Model	Berkeley-Trent Global Contaminant Fate Model
BIOWIN	A computer model to estimate biodegradation rates of chemicals. Available in EPI Suite from the US EPA
CAIPAP	Canadian Arctic Indigenous Peoples Against POPs
CanMETOP	Canadian Model for Environmental Transport of Organochlorine Pesticides
CCME	Canadian Council of Ministers of the Environment
CEMC	Canadian Centre for Environmental Modelling and Chemistry
CEPA	Canadian Environmental Protection Act
CFL	Circumpolar Flaw Lead
CLRTAP	Convention on Long-Range Transboundary Air Pollution
CMC	Canadian Meteorological Centre
COP	Conference of the Parties
CTD	Characteristic travel distance
CUP	Current use pesticide
D_{AW}	Air-water distribution coefficient
DEHM	Danish Eulerian Hemispheric Model
DEW	Distant Early Warning line – military radar facilities
DF	Digital Filtration Technique
DLCU	DEW-line Clean Up
DL-PCB	Dioxin-like polychlorinated biphenyl
DND	Department of National Defence
DOC	Dissolved organic carbon
D_{OW}	Octanol-water distribution coefficient
DRT	Distant residence time
DSL	Domestic Substance List
EAO	Eastern Arctic Ocean
EBC	Equivalent black carbon
EC	Environment Canada
EF	Enantiomer fraction
ENSO	El Niño-Southern Oscillation

Acronyms	Full name
EPI	Estimation Program Interface
F	Flux
FA	Fatty acid
FAV	Final adjusted value
FR	Fugacity ratio
FRs	Flame retardants
FTS	Flowthrough sampler
FWI	Fresh Water Institute
GAPS	Global Atmospheric Passive Sampling
GC	Gas chromatography
GFF	Glass fiber filter
GMP	Global Monitoring Plan
H or HLC	Henry's law constant
HENRYWIN	A computer model for estimating air-water partition coefficients and Henry's Law Constants. Available in EPI Suite from the US EPA
HPLC	High performance liquid chromatography
HPV	High Production Volume
IGS	Inert gas stripping
INAC	Indian and Northern Affairs of Canada
INCATPA	Intercontinental Atmospheric Transport of Anthropogenic Pollutants to the Arctic
IPCS	International Program for Chemical Safety
IPY	International Polar Year
IRPTC	the International Registry of Potentially Toxic Chemicals
ITK	Inuit Tapirit Kanatami
K_{AW}	Air/water partititon coefficient
K_{IA}	Surface/air sorption coefficient
K_{OA}	Octanol/air partition coefficient
KOAWIN	A computer model for estimating octanol-air partition coefficients. Available in EPI Suite from the US EPA
K_{OW}	Octanol/water partition coefficient
KOWWIN	A computer model for estimating octanol-water partition coefficients. Available in EPI Suite from the US EPA
K_{P}	Particle-gas partitioning coefficient
K_{PA}	Particle/air partition coefficient
$K_{Snow-Air}$	Snow-air partition coefficient
LDV	Literature-derived value
LCC	Local contaminants concerns
LOAEL	Lowest Observable Adverse Effects Level
LOD	Limit of detection – see also MDL
LOQ	Limit of quantification (usually defined as 10 x SD of blank values)
LROT	Long-range oceanic transport
LRTAP	Long-Range Transboundary Air Pollution
LRTP	Long range transport potential
LSER	Linear solvation energy relationship
MDL	Method detection limit (usually defined as 3 x SD of blank values)
MEDIA	Multicompartment Environmental Diagnosis and Assessment
MSC	Meteorological Service of Canada

Acronyms	Full name
MTC	Mass transfer coefficient
NAAO	North American Arctic Ocean
NAFTA	North American Free Trade Agreement
NAO	North Atlantic Oscillation
NCP	Northern Contaminants Program
NILU	Norwegian Institute for Air Research
NLET	National Laboratory for Environmental Testing
NOAA	National Oceanic and Atmospheric Administration
NOAEL	No Observed Adverse Effects Level
NPHP	North Pacific High Pressure
OECD	Organisation for Economic Co-operation and Development
OSPAR	The Convention for the Protection of the marine Environment of the North-East Atlantic
PAS	Passive Air Sampler
PB&T	Persistent, toxic and bioaccumulative
PCA	Principal component analysis
P_L	Liquid-phase vapour pressure
PML	Polar mixed layer
POC	Particulate organic carbon
POP	Persistent organic pollutant
P_{OV}	Overall persistence
pp-LFERs	Polyparameter linear free energy relationships
P_S	Solid phase vapour pressure
PUF	Polyurethane foam
QSPR	Quantitative structure-property relationship
RP-HPLC	Reverse phase high performance liquid chromatography
S_A	Solubility in air
SI	Stable isotope ratio ($\delta^{13}C$, $\delta^{15}N$)
SIP	Sorbent impregnated polyurethane
S_O	Solubility in octanol
SOC	Semivolatile organic compound
sp-LFER	Single-parameter linear free energy relationship
SSA	Specific surface area
S_W	Solubility in water
TEQ	Toxic equivalent
TL position	Trophic level, the position an organism occupies in a food chain
TSMP	Toxic Substances Management Policy
TSP	Total suspended particles
UN-ECE	The United Nations Economic Commission for Europe
UNEP	The United Nations Environment Programme
ΔH_{EX}	Enthalpy of air-surface exchange
ΔH_{SUB}	Enthalpy of sublimation
ΔH_{VAP}	Heat of vapourization
ΔS_{VAP}	Entropy of vapourization

CHAPTER 1

Introduction

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Photo: James Ford/ArcticNet

CHAPTER 1

Introduction

Coordinating authors: Derek Muir and Perihan Kurt-Karakus

1.1. POPs in the Canadian Arctic – Background, Program Design and Context

Contributors: Derek Muir and Perihan Kurt-Karakus

Indian and Northern Affairs of Canada (INAC), now Department of Aboriginal Affairs and Northern Development Canada (AANDC), established the Northern Contaminants Program (NCP) in 1991 in response to concerns about human exposure to elevated levels of contaminants in wildlife species that are important to the traditional diets of northern Aboriginal peoples (Figure 1.1). The program's key objective is ***"to work towards reducing and, where possible, eliminating contaminants in traditional/country foods, while providing information that assists individuals and communities in making informed decisions about their food use (INAC 2010)"***.

The primary goal of the NCP has been to develop a sound scientific basis by which (1) to monitor contaminant levels and trends in the Arctic environment and assess the influence of environmental change on exposure and effects of contaminants on Arctic ecosystems, (2) to support the assessment of Human Health risks with information on levels and trends of contaminants in traditional/country foods, (3) to produce scientific information that supports national and international chemical management initiatives to reduce or eliminate the sources of such chemicals.

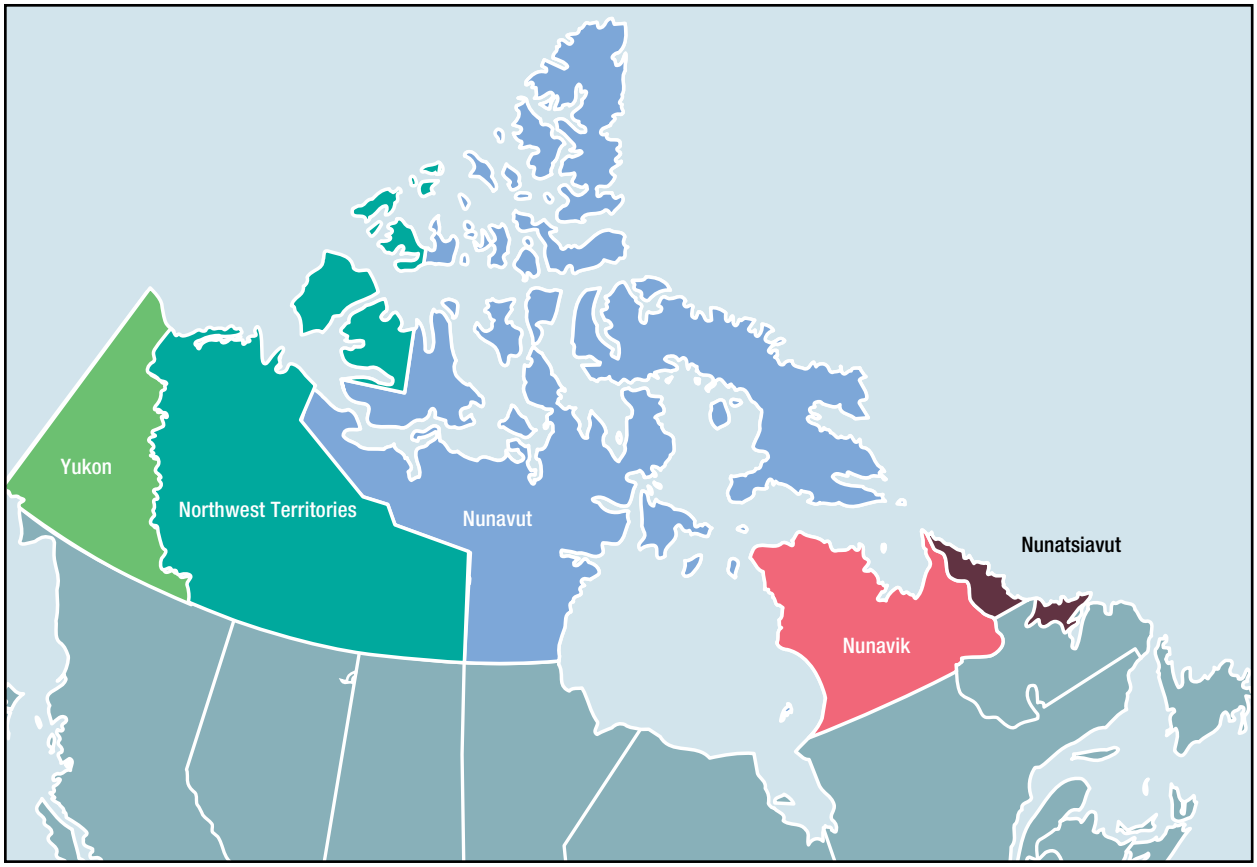

FIGURE 1.1

Five northern regions within the geographical boundary of the Northern Contaminants Program (NCP).

Under the first phase of the NCP (NCP-I, 1991–1996), research was focused on gathering the data required to determine the levels, geographic extent, and source of contaminants in the northern atmosphere, environment and its people, and the probable duration of the problem. Chlorinated industrial organic compounds, chlorinated pesticides, polycyclic aromatic hydrocarbons, metals, and radionuclides were the categories of contaminants studied. NCP-I assessed the sources, occurrence and pathways of contaminants entering the Arctic based on concentrations in biota and the humans results of NCP-I were summarized in the first Canadian Arctic Contaminants Assessment Report (Jensen et al. 1997).

The second phase of NCP (NCP-II, 1997–2002) focused upon questions about the impacts and risks to human health that might result from current levels of contamination in key Arctic food species as well as the temporal trends of persistent organic pollutants (POPs) of concern in key indicator Arctic species and air (Bidleman et al. 2003). The list of POPs in Phase III included approximately 100 "legacy" contaminants, including polychlorinated biphenyls (PCBs), and chlorobenzenes (CBz), as well as organochlorine pesticides (OCPs), and hexachlorocyclohexanes (HCHs) that were measured in most studies funded under NCP-II. Additionally, the first work began on brominated flame retardants (BFRs), polybrominated diphenyl ethers (PBDEs), short-chain chlorinated paraffins (SCCPs), and polychlorinated naphthalenes (PCNs) (Table 1.1).

The scientific studies conducted under NCP-I and NCP-II not only provided considerable understanding about the pathways of POPs to and within the Arctic, but they also provided the crucial underpinning to convince the international community to institute regional controls for persistent organic pollutants, first under the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP) and subsequently under the global United Nations Environment Programme (UNEP) Stockholm Convention on Persistent Organic Pollutants which was negotiated in the period 1997–2001. Canada was the first country to ratify the Stockholm Convention that came into force in 2004, requiring control of initially twelve POPs with additional POPs being added in subsequent years (since 2009, an additional 11 POPs have been added to the Annexes of the convention; See Section 1.3.2).

Photo: Derek Muir

TABLE 1.1. Reported major groups of POPs in environmental compartments of the Canadian Arctic in NCP-I (1991–96), NCP-II (1997–2002) and NCP-III or in other studies (2003–2011)

	Air		Seawater	Terrestrial Plants	Sediments	Invertebrates	Fish		Seabirds	Terrestrial Mammals	Marine Mammals		
	Active	Passive			Marine + lake	Marine + freshwater	Marine	Lake			Beluga Narwhal	Ringed seals	Polar Bears
PCBs[1]													
OCPs[2]													
HCB													
Other CBz													
PCDD/Fs													
PBDEs													
Other BFRs													
Endosulfan													
CUPs[3]													
PFOS													
Other PFASs													
Chlorinated paraffins													
Coplanar PCBs													
PCNs													
Musks													
Legend	NCP-I	NCP-II	NCP-III	NCP-I, -II, -III	NCP-I, -II	NCP-II,-III	No measurement						

[1] various congeners depending on the study; [2] DDTs, HCHs, chlordanes, toxaphene; [3] Current use pesticides such as dacthal, chlorothalonil, chlorpyrifos, pentachloroanisole (PCA, metabolite of pentachlorophenol), pentachloronitrobenzene, trifluralin.

The abiotic studies were instrumental in defining contaminant levels in abiotic arctic media, in revealing the pathways connecting these contaminants back to their sources and in defining many of the processes that make the Arctic particularly vulnerable to persistent, semi-volatile contaminants.

The combination of long-range transport, high levels of POPs accumulating in the food chain, and the fact that indigenous people relying on the foods may exceed exposure guidelines in some cases, make the Canadian Arctic a unique study area. These factors have led to arctic monitoring data on new chemicals being regarded as critical evidence when assessing the need to add new substances to the Stockholm and UNECE LRTAP Conventions. The NCP represents Canada's main contributor of contaminants related science to the circumpolar Arctic Monitoring and Assessment Programme (AMAP). The NCP, in partnership with Canadian indigenous peoples, works very closely with AMAP and other Arctic nations on collaborative monitoring and research activities, and on the preparation of scientific assessments. Moreover, partnership with the aboriginal people most affected by the contaminants, makes it a very special government-run program.

Under Phase III, a major change in the Environmental Monitoring was to design biological sampling programs with the goal of being able to detect a 10% annual change in contaminant concentration over a period of 10–15 years with a power of 80% and confidence level of 95% (INAC 2004). This involved moving to annual sampling for key species (beluga, ringed seals, seabirds, arctic char) and, for beluga and ringed seals, a reduction in the number of locations sampled. As of 2010-11 the goal was changed to a detection of a 5% change over a 10-15 year period (INAC 2010). Statistical power is discussed further in Section 4.2. Starting in 2009, analysis of high volume air sample extracts from Alert was reduced to one sample every month, archiving remaining sample extracts. The list of individual compounds analysed was also expanded

particularly for polyfluoroalkyl substances (PFASs), BFRs and current use pesticides (CUPs) (see Glossary for individual compounds).

1.2. Goals and Context for this Assessment

One of the main objectives related to monitoring POPs, which are already regulated under the Stockholm POPs Protocol and UNECE LRTAP convention, is to assess how the contaminant levels in the environment are reacting in response to actions taken under the conventions, and thus assess the effectiveness of these actions.

The overall goal of this report is to review and determine the current state of knowledge on the levels, trends, and biological effects of POPs in the physical and biological environment of the Canadian Arctic, specifically in the Yukon, Northwest Territories, Nunavut, Nunavik and Nunatsiavut (Figure 1.1). The focus is on all studies of POPs published or reported since approximately 2002, encompassing results not previously available for the assessments of the physical and biological environments published in 2003 (Bidleman et al. 2003, Fisk et al. 2003). Related goals are to identify knowledge gaps and make recommendations for the design of the Environmental Monitoring and Research component of the NCP.

In preparing the report, we have drawn on results from Phase III of the NCP (2003–2011) as well as on any other published or unpublished studies that the editors and contributing authors were aware of. The review and overview articles in the recent AMAP POPs assessment (de Wit and Muir 2010) are also a source of information for this report.

All of the NCP funded environmental monitoring studies participate in the NCP Quality Assurance (QA) Program which evaluates the performance of the laboratories generating the data on POPs. Chapter 6 describes the results of QA studies from 2004–2011. The quality of the data in non-NCP funded studies was considered on a case by case basis by the editors and contributing authors. No data needed to be excluded from the report because of QA concerns.

While the data for concentrations of POPs in wildlife are intended to support ongoing assessments of human health risks, this report does not directly consider human exposure or possible impacts of POPs on human health. NCP's Canadian Arctic Contaminants and Health Assessment report was published in 2009 (Donaldson et al. 2010). On the circumpolar level, AMAP published a human health assessment in 2009 as well (AMAP 2009).

1.3. Design of the POPs Environmental Measurements

1.3.1. The core monitoring program

The NCP "Blueprint", updated in 2010–2011 following an external review (INAC 2010), provides the broad outline of the environmental measurements program for POPs. The media and species monitored are present in Table 1.1 while sampling frequency and major locations are provided in Table 1.2 and

TABLE 1.2. Overview of NCP POPs monitoring program media 2003–2011

Media	Locations	Sampling years[1]	Frequency
Air – hi volume	Alert	1992–present	7 day continuous
Air – passives	Up to 7 arctic/sub-arctic locations	2005–present	Quarterly continuous
Seawater	Beaufort Sea	2008	Single study
Arctic char (searun)	Cambridge Bay, Pond Inlet , Nain	2004–2011	Annual
Arctic char (landlocked)	Lakes Resolute, Char, Amituk and Hazen	2004–2011	Annual
Burbot	Fort Good Hope, Great Slave Lake West Basin and East Arm	2004–2011	Annual
Lake trout	Lake Laberge, Kusawa Lake, Great Slave Lake West Basin and East Arm	2004–2011	Annual
Caribou	Northern Yukon and Southwestern Nunavut (Porcupine and Qamanirjuaq herds)	2006, 2008	Single study
Ringed seals	Arviat, Resolute, Sachs Harbour and other locations to 2009	2004–2011	Annual
Beluga	South Beaufort, Cumberland Sound, West Hudson Bay	2004–2011	Annual
Polar bears	West Hudson Bay and other locations	2004–2011	Annual
Seabirds (thickbilled murre, blacklegged kittiwakes	Prince Leopold Island, Coats Island	2004–2011	Annual

[1]All programs include data from earlier years based on existing data or reanalysis of archived samples

Figure 1.1 respectively. In addition to the core long-term monitoring program described in Table 1.2, NCP has supported many short-term projects which include the measurements of POPs, particularly in food webs.

1.3.2. Defining "New POPs"

A major goal of the contaminants monitoring program is the identification of "new POPs". For the purposes of this assessment, we broadly define these as any organic chemical not in the original "dirty dozen" listing from the Stockholm Convention as of 2004. The general classes of these chemicals are provided in Table 1.1 and Table 1.3 provides a more detailed list of chemicals that have been included in contaminant measurements over the period 2003–2011. Not all have been detected and many may never be classified under the Stockholm Convention. Among the chlorinated organics, PCNs are now widely measured and chlorinated paraffins have been determined in seals, seabirds, and beluga. Measurements of CUPs such as dacthal, pentachloronitrobenzene (PCNB) and endosulfan, which are reported in air and seawater (see Chapter 3, Section 3.1.4.4.), are limited in marine biota.

TABLE 1.3. "New POPs" surveyed in Arctic abiotic and biological samples during the period 2003–2011[1].

Class	Chemical name	Abbreviation	Air and sea-water	Seals	Sea-birds	Beluga	Polar bears
OC	3,4,5-trichloroveratrole	TrCV	✓	nd			
OC	3,4,5,6-tetrachloroveratrole	TeCV	✓	nd			
OC	hexachlorobutadiene	HCBD		✓			
BFR	hexabromocyclododecane	HBCD	✓	✓		✓	
BFR	allyl 2,4,6-tribromophenyl ether	ATE		nd			
BFR	2-bromoallyl 2,4,6-tribromophenyl ether	BATE		nd			
BFR	pentabromobiphenyl	BB-101		✓			✓
BFR	bis(2-ethyl-1-hexyl)tetrabromophthalate	BEHTBP		✓		✓	
BFR	1,2-bis(2,4,6-tribromophenoxy)ethane	BTBPE		✓			
BFR	2,3-dibromopropyl-2,4,6-tribromophenyl ether	DPTE		nd			
BFR	2-ethyl-1-hexyl-2,3,4,5 tetrabromobenzoate	EHTeBB		nd		✓	
BFR	hexabromobenzene	HBB		✓			✓
BFR	octabromotrimethylphenylindane	OBIND		nd			
BFR	pentabromobenzyl acrylate	PBBA		nd			
BFR	pentabromobenzene	PBBe		nd			
BFR	2,3,4,5,6-pentabromoethylbenzene	PBEB		nd			
BFR	pentabromotoluene	PBTo		nd			
BFR	2,3,5,6-tetrabromo-p-xylene	pTBX		nd			
BFR	tetrabromo-o-chlorotoluene	TBCT		nd			
BFR	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	TBECH		nd		✓	
BFR	di-hepta-brominated diphenyl ethers	PBDEs	✓	✓	✓	✓	✓
BFR	octa-, nona, deca BDEs	PBDEs	✓	✓	✓		
NP	methoxy-brominated diphenyl ethers	MeO-BDE		✓		✓	
CFR	anti-Dechlorane Plus	anti-DP		nd			
CFR	syn-Dechlorane Plus	syn-DP		nd			
CFR	shortchain chlorinated paraffins	SCCP		✓	✓	✓	
CFR	chlorinated naphthalenes	PCNs	✓	✓	✓	✓	✓
CUP	dacthal	DCPA	✓	✓			
CUP	chlorothalonil	CHT	✓				
CUP	chlorpyrifos	CPF	✓				
CUP	pentachloronitrobenzene	PCNB	✓				

TABLE 1.3. "New POPs" surveyed in Arctic abiotic and biological samples during the period 2003–2011[1]. *(continued)*

Class	Chemical name	Abbreviation	Air and sea-water	Seals	Sea-birds	Beluga	Polar bears
CUP	pentachlorophenol/anisole	PCA	✓	✓		✓	
CUP	trifluralin		✓				
CUP	tefluthrin		✓				
CUP	endosulfan	Endo	✓	✓		✓	
CUP	endosulfan sulfate	ES	✓	✓		✓	
PFAS	perfluorocarboxylates	PFCAs	✓	✓	✓	✓	✓
PFAS	perfluoroalkylsulfonates	PFSAs	✓	✓	✓	✓	✓
PFAS	perfluorotelomer alcohols	FTOHs	✓				
PFAS	perfluorosulfonamido-alcohols	FTSOHs	✓				
Si	cyclic methyl siloxanes	D3 - D6	✓				
Si	linear methyl siloxanes	L3-L5	✓				

[1]nd=not detected; ✓=detected;. OC=organochlorine, BFR=brominated flame retardant; CFR=chlorinated flame retardant; CUP=current use pesticide; NP=natural product; PFAS=poly- and perfluoroalkylsubstances; SI=siloxanes

1.4. Canadian and International Policy Initiatives Related to POPs

Canada has a long history of regulation and management of toxic substances under the *Canadian Environmental Protection Act* (CEPA), the *Pest Control Products Act*, and the *Fisheries Act* as well as under provincial legislation. The update of CEPA in 1999 required the screening of all 23,000 substances on the Canadian Domestic Substances List (DSL). The categorization of over 10,000 organic chemicals on the DSL by 2006 contributed to the bans on "penta" and "octa" brominated diphenyl ethers and perfluorooctane sulfonate (PFOS), which had been on the DSL since its creation in 1986, as well as to the identification of many other chemicals in commerce that were potentially persistent, bio-accumulative and toxic (PB&T). The science based criteria for evaluating whether chemicals were potential POPs were first articulated in the Toxic Substances Management Policy (TSMP) (Environment Canada 1995). The major goal of this policy was to "virtually eliminate" PB&T substances and to manage other toxic substances throughout their life cycle. The TSMP defined, for the first time, a half-life in air of 2 days or more as being indicative of potential for "atmospheric transport to remote regions such as the Arctic". This criterion was later adopted by the Stockholm Convention to define POPs and is a major characteristic which distinguishes such chemicals from other toxic substances.

The federal government has supported research to understand sources of POPs, POPs vs. ecosystem interactions, processes within the ecosystems, ultimate fate of POPs and their effects on the environmental compartments, living organisms and humans through initiatives such as the "Green Plan" (1990–1995), which funded NCP Phase 1, the Toxic Substances Research Initiative (TSRI) (1999–2003), the Pesticide Science Fund (2003–2005), the Chemicals Management Plan (CMP) (2008–2011) as well as with the Strategic Grants program of the Natural Sciences and Engineering Research Council. Under these programs the ability to detect POPs in atmospheric samples, to track the accumulation of these chemicals up the food chain, to assess biological effects as well as human exposure, has been improved and refined. These programs have benefited the NCP. For example, under the TSRI, the first studies of PBDEs and of PFOS and other perfluorinated chemicals in the Canadian environment were undertaken. Under the CMP, the environmental fate and distribution of many other chemicals that meet the characteristics of POPs under the TSMP criteria have been studied, including other brominated flame retardants and cyclic siloxanes, which are discussed in this report.

The recognition during the late 1980s and early 1990s that POPs can reach remote locations and have a tendency to accumulate in these cold regions, i.e. polar regions and high altitudes, biomagnify in living organisms in these regions and can reach levels of concern in both humans and top predators far from the sources, led to international policymaking efforts to develop legally binding instruments. POPs are currently regulated globally under the Stockholm Convention and in the UNECE region under the

POPs protocol of the LRTAP Convention. Trade and movement of wastes and products containing POPs are globally regulated under the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.

The Executive Body of the LRTAP Convention adopted its Protocols on Persistent Organic Pollutants and Heavy Metals (including mercury) 24 June 1998 in Aarhus (Denmark). The LRTAP POPs protocol entered into force on 23 October 2003. As of March 2011, 31 countries are parties to the POPs protocol, 21 of which ratified it, including Canada (which ratified 24 June 1998) (UNECE 2012). The goal of the POPs Protocol is "to control, reduce, or eliminate discharges, emissions, and losses of persistent organic pollutants" (Article 2). To date, the POPs protocol covers a total of 23 chemicals. Some are subject to outright bans on production and use (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl (HBBP), mirex, and toxaphene) while others are scheduled for elimination at a later date (DDT, heptachlor, hexachlorobenzene, and PCBs). Presently, the protocol severely restricts use of DDT, HCHs (including lindane) and PCBs and, furthermore, emissions of polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), and hexachlorobenzene are to be reduced to below 1990 levels (UNECE 1998).

The United Nations Environment program (UNEP) began negotiations to reduce or eliminate emissions of twelve POPs on a global scale in Montreal, in June 1998, with the aim of including all countries in a single global agreement. The Stockholm Convention on Persistent Organic Pollutants was then adopted on 22 May 2001 and entered into force on 17 May 2004. It is the only legally binding global agreement, with 152 signatories and 179 parties as of July 2013 (UNEP 2013). Canada was instrumental in the negotiations of the Stockholm Convention, and was the first country to ratify it on 23 May 2001. The Stockholm Convention initially included the same 12 compounds covered by the UNECE LRTAP POPs Protocol. The amendments to list an additional 11 substances in Annexes A, B and/or C of the Stockholm Convention, have been adopted by the Conference of the Parties of the Convention (COP).

These new POPs are; α- and β-HCH, chlordecone, hexabromobiphenyl (HBBP), commercial pentabromodiphenyl ether and octabromodiphenyl ether, lindane, pentachlorobenzene, perfluorooctanesulfonate (PFOS) and related products, endosulfan and hexabromocyclododecane (HBCDD) (Table 1.4). HBCDD was listed in Annex A3 of the Convention in May 2013, with time-limited exemptions for production and use in expanded polystyrene and extruded polystyrene insulation foams in buildings. Short-chain chlorinated paraffins (SCCP) are still in varying stages of the review process for a POPs classification decision. Additional substances have been recently (2011-2013) added to the review process: hexachlorobutadiene, pentachlorophenol, decabromodiphenyl ether, dicofol, and chlorinated napthalenes.

One of the main objectives related to monitoring POPs is to assess how the contaminant levels in the environment are reacting in response to actions taken under the Stockholm Convention, and to assess the effectiveness of these actions. The Global Atmospheric Passive Sampling (GAPS) program (Harner et al. 2006), funded by Environment Canada, is a significant component of the Global Monitoring Plan of the Stockholm Convention and includes several Arctic air monitoring sites (Chapter 3, Section 3.15).

TABLE 1.4. Chemicals regulated under the Stockholm Convention and UNECE LRTAP Convention

Substance	STOCKHOLM CONVENTION				UNECE (LRTAP Convention		
	Originally included	Included by COP (May 09, '11, '13)	Annex	Under review	Originally included	Recognized as a POP[a]	Under review
Aldrin[1]	+		A		+		
Chlordane[1]	+		A		+		
Dieldrin[1]	+		A		+		
Endrin[1]	+		A		+		
Heptachlor[1]	+		A		+		
Hexachlorobenzene (HCB)[3]	+		C		+		
Mirex[1]	+		A		+		
Toxaphene[1]	+		A		+		
Polychlorinated biphenyls (PCBs)[3]	+		C		+		
Dichlorodiphenyltrichloroethane (DDT)[1]	+		B		+		
Polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs)[3]	+		C		+		
Chlordecone[1]		+	A		+		
Hexachlorocyclohexanes (HCHs)[1,3]		+	A		+		
Hexabromobiphenyl (HBBP)[2]		+	A		+		
Polycyclic aromatic hydrocarbons (PAHs)[3]					+		
Pentabromodiphenyl ether (PentaBDE)[2]		+	A			+	
Octabromodiphenyl ether (OctaBDE)[2]		+	A			+	
Pentachlorobenzene (PeCB)[1,2]		+	A and C			+	
Perfluorooctane sulfonate (PFOS) (Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride)[2]		+	B			+	
Hexachlorobutadiene[2,3]				+		+	
Polychlorinated naphthalenes (PCNs)[2]				+		+	
Short-chain chlorinated paraffins (SCCP)[2]				+		+	
Endosulfan[1]		+	A				+
Hexabromocyclododecane (HBCDD)[2]		+	A				+
Dicofol[1]				+			+
Trifluralin[1]							+
Pentachlorophenol (PCP)[1]				+			+

[1] Agricultural chemical; [2] Industrial chemical; [3] By-product; [a]UNEP ECE 6th meeting of the Task Force in Vienna, Austria in 4-6 June 2007

There are also many regional initiatives which result in monitoring, assessment and regulation of POPs. The North American Agreement On Environmental Cooperation has supported initiatives such as the modelling of atmospheric transport of dioxins to the Arctic and a study of the status of PCBs in Mexico, the USA and Canada. Under this agreement Canada, Mexico and the United States have developed regional action plans on lindane, chlordane, DDT and PCBs. In Europe, the Oslo and Paris Commission OSPAR Convention for the protection of the Northeast Atlantic marine environment (involving Western European governments and the European Commission) and the Helsinki Convention for the protection of the Baltic Sea (involves Baltic Sea states), maintain extensive monitoring programs that include POPs and other PB&T substances and which are models for the design of NCP monitoring.

Perhaps the most important regional initiative related to POPs in the Arctic is the Arctic Council, an intergovernmental forum that promotes cooperation, coordination and interaction among the 8 circumpolar countries. The Arctic Council has supported work on POPs through the AMAP working group, as previously mentioned, as well as via the Arctic Contaminants Action Program (ACAP) working group. ACAP activities have included inventories of PCBs in Russia.

1.5. The Aboriginal Perspective

Contributor: Eva Krümmel

1.5.1. How are Aboriginal peoples affected?

The contaminant levels in the environment, which are described in this report, affect Aboriginal peoples particularly through direct consumption of country food, as well as through the cultural, social and economic significance of hunting and sharing country food. Country food in northern communities consists of fish and marine mammals such as seals, whales and polar bears, as well as terrestrial animals such as caribou, ptarmigan, geese, eggs, and a selection of berries. As described in later chapters, although many contaminant concentrations in the Arctic environment have declined in recent years, some of the contaminant concentrations in animals consumed as country food are still high enough to exceed consumption guidelines. Due to their high reliance on country foods, some northern Aboriginal peoples have been found to have elevated PCBs and mercury based on measurements of cord blood and mother's milk (AMAP 2009, Donaldson et al. 2010). Possible health effects related to contaminant exposure include endocrine disruption, neurobehavioral effects, liver toxicity, and reproductive effects (Van Oostdam et al. 2005, AMAP 2009, Donaldson et al. 2010,). Due to possible developmental health effects of the contaminants, pregnant mothers and the developing child are especially vulnerable.

However, since country foods are rich in healthy fatty acids (such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) omega-3 fatty acids), as well as nutrients (such as selenium), which are thought to protect against the harmful effects of contaminants, the consumption of country foods is generally promoted. Nevertheless, Deutch et al. (2007) recently recommended not to increase Greenlandic country food consumption beyond the current average level of 20–25% (by solid weight, corresponding to a relative energy contribution between 9–14%), because of the possible negative health effects of contaminants. In northern Canada, country food consumption may attribute up to 30% of the overall energy consumed, but can be as low as 4% for children (AMAP 2009).

The avoidance or reduction in country food consumption can exacerbate the problem of an already occurring nutrition transition, further adding to the food insecurity already experienced in northern communities (Egeland et al. 2010). Nutrition transition is a global phenomenon and has been described as the enhanced replacement of nutritious, traditional diets with low quality pre-processed and 'junk' foods (Damman et al. 2008). Many studies have reported a decline in country foods in northern communities throughout Canada particularly among the younger generations (Johnson-Down and Egeland 2010). Although the decline in country foods is often accompanied by a decline in contaminant exposure and associated health risks (Deutch et al. 2007), it also decreases the intake of many essential nutrients and fatty acids, thereby increasing the risk for health problems such as coronary heart disease, which was previously rarely found in Arctic Indigenous peoples (Bersamin et al. 2006). A more sedentary life style, less activity due to decreased hunting, and higher intake of pre-processed foods rich in sugars and saturated fatty acids also contribute to a rising prevalence of obesity and related diseases, including diabetes among northern Aboriginal peoples (Chen et al. 2009, Johnson-Down and Egeland 2010). On the other hand, there is mounting evidence that the contaminants which are currently found in country food may also cause an increased risk in diabetes (Lee et al. 2006, Everett et al. 2007, Carpenter 2008, Rignell-Hydbom et al. 2009, Lee et al. 2010,

Grandjean et al. 2011). One study, however, suggested that the consumption of some fish species may have a protective effect (Philibert et al. 2009), which further highlights the complexity of the problem and the need for additional investment in the issue of food security.

Apart from the nutritional value, hunting and the consumption of country food is part of a culture reflecting the connection with and reliance on the environment which Arctic Aboriginal peoples have developed over millennia. It is, therefore, not only manifested in cultural and social practices and important for health and well-being, but is also part of northern Aboriginal peoples' identity. Recognizing the importance of country food for northern Aboriginal people, local health officials often try to promote country foods low in contaminants, such as Arctic char, caribou and seal meat. However, communication of such detailed information is difficult to realize in a successful manner (Furgal et al. 2005, Myers and Furgal 2006). In addition, the availability, abundance and accessibility of given food items varies greatly in the north, and depends on season, animal migration, population densities, and other factors. The overall goal, therefore, is to diminish contaminant concentrations in the environment such that they do not pose any health risk, no matter what and how much is consumed or by whom.

1.5.2. New threats

Currently, the Arctic is experiencing significant changes due to climate warming, with some scientists even predicting ice-free summers as early as 2013 (Whelan et al. 2007). Climate change will have some direct and indirect implications for contaminant cycling, deposition and processing (Grannas et al. 2013, Macdonald et al. 2005, Noyes et al. 2009). New challenges will also arise from increased development, transportation and associated local contaminant sources. These topics are being dealt with in later sections of this report. Local sources of contaminants also include those associated with a different way of life connected to globalization and increased development in the Arctic. Changes in life style in the Canadian Arctic are still of a very recent nature. The government implemented relocation policies in the early 1960's and caused the originally nomadic Aboriginal peoples living in the Arctic to settle down (Damman et al. 2008). Within only two generations, Aboriginal Arctic peoples went from the use of temporary shelters and living off the land with very limited contact to the outside world to remaining in stationary houses and using stoves, fridges, TVs and computers, resulting in an increased reliance on supplies brought in from the south. The new life style also introduced new sources of contaminants: plastics with compounds such as phthalates and bisphenol-A, furniture and electronic equipment which contain flame retardants and perfluorinated compounds, cosmetics and antibacterial soaps containing a large variety of chemicals, etc. Dump sites in the Arctic are already a local source of PBDEs, as described in Chapter 3, Section 3.4.2.1, and municipal landfill leachates have been identified as a significant source for new and emerging pollutants (Eggen et al. 2010). Future studies and efforts towards a clean Arctic environment will need to take these additional exposures from local sources into account.

1.5.3. Importance of international action with regards to contaminants

The previous section explained in detail the international efforts to reduce contaminant concentrations in the Arctic environment. Global treaties are of paramount importance for Arctic Aboriginal peoples, especially because the contaminants that have been found to be problematic in the Arctic today have largely not been used or produced locally but have undergone long-range transport (mostly from industrialized regions in North America, Europe and Asia) and biomagnified up the food chain due to their persistence. This was recognized when the Stockholm Convention was negotiated, as described in more detail in the NCP-II assessment report ("Knowledge in Action", Section 6.2.5.). Arctic Aboriginal peoples, working in partnership with the Canadian government, had a significant influence on the negotiations of the Stockholm Convention. The Arctic Aboriginal peoples also participating in the NCP (Inuit, Dene, Metis and Yukon First Nations) had formed a coalition called Canadian Arctic Indigenous Peoples Against POPs (CAIPAP), financed through the NCP and Environment Canada (Fenge 2003). The success of the engagement of Arctic Aboriginal peoples in the Stockholm Convention is particularly visible by the specific mention of the vulnerability of the Arctic and its people in the preamble of the treaty. The Government of Canada took the commitment to its stakeholders one step further by inviting non-governmental organizations (NGO's) to be part of their delegation during the negotiation process. This included representatives from one Aboriginal organization, one environmental organization, and one representative from industry and this practice has continued since then.

Photo: Isabelle Dubois/ArcticNet

As described in later sections in this report, the Stockholm Convention has been quite successful. Some of the legacy contaminants have declined significantly in the Arctic since the creation of the treaty. Furthermore, new contaminants have been added to the list, and negotiations to add more chemicals are ongoing.

However, the process of adding new compounds is lengthy and especially difficult if the chemical to be added is widely used, with only limited alternatives available or regarded as cost effective. The POP Review Committee (POPRC) meets every year to review proposals for new chemicals that have been submitted for addition to the Stockholm Convention. The screening process for the addition of new chemicals includes four criteria that must be fulfilled for the chemicals to be added to the Stockholm Convention: The chemical needs to be (1) persistent, (2) bioaccumulative, has to have (3) potential for long-range transport, and (4) adverse effects to human health or the environment. Further, under Article 8 ("Listing of chemicals in Annexes A, B and C"), paragraph 7, the Stockholm Convention states that "…the Committee decides:

(a) That the chemical is likely ***as a result of its long-range environmental transport*** *to lead to significant adverse human health and/or environmental effects such that global action is warranted, the proposal shall proceed." (Emphasis added)*

The latter paragraph, in particular, regularly leads to difficult negotiations where the argument is often made that a chemical has been found in too small concentrations in the Arctic to be of a health threat, and therefore should not be listed. This argument, of course, is inconsistent with the acknowledgement in the Stockholm Convention preamble that "*precaution underlies the concerns of all the Parties and is embedded within this Convention*", which attempts to prevent a health risk from developing in the first place. It also does not take into account the potential of synergistic or cumulative impacts of the complex mixture of contaminants found in the Arctic.

Furthermore, the convention states under Article 3, Paragraph 3, that:

"Each party…shall take measures to regulate with the aim of preventing the production and use of new pesticides or new industrial chemicals which, … exhibit the characteristics of persistent organic pollutants."

Nevertheless, no such preventative measures seem to be undertaken sufficiently by the parties. To the contrary, many of the chemicals that were listed after banning the original 12 "legacy" POPs (4), have been introduced or scaled up in production and use to (at least partly) replace the ones that were banned (for example HBCDD and other BFRs replaced PentaBDEs in many uses). In this way, the

Stockholm Convention is a purely reactive measure, and it is a constant effort to keep up with research and analysis with regards to newly introduced chemicals that are heavily produced and used globally. In many cases, it takes several years before adequate techniques for analysis have been developed sufficiently to show that chemicals have made it into the Arctic, and it may take some additional years to show that those chemicals pose a risk to health and the environment. This is especially problematic in the case of highly persistent chemicals such as perfluorinated substances, which are not known to break down under any naturally occurring environmental conditions.

Another weakness of the Stockholm Convention is the option for restricted uses. When the Convention was created, Article 4 for specific exemptions was included particularly for DDT, because it was seen as a chemical of great importance for human health in the fight against malaria. While concentrations of DDT in the environment have been declining recently, it can be expected that they will remain at a stagnant level and may even increase again with possible enhanced uses, unless the use and production of DDT are completely eliminated. Although DDT has been phased out by many countries since its inclusion in the Stockholm Convention, it continues to be used in some African countries, and recently several other African countries have indicated at the Stockholm Convention COP in May 2009 that they intended to reintroduce the use of DDT. A recent study in Mesoamerica found some high DDT concentrations in children, particularly in Mexico, where DDT was used until the year 2000 (Pérez-Maldonado et al. 2010). Furthermore, DDT/DDE ratios in some areas and matrixes were found to be high, pointing to recent uses, and the authors point out that DDT is still available in some warehouses for general pest control (Pérez-Maldonado et al. 2010).

While CAIPAP never supported a ban of DDT that would put lives at risk in other parts of the world (Fenge 2003), alternatives do exist and need to be more utilized and heavily promoted. In the case of perfluorinated substances, an extensive list of use exemptions has been created, not because of its importance to human health, but largely out of rather short-term economical considerations. Since long-term economical considerations of human and environmental health consequences are either very difficult or even impossible to assess, emphasis is usually placed on the cost of possible alternatives, which are in many cases higher compared to the chemical in question.

As with DDT, the ongoing restricted uses will hamper efforts to eliminate these substances in the environment. In the case of perfluorinated substances, this is of particular concern because they are extremely persistent and do not break down unless they are incinerated at very high temperatures and under very specific and controlled conditions.

These examples show that efforts to eliminate all uses for chemicals in the Stockholm Convention are important to prevent resurgence and achieve elimination of the contaminants. As mentioned above, the Arctic is currently undergoing quite rapid changes, and local sources of contaminants will be more abundant and likely make it more difficult in the future to distinguish between locally originating versus long-range transported pollutants. Further, as recently published by Statistics Canada (Bushnik et al. 2010), non-persistent chemicals such as bisphenol-A can be found in significant levels in over 90% of the Canadian population and are becoming a threat due to permanent exposure to the chemical, which is widely used in plastic products. Since the life style of Arctic Aboriginal peoples today is much closer to that of southerners than it used to be 50 years ago, a similar exposure to these chemicals can be expected, adding to the overall contaminant loading of Arctic Aboriginal peoples. As contaminants in daily products also undergo long-range transport in the widest sense, international agreements such as the Stockholm Convention may have to take those chemicals into account in the near future.

Finally, it should be mentioned that the Stockholm Convention is still lacking a compliance mechanism which would hold parties accountable if they fail to adhere to the provisions regulated in the treaty. Negotiations for a compliance mechanism have been long and difficult, and will likely continue past COP6 in 2013. In order to ensure the Stockholm Convention's success in the long-term and allow for protection of the Arctic environment and Arctic Aboriginal peoples in the future, a strong and meaningful compliance mechanism in the treaty will be critical.

1.6. Conclusions and Recommendations

- A major goal of the Arctic contaminants studies on POPs is the identification and assessment of the spatial and temporal trends of "new POPs" which we have defined broadly as any organic chemical not in the original "dirty dozen" listing from the Stockholm Convention.
- The Stockholm Convention has been very successful in reducing levels of many legacy POPs in the Arctic. However, the process for adding chemicals is slow and it is unclear whether the Convention can respond to new contaminant threats.
- The information in Chapters 2 to 5 draws on the peer reviewed literature where possible but also on other published or unpublished studies that the editors and contributing authors were aware of. Thus some results and conclusions in the following chapters must be regarded as preliminary.

Photo: Eric Loring

- This expansion of measurements of new organic contaminants in the NCP Phase III presents challenges for those laboratories involved in measurement programs due the analytical burden (i.e. method development) and raises questions about what criteria should be used to decide on the need for continued measurements of specific legacy and "new"POPs.
- The results on POPs from the Canadian Arctic are important for chemical managements in Canada and internationally. A lack of timely data can significantly delay national or international efforts to regulate chemicals, which is particularly of importance for those that are produced and used in high volumes. There needs to be better coordination between the regulatory/policy development requirements for information, scientific programs which fund the science, and scientists who are conducting the work.
- Comparisons with other regions of the Arctic or with mid-lattitude measurements of POPs are limited because the overall goal of this report is to review and determine the current state of knowledge on the levels, trends, and biological effects of POPs in the physical and biological environment of the Canadian Arctic, specifically in the Yukon, Northwest Territories, Nunavut, Nunavik and Nunatsiavut
- This report does not directly consider human exposure or possible impacts of POPs on human health as these have been assessed separately.
- The NCP partnership with Aboriginal peoples has been very successful so far and that this work needs to be continued.
- There is a need of better interdisciplinary cooperation to link general changes in the Arctic (for example those related to climate change) with impacts on contaminant cycling, deposition, bioaccumulation, and toxicity (for example through multiple stressors, and complex contaminant mixtures as found in the Arctic environment).
- There is a need for research groups/programs conducting contaminants research in the Canadian Arctic to integrate their resources and collaborate so that these new challenges can be met efficiently.

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CHAPTER 2

Properties, Sources, Global Fate and Transport

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Photo: Philippe Bourseiller/ArcticNet

CHAPTER 2

Properties, Sources, Global Fate and Transport

Coordinating authors: Terry Bidleman and Perihan Kurt-Karakus

2. 1. Physicochemical Properties of POPs

Coordinating authors: Terry Bidleman and Perihan Kurt-Karakus

2.1.1. Introduction

Part II of the second Canadian Arctic Contaminants Assessment Report (CACAR-II) began with a section on "Physicochemical Properties of Persistent Organic Pollutants", which identified key physicochemical (pchem) properties, provided the rationale for their measurement or prediction and tabulated literature citations for chemicals that are of concern to the NCP (Bidleman et al. 2003). The section also discussed temperature dependence of pchem properties and their applications to describing partitioning in the physical environment.

There is, and will continue to be, emphasis on predictive approaches to screening chemicals for persistence, bioaccumulation and toxic (PB&T) properties, as well as long-range atmospheric transport (LRAT) potential (Brown and Wania 2008, Czub et al. 2008, Fenner et al. 2005, Gouin and Wania 2007, Howard and Muir 2010, Klasmeier et al. 2006, Matthies et al. 2009, Muir and Howard 2006). This has created the need for determining pchem properties of new and emerging chemicals of concern.

Predicting gas exchange cycles of legacy persistent organic pollutants (POPs) and new and emerging chemicals of concern places a high demand on the accuracy of pchem properties, particularly the air/water partition coefficient, K_{AW}. Hexachlorocyclohexanes (HCHs) in Arctic Ocean surface waters

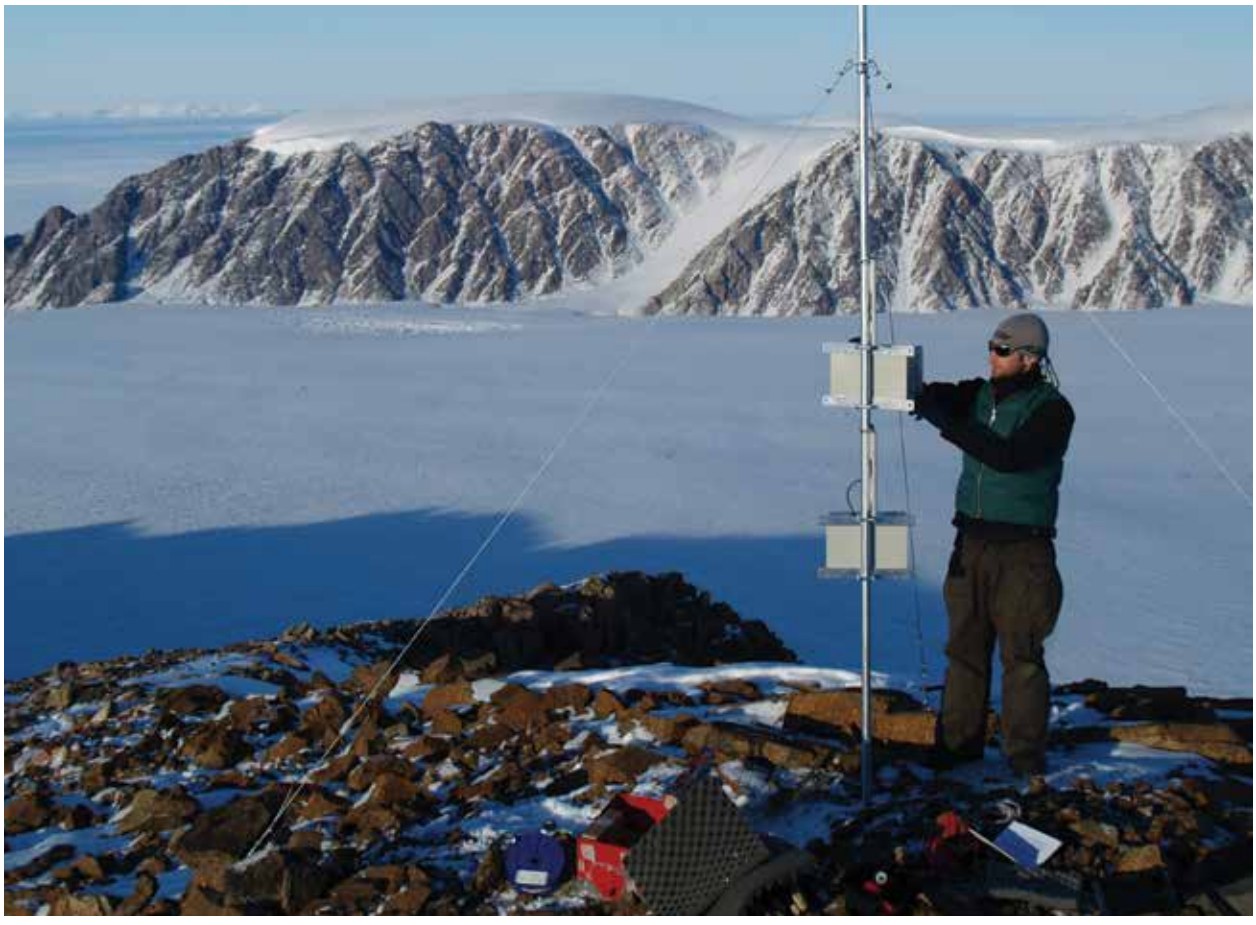


Photo: Alex Gardner/ArcticNet

are close to air-water equilibrium, with excursions toward net volatilization or deposition that vary with location and season (Hargrave et al. 1993, Jantunen et al. 2008a, Lohmann et al. 2009, Su et al. 2006, Wong et al. 2011) while hexachlorobenzene (HCB) (Lohmann et al. 2009, Su et al. 2006, Wong et al. 2011) and some current use pesticides (CUPs) (Wong et al. 2011) are undergoing net deposition. The predicted Arctic Contamination Potential (ACP) for persistent organic chemicals is strongly influenced by ice cover due to its effect on air-water gas exchange (Meyer and Wania 2007).

Many advances have taken place and numerous papers have been published since CACAR-II, which present new measurements and predictions of pchem properties. This section does not attempt to provide a comprehensive review of the field, or to compile pchem properties from the many studies. The approach taken is to highlight the reports which are most relevant to polar science, particularly in areas of improving reliability of pchem properties for POPs, improving experimental techniques and comparing predictive methods. The section ends with a discussion of polyparameter linear free energy relationships (*pp*-LFERs), which goes beyond partitioning descriptions based on single pchem properties by taking into account specific chemical interactions that can take place in air-surface and water-surface exchange processes. A detailed list of chemical names and nomenclature are provided in the Glossary.

2.1.2. Key physicochemical properties and interrelationships

Key properties for describing phase partitioning in the environment are the three solubilities (mol m^{-3}) of liquid-phase chemicals in air, water and octanol (S_A, S_W, S_O), and three dimensionless partition coefficients between octanol/water (K_{OW}), octanol/air (K_{OA}) and air/water (K_{AW}) (Cousins and Mackay 2001). K_{OW} is a measure of hydrophobicity and is used as a correlation property in bioaccumulation assessments and for partitioning between water and sediment organic carbon. K_{OA}, S_A or liquid-phase vapour pressure ($P_L = S_A RT$, Pa), are correlation properties for describing absorption of organic compounds to aerosols. K_{OA} has further applications in modeling soil-air exchange and bioaccumulation through the respiratory exchange. The dimensionless Henry's law constant K_{AW} ($K_{AW} = H/RT$, where H has units Pa m^3 mol^{-1}), is used to estimate the direction and rate of air-water gas exchange and precipitation scavenging.

The six properties form the triangular relationship in Figure 2.1 (modified from Åberg et al. 2008). A complication arises with K_{OW}, which is experimentally measured using octanol and water that are mutually saturated with the other solvent and thus is different from the partition coefficient which is based on the ratio of solubilities in the pure solvents, $K^*_{OW} = S_O/S_W$. The "wet octanol" K_{OW} is used for the prediction of phase partitioning in the environment, but "dry octanol" K^*_{OW} is needed to estimate other properties according to Figure 2.1, and relationships have been proposed to interconvert K_{OW} and K^*_{OW} (Beyer et al. 2002, Li et al. 2003a, Schenker et al. 2005).

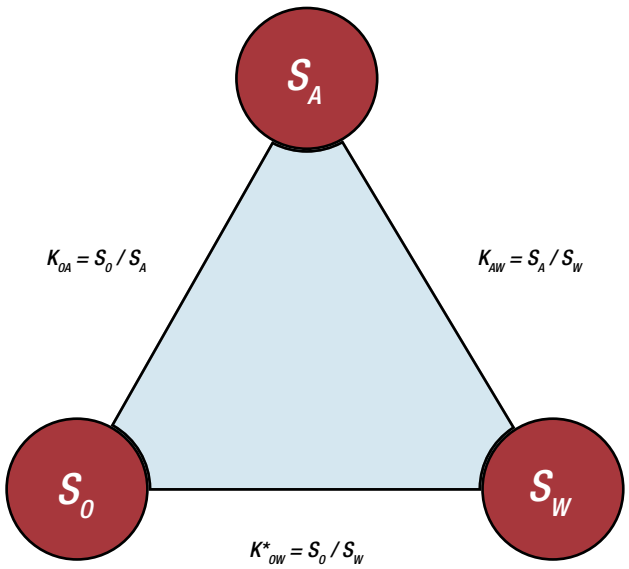


FIGURE 2.1

Relationships among solubilities and partition coefficients. Modified from Åberg et al. 2008.

2.1.3. Derivation of "thermodynamically consistent" pchem properties

Experimental values for the above pchem properties are often quite variable, especially for more hydrophobic chemicals, and selection of literature values for predicting environmental partitioning is problematic. A major advance since CACAR-II has been the generation of "thermodynamically consistent" pchem properties. The process begins by screening published properties data, rejecting outlying results and arriving at a set of literature-derived values (LDVs). The LDVs are adjusted for thermodynamic consistency by employing the relationships among solubilities and partition coefficients in Figure 2.1 and minimizing the errors in each LDV by using iterative (Beyer et al. 2002, Li et al. 2003a, Schenker et al. 2005, Shen and Wania 2005, Xiao et al. 2004) or least squares (Åberg et al. 2008, Schenker et al. 2005) approaches. The result is a set of final adjusted values (FAVs) with reduced uncertainties compared to the original data. LDVs for K_{OW} are converted to K^*_{OW} for thermodynamic adjustment (Figure 2.1), and the FAVs are recalculated to K_{OW} for reporting. The FAVs for K_{OW}, K_{OA}, K_{AW}, P_L and S_W at 25 °C are summarized in Annex Table A2-1 for PCB congeners (Li et al. 2003a, Schenker et al. 2005) and Annex Table A2-2 for pesticides (Muir et al. 2004, Shen and Wania 2005, Xiao et al. 2004). FAVs have also been derived for polycyclic aromatic hydrocarbons (PAHs) (Beyer et al. 2002) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs, PCDFs) (Åberg et al. 2008). Similar selection and adjustment procedures are used in these reports to derive LDVs and FAVs for the internal energy of phase changes, thereby allowing prediction of pchem properties at other temperatures.

Numerical uncertainty values have not been applied to the Wania group FAVs; instead, a subjective scale of 1 (low) to 5 (high) was assigned based on the number and perceived quality of individual literature results that went into the calculation of LDVs and FAVs (Li et al. 2003a, Shen and Wania 2005, Xiao et al. 2004).

2.1.4. Prediction of pchem properties

Experimental determination of pchem properties is labour-intensive and results often vary depending on the laboratory and measurement technique. Prediction of pchem properties using quantitative structure-property relationships (QSPRs) offers an alternative and works synergistically with measurements to improve reliability. Moreover, modeling is the only feasible way to generate pchem properties for the tens of thousands of high production volume chemicals that need to be screened for their potential to persist, bioaccumulate and undergo long-range transport. Today's QSPR models range in complexity from semi-empirical, employing training sets of chemicals with known pchem properties for calibration, to those that are fully computational. A large number of papers on prediction of pchem properties have appeared since CACAR-II. The approach taken here is to give examples of studies that compare QSPRs, particularly for chemicals which are on Canada's Domestic Substance List (DSL) and/or are likely to be arctic contaminants. Because of their growing importance as arctic contaminants and the uncertainties involved in experimental measurement and prediction of pchem properties, a separate discussion of fluorinated chemicals is given in section 2.1.7.

The EPI (Estimation Program Interface) (U.S. EPA 2009) Suite QSPRs are widely used for predicting pchem properties and environmental fate, including K_{OW} (KOWWIN), K_{AW} (HENRYWIN), K_{OA} (KOAWIN), bioconcentration factor (BCFWIN), biodegradation (BIOWIN) and atmospheric oxidation (AOPWIN). The pchem properties modules in EPI Suite are based on fragment methods that assign a coefficient value for each identified fragment that contributes to the predicted property of the whole molecule. The applicability domain of fragment-based QSPRs is restricted to the structural features present in training sets of chemicals, which are typically less than 1,000 substances, but are 13,000 for KOWWIN (Muir and Howard 2006). Predictions are more uncertain for chemicals outside the training set domain because they rely on experimental properties of the chemicals in the training sets.

Large-scale screening of chemicals on Canada's DSL and other lists of commercial chemicals for bioaccumulation and LRAT potential, has been carried out using properties predicted from the EPI Suite QSPR models, covering 11,317 substances (Muir and Howard 2006) and subsequently, a largely non-overlapping list of 22,263 chemicals (Howard and Muir 2010). From the former list, the top 30 chemicals with persistent and bioaccumulative characteristics and the top 30 with LRAT potential were reported (Muir and Howard 2006). In the subsequent paper, Howard and Muir (2010) selected 610 priority substances as persistent and bioaccumulative on the basis of EPI Suite modeling and expert judgment.

Brown and Wania (2008) used two parallel screening methodologies, one based upon substance properties (either measured or estimated) and the other on the structural similarity to known arctic contaminants, to examine 105,584 chemicals from the EPI Suite

software (3) for Arctic Contamination and Bioaccumulation Potential (AC-BAP). They identified 120 high production volume (HPV) chemicals as being structurally similar to known arctic contaminants and/or had pchem properties that suggested they have arctic contamination potential. Most of these 120 chemicals were also identified by Howard and Muir (2010), indicating a high degree of agreement for screening level assessments.

2.1.5. Comparison of predictive methods

COSMOfrag (Hornig and Klamt 2005) was applied to estimate K_{OW} and K_{AW} for chemicals on Canada's DSL (Wittekindt and Goss 2009) and the results were compared to those from the EPI Suite models KOWWIN and HENRYWIN. For 1,800 compounds with experimental values of K_{OW}, the root mean square error (rmse) was 0.4 log units for KOWWIN and 0.76 log units for COSMOfrag. Comparison of COSMOfrag and KOWWIN predictions for 8,560 chemicals gave a rmse of 0.7 log units, with no bias on either side. Greater errors were encountered in predicting K_{AW}; the rmse in experimental vs. model comparisons was 0.90 log units for COSMOfrag and 0.92 log units for HENRYWIN. COSMOfrag and HENRYWIN predictions compared with an average deviation of 1.8 log units and HENRYWIN values an average bias of 0.15 log unit higher. COSMOfrag predicted 1,902 out of 8,560 compounds on Canada's DSL to have log $K_{OW} > 5$ (a commonly used indicator for bioaccumulation potential screening), while KOWWIN predicted 2,043 compounds with log $K_{OW} > 5$.

Results from EPI Suite, SPARC (Hilal et al. 2007), COSMOtherm (Eckert and Klamt 2002); (Klamt 2005) and ABSOLV (Clarke 2009) were compared by Zhang et al. (2010b) for predicting K_{OW}, K_{AW} and K_{OA} of 529 chemicals, and predicted properties were used to screen these chemicals against long-range transport potential (LRTP) and bioaccumulation potential (BAP) criteria, using thresholds for arctic contamination and bioaccumulation potentials (AC-BAP) (Brown and Wania 2008, Czub et al. 2008). Screening results based on the four methods were consistent for approximately 70% of the chemicals. EPI Suite identified more chemicals as bioaccumulative in the aqueous environment and in humans than other prediction methods. When screening for elevated LRTP, fewer chemicals were identified with EPI Suite, while SPARC identified more chemicals with elevated LRTP and less with elevated terrestrial and human BAP when compare to the other methods.

Rayne and Forest (2010a) evaluated KOWWIN and ALOGPS.2.1 (VCC Laboratories 2010), for predicting log K_{OW} of 1,545 chemicals on Canada's DSL which had experimental values available. The rmse values for KOWWIN and ALOGPS2.1, predicted vs. experimental log K_{OW}, were 0.37 and 0.35 log units, respectively. Log K_{OW} residuals for KOWWIN were evenly distributed with no significant trend, whereas ALOGPS2.1 residuals displayed a significant trend, decreasing in signed error magnitude with increasing log K_{OW}. Of the 83 compounds on a screened version of the DSL with known experimental log $K_{OW} > 5$, KOWWIN correctly classified 75 and ALOGPS.2.1 correctly classified 72. KOWWIN generated 11 false positives (predicting log $K_{OW} > 5$ when experimental log $K_{OW} < 5$) and 8 false negatives (predicting log $K_{OW} < 5$ when experimental log $K_{OW} > 5$), while ALOGPS generated 8 false positives and 11 false negatives. Performance was poorer for a suite of chemicals on the DSL list for which there were no experimental log K_{OW} values.

Experimental observations have shown that K_{AW} is much lower and K_{OA} is much higher for β-HCH than for the α- and γ-isomers (Xiao et al. 2004). Due to its lower K_{AW}, β-HCH was historically transported to the Arctic largely by ocean currents, whereas a combination of atmospheric and oceanic pathways delivered α-HCH (Li and Macdonald 2005, Li et al. 2002). The partitioning of HCH isomers was critically evaluated by Goss et al. (2008), who measured additional partitioning data for the three HCHs. Results revealed a distinctly different partition behaviour for β-HCH. The ability of various models to predict this behaviour from molecular structure was investigated. SPARC and EPI Suite failed to predict any isomeric differences. COSMOtherm correctly predicted the qualitative differences among the isomers, but in some cases, the predicted absolute values differed by more than 1 order of magnitude. In addition, the COSMOtherm software was used to predict partition data for the three isomers of HBCDD, revealing results similar to HCH. Staikova et al. (2005), found that large differences in the experimental K_{OA} for the isomers of HCH were found to correspond to similarly large differences in the out-of-plane polarizabilities of these substances.

2.1.6. Other predictive studies

Polychlorinated naphthalenes (PCNs) are contaminants of air and biota in polar environments (Bidleman et al. 2010), but few of the 75 PCN congeners have measured pchem properties. K_{OW}, K_{OA} and K_{AW} were predicted for all PCN congeners using QSPRs based on quantum mechanical calculations

of molecular properties and interactions (Puzyn and Falandysz 2007). Six QSPRs were run and calibrated against experimental values of K_{OW} and K_{OA}. The rmse values for the most successful model were 0.065 and 0.091 log units.

Partial least squares (PLS) regression with 18 molecular descriptors was used to develop QSPRs based on directly measured K_{OA} values of selected chlorobenzenes, PCBs, PCNs, PCDD/Fs, PBDEs and OCPs. An optimization procedure resulted in two temperature-dependent universal predictive models that explained at least 91% of the variance of log K_{OA} (Chen et al. 2004).

Principal component analysis and PLS regression was used to develop models for the P_L of polychlorinated diphenyl ethers (PCDEs) and PBDEs (Öberg 2002). All congeners of PCDEs and PBDEs were characterized by 795 molecular descriptors and two principal components accounted for about two thirds of the variance within each group. Bilinear calibration models were developed that could explain 99.4% of the variance in the external validation test sets. Values of P_L were subsequently predicted for all congeners that were adequately described by these calibration models. The type and number of halogen atoms in the molecule were the main factors influencing the vapour pressures of halogen substituted diphenyl ethers, but the variations in substitution pattern was also shown to be a significant factor.

QSPRs were developed for chlorobenzenes, PCBs, PCDD/Fs and PAHs using the simple molecular descriptors carbon number, chlorine number and, for PCBs, ortho-chlorine number (Van Noort 2009a). The models were applied to predict the P_L, heat of vapourization (ΔH_{VAP}) and the entropy of vapourization (ΔS_{VAP}); the latter two parameters allow the temperature dependence of P_L to be estimated. Predictions of P_L agreed, within 0.12-0.3 log units, with those determined by gas chromatography (GC) methods. These descriptors, along with the melting point, were also applied to predict water solubilities and vapour pressures of solid-phase chlorobenzenes, PCBs, PCDD/Fs, PAHs and phenolic compounds, with a standard error of about 0.2 log unit (Van Noort 2009b).

A model based on five fragment constants and one structural correction factor was developed for predicting log K_{OA} at temperatures ranging from 10 °C to 40 °C (Li et al. 2006). The model was validated as successful by statistical analysis and external experimental log K_{OA} data. Compared to other quantitative structure–property relationship methods, the fragment model was reported to be much easier to implement. As aromatic compounds that contain C, H, O, Cl, and Br atoms were included in the training set, the fragment model applies to a wide range of chlorinated and brominated aromatic pollutants, such as chlorobenzenes, PCNs, PCBs, PCDD/Fs, PAHs, and PBDEs. The model predicted log K_{OA} with a standard error of about 0.2 units.

Solvation parameters were predicted for the 209 PCB congeners (Abraham and Al-Hussaini 2005). The solvation parameters were the sum of the solvent-solute interactions: solute excess molar refractivity, solute dipolarity/polarizability, hydrogen bond acidity and basicity, McGowan characteristic volume, and the air/hexadecane partition coefficient. The solvation parameters were, in turn, used to estimate K_{OW}, K_{OA} and K_{AW}. Predicted pchem properties were compared to available LDV and FAV values for PCB congeners (Li et al. 2003a), with the outcome that average absolute errors (in log units) ranged from 0.06–0.34, or agreement within a factor of two or better.

Henry's law constants ($H = RT \cdot K_{AW}$, Pa m^3 mol^{-1}) were predicted for the 209 PCB congeners using the quantum mechanical Continuous Solvation models COSMO-SAC and SM6 (Phillips et al. 2008) and the results were compared to predictions made with the SPARC Abraham solvation (Abraham and Al-Hussaini 2005) and the Burkhard (1985) semi-empirical models. At 25 °C, COSMO-SAC and SM6 models predicted similar values, which were consistent with all but one of the available sets of measurements, and had smaller rmse values than the other models tested.

A QSPR model for K_{OA} of hydroxylated and methoxylated PBDE congeners (OH/MeO-PBDEs), based on 16 fundamental quantum chemical descriptors, was developed by Zhao et al. (2010). The molecular weight and energy of the lowest unoccupied molecular orbital were found to be the main factors governing K_{OA}. K_{OA} were also determined for 29 OH/MeO-PBDEs using GC compared to predicted values. The relative errors in log K_{OA} ranged from 0.04% to 8.1%.

An empirical linear relationship between the average polarizability of chlorinated aromatic and aliphatic compounds and their log P_L was tested for its capability to predict log P_L at 25°C for a diverse set of other nonpolar organic compounds, including brominated benzenes, aromatic hydrocarbons, chlorinated toluenes, HCHs, and *p,p'*-DDT (Staikova et al. 2005). The model showed generally excellent agreement with experimental data over a 10 order-of-magnitude range in P_L, with an average error of less than 0.5 log unit, and accounted for the

differences in K_{OA} of the HCH isomers. Results suggested that a single theoretically derived parameter is sufficient to estimate (within an order of magnitude) the volatility of a wide variety of organic compounds whose primary interactions are dispersive in nature.

The importance of considering the dissociation of ionizing compounds in evaluating their LRTP and bioaccumulation was pointed out by Rayne and Forest (2010b), Fu et al. (2009) and Kah and Brown (2008). For ionizable compounds (e.g., acid and anion forms, represented by HA and A^-, respectively), their "effective" pH-dependent distributions between octanol/water and air/water are:

$$K_{OW} \text{ or } K_{AW} = [HA]_O/[HA]_W \text{ or } [HA]_A/[HA]_W \quad \text{(neutral form)} \qquad \text{Eq. 1}$$

$$D_{OW} \text{ or } D_{AW} = [HA]_O/[HA + A^-]_W \text{ or } [HA]_A/[HA + A^-]_W \quad \text{(acid-base pair)} \qquad \text{Eq. 2}$$

Organic ions are capable of crossing cell membranes (Fu et al. 2009) and partitioning into octanol or lipids can also involve the ionic form, in which case D_{OW} and K^i_{OW}, the partition coefficient for the ionic form, are written:

$$D_{OW} = [HA + A^-]_O/[HA + A^-]_W \qquad \text{Eq. 3}$$

$$K^i_{OW} = [A^-]_O/[A^-]_W \qquad \text{Eq. 4}$$

$$D_{OW} = [K_{OW} + K^i_{OW} \cdot 10^{(pH\text{-}pKa)}]/[1+10^{(pH\text{-}pKa)}] \qquad \text{Eq. 5}$$

or the algebraically equivalent form:

$$D_{OW} = f_n K_{OW} + f_i K^i_{OW} \qquad \text{Eq. 6}$$

where f_n and f_i are the neutral and ionized fractions of the compound (Fu et al., 2009; Kah and Brown, 2008). Similar relationships can be written for the partition and distribution coefficients between soil or sediment organic carbon/water (K_{OC}, D_{OC}). Rayne and Forest (2010b) used SPARC to predict D_{OW} and D_{AW} as functions of pH for eleven acidic compounds that have been proposed as potential arctic contaminants, with the result that many have D_{OW} or D_{AW} values at pH 6–8 which are substantially lower than the K_{OW} or K_{AW} of the neutral form. They conclude that the acidity/basicity of all compounds at relevant pH values (varying depending on the nature of the freshwater, marine, soil, atmospheric, or biological systems) must be taken into consideration in any K_{OW} and K_{AW} based screening assessment for arctic contamination potential.

2.1.7. Partitioning properties of fluorinated chemicals

Arp et al. (2006) predicted partitioning properties of fluorinated chemicals, including fluorotelomer alcohols and olefins (FTOHs, FTolefins), methyl and ethyl perfluorosulfamidoethanols (MeFOSEs, EtFOSEs), methyl perfluorosulfamidoethylacrylate (MeFOSEA), and perfluoralkyl carboxylic and sulfonic acids (PFCAs, PFSAs) using EPI Suite, ClogP, SPARC (versions 2005 and 2006) and COSMOtherm. In estimating P_L, K_{AW}, and K_{OW}, SPARC and COSMOtherm made predictions usually within 1 order of magnitude of the experimental value, while EPI Suite and ClogP performed with less accuracy. The least accurate predictions were found using ClogP for the fluorotelomer alcohols, where the estimated values were off by two to almost five orders of magnitude.

A critical review of pchem properties of PFCAs and PFSAs, which also included other fluorinated chemicals (FTOHs, MeFOSE and EtFOSE), was conducted by Rayne and Forest (2009b). Properties were predicted using EPI Suite, SPARC, ClogP, AlogPS 2.1 and other QSPRs. Annex Table A2-3 lists predicted properties (K_{OW} or D_{OW}, K_{AW} or D_{AW}, K_{OC} or $D_{OC,}$ K_{OA}, P_L) for PFCAs and PFOSA, summarized from Rayne and Forest (2010a, b) and Arp et al. (2006). Predictions are compared to experimental values, where available. As noted above, K_{OW} and K_{AW} values refer to the properties of the neutral form only (typically estimated by models such as QSARS) whereas D_{OW} and D_{AW} characterize the overall partitioning behaviour of the acid-base pair. D_{OW} and its pH dependence can be estimated directly by some models (e.g., SPARC), following the general equation Eq. 7.

$$D_{XY} = f_n K_{XY\text{-}n} + f_i K_{XY\text{-}I} \qquad \text{Eq.7}$$

Empirical partition property values of ionizing chemicals generally represent the overall partitioning behaviour of the compound (i.e., D_{XY}) but experimental techniques can be used to estimate the behaviour of individual species (see below). For the PFCAs, D_{AW} has only been measured for PFOA (Kutsuna and Hori 2008, Li et al. 2007). The measurements were made in sulphuric acid solutions and may represent K_{AW}, although there is discussion as to whether the pH was low enough to completely suppress ionization (Kutsuna and Hori 2008, Li et al. 2007, Rayne and Forest 2009b).

Rayne and Forest (2009a,b) reviewed experimental measurements of sorption to sediments and inorganic surfaces such as sand and clay, and predicted partitioning between organic carbon and water using QSPRs (Rayne and Forest 2009b). Results for log K_{OW} and log D_{OW} were generated by AlogPS2.1, and the 2007 versions of SPARC. Empirical log D_{OC} values for a series of PFCAs and PFSAs, measured at pH 5.7–7.6 (Higgins and Luthy 2006), were correlated to these properties, and from the

Photo: Simon Belt/ArcticNet

regression equations estimates, were made for other PFCAs. Although Rayne and Forest (2009b) refer to their predictions as "log K_{OC}", they appear to be log D_{OC}, since the correlations were developed from the Higgins and Luthy (2006) data. They are listed as D_{OC} in Annex Table A2-3. Other "log K_{OC}" or log D_{OC} values for trifluoroacetic acid (TFA), PFOA and PFOS are provided in Table 1 of their paper, based on the log K_{OW} and log D_{OW} results from the programs listed above and the published regression equations.

Partitioning of PFCAs and PFSAs between octanol and water have been experimentally measured by only one group (Jing et al. 2009). Their partition coefficients were classified as "log D" by Rayne and Forest (2009b), and are reported as such in Annex Table A2-3, but are actually neither D_{OW} nor K_{OW} as defined by Eq. 1-3. Rather, Jing et al. (2009) estimated partitioning of perfluorinated carboxylate and sulfonate oxoanions, and not neutral species, between the two phases using cyclic voltammetry to follow the ionic forms.

Predicted properties of PFCAs and PFOSA vary by several orders of magnitude among the different QSPRs and often deviate substantially from experimental values. The discrepancies may be inherent in the models themselves and also related to uncertainties in the measured/predicted ionization constants (pK_a) of the chemicals, which are necessary for predicting D_{OW} or D_{AW}. Rayne and Forest (2010a, b) point out that model estimates are sensitive to the version used; for example, predictions of log K_{OW} using more recent versions of SPARC and ClogP have changed by up to two units from the estimates provided by Arp et al. (2006). Rayne and Forest (2009b) state that the physicochemical properties and partitioning behaviour for the linear PFCAs and PFSAs are poorly understood and widely debated, and even less is known about the numerous branched congeners with varying chain lengths.

Due to the uncertainty in key partitioning property data, it is important to characterize the impact of the input uncertainty on conclusions that are based on model output (e.g., conduct sensitivity and uncertainty analyses). In some cases, such as assessing the long-range oceanic transport potential of perfluorinated acid (Wania 2007), key model output is not sensitive to the uncertainty in partitioning property data. In other cases, such as characterizing aerosol-air partitioning or atmospheric deposition of perfluorinated acids, the uncertainty in partitioning property data may result in high variability in model output (and hence higher uncertainty in the conclusions based on the study). Predicted pchem properties for some non-ionic perfluorinated chemicals from

Rayne and Forest (2009b) and Arp et al. (2006) are summarized with experimental values in Annex Table A2-4. As for the PFCAs and PFOSA, a wide range of properties is estimated from various models. Rayne and Forest (2009b) again point out that model performance has changed over time, and that the more recent versions of SPARC and EPI Suite provide estimates of P_L, K_{OA} and K_{AW} with better than an order of magnitude accuracy, often agreeing with experimental values.

Rayne et al. (2009) have summarized second-order reaction rate constants of perfluorinated compounds with atmospheric OH radicals and predicted rate constants for OH, NO_3 and O_3 reactions .The solid-phase vapour pressure (log P_S/Pa -2.52, 25°C) and enthalpy of sublimation (ΔH_{SUB}, 90.9 kJ mol^{-1}) were measured for ammonium perfluorooctanoate (Barton et al. 2009). Log P_S/Pa and ΔH_{SUB} of PFOA were reported as -0.14 (27°C) and 88.9 kJ mol^{-1} (Barton et al. 2008). Log P_S/Pa at 23°C was reported for MeFOSE (-3.40), EtFOSE (-2.77), and MeFOSA (-3.39) (Shoeib et al. 2004).

2.1.8. Polyparameter linear free energy relationships

Partitioning of chemicals to environmental matrices is most often described by relationships of the type below where K_i is the equilibrium partition coefficient of substance i between two phases (particle/gas, water/sediment, water/biota, snow/air, etc.) and P_i is a pchem property (P_L, K_{AW}, K_{OW}, K_{OA}) of substance i.:

$$\text{Log } K_i = \text{mlog } P_i + \text{b} \qquad \text{Eq. 8}$$

Such single-parameter linear free energy relationships (sp-LFERs) cannot take into account the complex physical-chemical interactions involved in adsorption or absorption. They are generally applicable only within a single compound class and provide no means to understand the variability of substances across compound classes or among different sorbents (Goss and Schwarzenbach 2001). Polyparameter linear free energy relationships (pp-LFERs), or linear solvation energy relationships (LSERs) have been proposed to fit partitioning data for a wide variety of compound classes (Breivik and Wania 2003, Brown and Wania 2009, Goss 2005, Goss and Schwarzenbach 2001). The pp-LFER equation has the form (Arp et al. 2008d, Brown and Wania 2009, Goss 2005):

$$\text{Log } K_i = sS_i + aA_i + bB_i + lL_i + vV_i + c \qquad \text{Eq.9}$$

A similar equation is used to calculate the enthalpy of phase change. Upper case letters are compound descriptors and lower case letters are phase descriptors. The terms represent the different types of interactions between the solute and the two phases which contribute to the partitioning. Specific interactions of the solute are described by the Abraham descriptors *S* (polarizability/dipolarizability), *A* (acidity: electron acceptor, hydrogen bond donor), and *B* (basicity: electron donor, hydrogen bond acceptor). Nonspecific (Van der Waals) interactions are described by *L* (logarithm of the hexadecane/air partition coefficient) and *V* (McGowan molecular volume) for absorptive processes. The corresponding phase descriptors quantify the relative affinity of the two phases for these kinds of interactions; *c* is a fitting constant.

Partitioning descriptions by pp-LFERs have been applied to sorption of vapour-phase organic chemicals to aerosols (Arp et al. 2008a, Arp et al. 2008b, Götz et al. 2007, Götz et al. 2008, Roth et al. 2005), soil humic acid (Niederer et al. 2006a,b), and to organic carbon/water partitioning (K_{OC}) (Bronner and Goss 2011a,b, Faria and Young 2010, Nguyen et al. 2005, Schüürmann et al. 2006). Solute descriptors have been measured or estimated for environmentally relevant chemicals, including pesticides and pharmaceuticals (Bronner and Goss 2011b, Tülp et al. 2008), PCBs (Abraham and Al-Hussaini 2005) and other chemicals (references in Brown and Wania (2009)). Phase descriptors (partitioning among air, octanol and water, and between aerosol/air, humic acid/air and humic acid/water) have been published by these and other works and are tabulated by Brown and Wania (2009).

Comparison of a pp-LFER with a sp-LFER, based on K_{OA} for predicting particle/air partition coefficients (K_{PA}), showed that the two models gave similar results for nonpolar solutes (PCBs, DDT compounds) and in cases where the interaction with aerosols was dominated by absorption into organic matter. Substantial differences were seen for polar pesticides and for low-organic aerosols. The pp-LFER model predicted that PCBs and DDTs would be approximately 95% associated with the organic fraction, while polar pesticides would partition 60% or more to the mineral fraction (Götz et al. 2007). The pp-LFER approach was preferred over K_{OA} in a geographically resolved global transport model with a variety of aerosol types. This was the case particularly in regions with low organic matter aerosols (deserts, arctic, and some oceanic regions) (Götz et al. 2008). An experimental-modeling study showed that pp-LFERs provided a better description of interactions between vapour-phase n-alkanes, PCBs and OCPs and the organic matter of aerosols (Arp et al. 2008b, Arp

et al. 2008c). Predictive methods failed to account for the particulate fraction of PAHs due to the presence of a nonexchangeable fraction (Arp et al. 2008c).

Prediction of K_{PA} from the molecular structures of sorbates and aerosol organic matter was carried out using COSMOtherm and SPARC (Arp and Goss 2009a, b). Using a validation set of 1,400 experimentally determined K_{PA} values for polar, apolar, and ionic compounds ranging over 9 orders of magnitude (including semi-volatile compounds such as PCDD/Fs, pesticides, and PBDEs), SPARC and COSMOtherm were generally able to predict K_{PA} values well within an order of magnitude over an ambient range of temperature and relative humidity (Arp and Goss 2009a). However, these methods consistently predicted values below the observed partitioning of PFCAs to aerosols. This is likely due to additional partition mechanisms, unique to surfactants, not being accounted for in the model, namely aggregate formation and water surface adsorption (Arp and Goss 2009b).

Niederer et al. (2006a, b) investigated vapour sorption of 188 chemicals on Leonardite humic acid. The sp-LFER Karickhoff model based on K_{OA} gave good interpretation of the results for nonpolar compounds, but not for polar ones. A good description of the whole data set was achieved with a pp-LFER that explicitly accounts for the nonpolar (van der Waals and cavity formation) and polar (electron donor/acceptor) interactions between the sorbate molecule and the sorbent phase. With this pp-LFER model, most of the humic acid/air partition coefficients could be predicted within a factor of 2. In a subsequent study (Niederer et al. 2007), experimental soil/air partition coefficients measured in 10 different humic and fulvic acids were successfully described by pp-LFERs. A pp-LFER model for soil-water partitioning was calibrated with experimental data for 79 polar and nonpolar compounds that covered a wide variety of intermolecular interactions (Bronner and Goss 2011a). The model was applied to 50 pesticides and pharmaceuticals, for which experimental data were also available, with a model agreement rmse of 0.4 log units.

Breivik and Wania (2003) modified a level III fugacity model to use five LSERs instead of sp-LFERs based on P_L, S_W and K_{OW}. A comparison of modified and unmodified models showed that the approach chosen to simulate environmental phase partitioning can have a large impact on model results, including long-range transport potential, overall persistence, and concentrations in various media The authors argued that pp-LFER based environmental fate models are applicable to a much wider range of organic substances, in particular those with polar functional groups.

The issue was revisited by Brown and Wania (2009) in a comparison of pp-LFERs and sp-LFERs for a suite of chemicals with varied molecular structures within the CoZMo-POP2 framework: a non-equilibrium, non-steady state multimedia fate model. Differences in chemical space plots arose mainly in the environmental phases that contained only a small fraction of chemical. K_{OC} calculated from sp- and pp-LFERs were closely correlated, while more scatter was noted for particle/gas partitioning in the atmosphere. Overall, the absolute differences between the two models were relatively small compared to the precision associated with model parameterization. The authors recommended that when using a multimedia fate model as an evaluative or predictive tool, the choice of using a sp- or pp-LFER should be based on the quality of the available chemical input values.

2.1.9. Assessment

- Pchem properties for legacy POPs are reasonably well established, but uncertainties remain, particularly for perfluorinated chemicals and probably for other polar compounds. Future progress will continue to rely on experimentation and modeling, critical evaluation and analysis of data to obtain thermodynamic consistency.
- The concluding statement of Arp et al. (2006) is relevant: "*One can never be too confident about using models that predict partitioning parameters for untested compound classes, even if the models have been validated for thousands of compounds. Thus, upon the emergence of new compound classes, there should be a special bias to experimentally test the partitioning behaviour of chemicals belonging to this class*".
- Regarding the application of pchem properties in decision-making, Zhang et al. (2010b) remarked that screening and categorization methods that rely on a decision as to whether a chemical's predicted property falls on either side of a threshold are likely to lead to a significant number of false positive/negative outcomes. They suggested that screening should rather be based on numerical hazard or risk estimates that acknowledge, and explicitly take into account, the uncertainties of predicted pchem properties.

2.2. Usage and Emissions of POPs, CUPs and New Chemicals (Post-2002 Data)

Coordinating authors: Yi-Fan Li and Perihan Kurt-Karakus

2.2.1. Introduction

A major focus of the NCP has been to identify global sources of contaminants and quantify emissions for use in global mass budget models. Under NCP-I, rough estimates of total global use were made for several compounds including PCBs, DDT, toxaphene, lindane, chlordane, aldrin, dieldrin, and endosulfan. Most of this information, which includes historic, present, and predicted global use or sales, has been obtained from United Nations and government reports, scientific publications, Battelle Europe, the International Registry of Potentially Toxic Chemicals (IRPTC), and some joint international projects. Under NCP-II the inventory of organochlorine pesticides was updated and enhanced with the addition of data for β-HCH [globally gridded (1° x 1° latitude/longitude)], toxaphene, and DDT. Additionally, estimates of actual emissions to the atmosphere were made on a global scale for HCHs and, in the United States (US), for toxaphene. Estimates of residues left in US agricultural soil were also made for toxaphene and mapped on a grid (1/6° x 1/4° latitude/longitude). In most parts of the world, technical HCH was replaced by lindane (γ-HCH) in the late 1970s and 1980s thereby reducing the amount of α- and β-HCH emissions.

The Stockholm Convention entered into force on 17 May 2004 and initially listed twelve chemicals, so-called "dirty dozen" (Chapter 1, Table 1.4). The dirty dozen "legacy" POPs were first produced and/or used many decades ago and large number of studies reported their persistence, bioaccumulative properties and potential for long range transport, hence they have been globally banned or restricted by the Stockholm Convention since 2004. In 2009, nine more substances were added to the Convention (Chapter 1, Table 1.3), and two more (endosulfan and HBCDD) were added in 2011 and 2013, respectively. The 23 POPs included to date belong to three groups:

- pesticides used in agricultural applications;
- industrial chemicals used in various applications; and
- chemicals generated unintentionally as a result of incomplete combustion and/or chemical reactions.

Some chemicals such as HCB, pentachlorobenzene (PeCBz), and PCBs fit more than one of general categories listed above whereas some chemicals such as Penta-BDEs and Tetra-BDEs are listed together in elimination or control Annexes of the Stockholm Convention.

Occurrence and distribution of POPs in the environment is strongly related with their global production and usage pattern. For instance, occurrence and release of pesticide POPs are often related to their former applications in main agricultural areas of the world (Li 1999a, von Waldow et al. 2010) whereas non-pesticide POPs are highest in industrialized countries in the Northern Hemisphere. Once released into the environment, POPs are transported to regions far from source areas by air, ocean currents or animal vectors. Transport by ocean currents is particularly important for chemicals such as HCH isomers and PFASs that have higher water solubility ratios compared to classical POPs. Detection of these compounds in various arctic media has demonstrated the long-range transport capacity of these chemicals (Hung et al. 2010, Muir et al. 1999, Weber and Goerke 2003).

In this section, we provide up-to-date information (to early 2011) on usage and emissions of both legacy and emerging POPs. Selected values resulting from extensive research and literature reviews are presented in Table 2.1 (and Annex Table A2-5). It is important to note that a similar table of the production/usage data of certain POPs was provided in the AMAP 2002 POPs assessment report (Table 2.1. in AMAP 2004), therefore the data presented here covers the period between 2002–2011 where available.

In this chapter, we summarize the data for two groups of POPs. One is referred to as "legacy" POPs, the original "dirty" dozen listed in the Stockholm Convention—including intentionally produced POPs, unintentionally produced by-products and industrial POPs (Table 1.3); and the other is referred to as "new POPs", which for purposes of this assessment include chlordecone, hexachlorocyclohexane (HCH), penta- and octa- BDEs, PeCBz, hexabromocyclododecane (HBCDD), perfluorooctanyl sulfonate (PFOS), perfluorocarboxylates (PFCAs) such as perfluorooctanoate (PFOA), short-chain chlorinated paraffins (SCCPs), polychlorinated naphthalenes (PCNs) and other organic chemicals not previously reported in the Arctic (See Chapter 1, section 1.3.2).

TABLE 2.1. Estimates of the global historical usage, production or emission of selected POPs, by-products or potential POPs (thousands of tonnes) (updated after AMAP 2004)

Chemical	Use	Temporal Coverage	Estimated Amount produced [1]	Data Type Production (P) Usage (U) Emission (E) Soil residue (R)	Data Scale Global (G) Regional (R)	Mode of Release Atmospheric (A) Land (L) Water (W)	Comments	Reference[2]
Legacy organochlorine pesticides								
DDT	Insecticide	1940-2005	4,500	P	G			1
		1950-1992	2,600	U	G			2
		1940-2005	1,030	E	G		Emission from agriculture	1
Aldrin	Insecticide	1950-1992	500	U	G			3
Dieldrin	Insecticide	1950-1992	34	U	G			3
Chlordane	Insecticide	1945-1988	78	U	G			3
Toxaphene	Insecticide	1947-1986	720	P	G			4
		1950-1993	1,330	P	G			2
		1950-1992	1,330	U	G			2
		1947-1999	190	E	G	A		4
		1947-2000	407	E	G			1
Legacy industrial organochlorines and by-products								
HCB	Pesticide by-product	Mid 1990s	0.012-0.092 kt/y	E	G	A		5
PCBs	Various	1930-2000	1,326	P	G		Sum of PCB homologues (mon-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-PCBs	6
		1930-1992	1,200	U	G			3
PCDD/Fs	By-products	~2000	7.1-12.6 kg TEQ/y	E	G	A	Global Emission to air from different sources by 23 countries	7
		2004	77.4 kg TEQ	E	G	A, L, W		8
New POPs								
Technical HCH	Insecticide	1948-1997	10,000	U	G			9
α-HCH		1945-2000	6,000	U	G			1
		1980	290	U	G			10
		1990	59	U	G			10
		1945-2000	4,300	E	G			1
		1980	184	E	G			10
		1990	44	E	G			10
β-HCH		1945-2000	850	U	G			11
		1945-2000	230	E	G			11
Lindane	Insecticide	1950-1993	720	U	G			2
		2005	13.6	R	G		Soil residue	12
Chlordecone	Insecticide							
Pentachlorophenol (PCP)	Fungicide	2002	5	P	G			13

Chemical	Use	Temporal Coverage	Estimated Amount produced [1]	Data Type Production (P) Usage (U) Emission (E) Soil residue (R)	Data Scale Global (G) Regional (R)	Mode of Release Atmospheric (A) Land (L) Water (W)	Comments	Reference[2]
HCBD (hexachlorobutadiene)	Solvent for other chlorine containing compounds, intermediate	1982	10	P	G			14
Penta-bromodiphenyl ether (Penta-BDE)	Flame retardant	2001 2001	7.5	P P	G G			15
Deca-bromodiphenyl ether (Deca-BDE)	Flame retardant	2001	56	P	G			15
Octa-bromodiphenyl ether (Octa-BDE)	Flame retardant	2001	3.8	P	G			15
TBBPA	Flame retardant	2001	120	P	G			15
		2008	3.2	P	G		Sold by EBFRIP member companies	16
Polybrominated diphenyl ethers (ΣPBDEs)	Flame retardants	2001	67	P	G			15
Brominated flame retardants (ΣBFRs)	Flame retardants	2001	204	P	G			15
PFCAs	Surfactant and flame suppressant	1951-2004 1951-2004	4.4-8 3.2-7.3	P E	G G			17
POSF (perfluorooctane sulfonyl fluoride)	Surfactant and flame suppressant	1970-2002 1970-2012	96 45	P E	G G	A,W	Fom direct and indirect (PFOS precursors) sources	18
Polychlorinated naphthalenes (PCNs)	Flame retardants and by-product	1920s-1980s	50-150	P	G			19,20
		1925-1985	450	P, U	G			21
		2007	430-692 mg TEQ	E	G		Emission from coking industry	22
Endosulfan	Insecticide	1954-2002	338	U	G			1
		1954-2002	215	E	G	A		1
Hexabromocyclododecane (HBCDD)	Flame retardants	2001	16.7	P	G			15
		2002 2003 2008	21.5 22.0 8.9	P P P	G G G			16 24 25
		2008	3.2	P	G		Sold by EBFRIP member companies	16
Current use pesticides								
Dicofol	Insecticide	2000s	5.5 kt/y	P	G		Global dicofol production including China	23

[1] Units are in kilotonnes total production for the period indicated in column 3 unless otherwise indicated

[2] References: 1: Li and Macdonald (2005); 2: Voldner and Li (1995); 3: Barrie et al. (1992); 4: Li (2001); 5: Bailey (2001); 6: Breivik et al. (2007); 7 : Fiedler (2007); 8: Li et al. (2010); 9 : Li (1999b); 10: Li et al. (2000); 11: Li et al. (2003b); 12: Li and Ren (2008); 13: U.S. EPA (2008)14 : WHO (1994b); 15: Birnbaum and Staskal (2004); 16: BSEF (2009); 17: Prevedouros et al. (2006); 18: Paul et al. (2009); 19 : Falandysz (1998); 20 : Hayward (1998); 21: Li (2011); 22: Liu et al. (2010a); 23: Hoferkamp et al. (2010); 24: BSEF (2003); 25: Morose (2006)

2.2.2. Legacy POPs

Chemicals discussed under the title of "legacy" POPs are pesticide POPs including aldrin, dieldrin, endrin, heptachlor, mirex, toxaphene, chlordane, DDT, HCB, and the industrial POPs including HCB, PCBs, and by-products PCDD/Fs. HCB is classified as both a pesticide and an industrial POP due to its historic use and production as a by-product. We outline estimated global production/usage/emissions of these chemicals as well as country-specific information for certain chemicals.

2.2.2.1. DDT

Li and Macdonald (2005) estimated the total global DDT production from the 1940s to the present at around 4,500 kt. The 7 countries with the highest historical DDT use are listed in Table 2.2. Although production and legal use of DDT no longer take place in North America, DDT is the only pesticide on the POPs list that is produced and applied in appreciable amounts for malaria control in other regions of the world. Hence, there are still large amounts of this chemical and its metabolites found cycling in various

TABLE 2.2. Top 7 countries for overall DDT use (Li and Macdonald 2005)

Country	Usage in agriculture (kt)	Usage in public health (kt)	Overall usage (kt)
United States	590	55	645
India	75	430	505
Former Soviet Union	320	?	320
Indonesia	20	293	313
China	260	10	270
Mexico	180	71	251
Brazil	106	106	212
Total	1606	910	2516

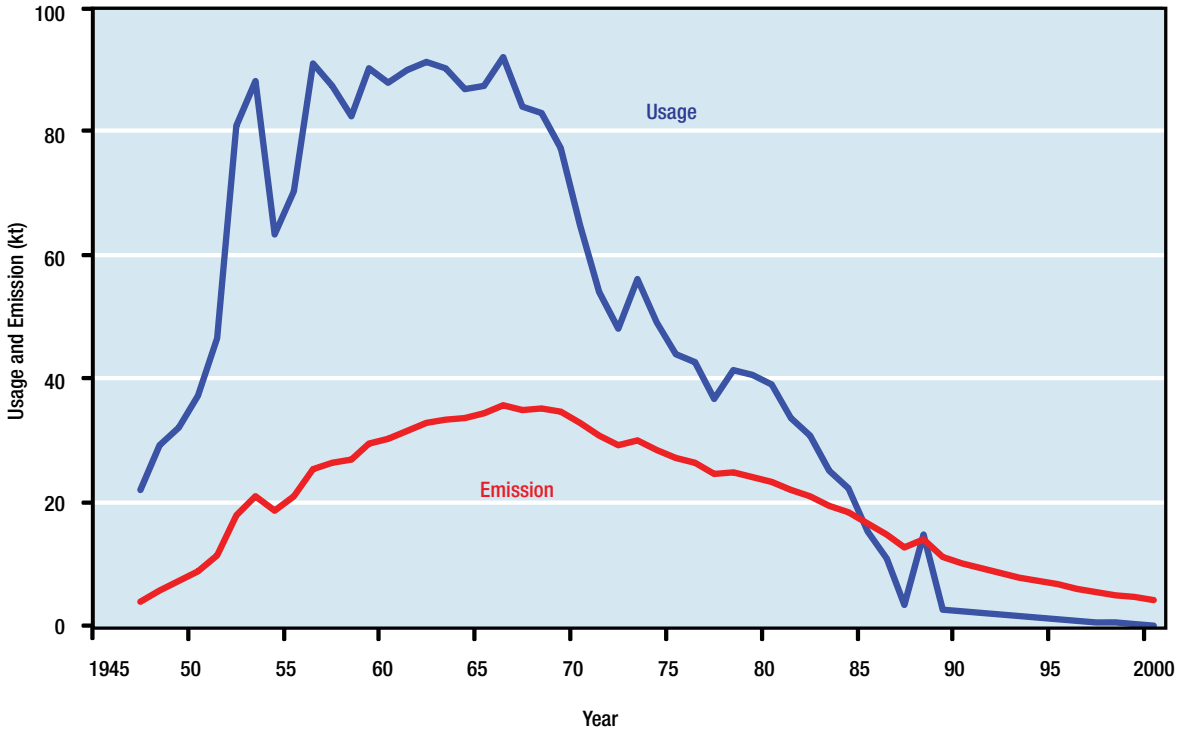


FIGURE 2.2

Temporal trend of DDT usage in agriculture and emissions due to agricultural uses from 1947 to 2000. The total usage is 2600 kt, and total emissions are 1030 kt for this period. Reproduced from Li and Macdonald (2005).

environmental compartments. Long-range transport, especially atmospheric transport, delivers some amounts of the DDT chemicals to North American environments, including Canada's North, even today. Also, it should be mentioned that the pesticide dicofol, which is still in use primarily as an acaricide to control mites, is quite closely related to DDT and has in the past contained substantial quantities of this chemical (up to 15%). Since 1986, dicofol has been required to contain no more than 0.1% DDT, and so it is no longer a significant source of DDT emission to the environment. The UNECE LRTAP Convention has proposed that dicofol be banned by 2010–2020 (Denier van der Gon et al. 2007, Hoekstra et al. 2006).

The temporal trends of global DDT usage in agriculture and emissions due to agricultural applications from 1947 to 2000 (Figure 2.2) shows that use and emissions have decreased continuously since the end of the 1960s and the beginning of the 1970s, when the United States and other western countries banned DDT for agriculture. The total emission of DDT from agricultural applications is estimated to be 1030 kt between 1947 and 2000.

2.2.2.2. Toxaphene

Toxaphene was one of the most heavily used pesticides on a global basis with an estimated cumulative usage of 1,330 kt (Voldner and Li 1995). Of the top 10 countries contributing to toxaphene usage (Table 2.3), the US consumed the largest amounts (490 kt) followed by the former Soviet Union (254 kt). Figure 2.3 shows the temporal trends of toxaphene usage and emission from 1947 to 2000, both of which have decreased continuously since the middle of the 1970s mainly due to reduced use in the United States. Total global toxaphene emissions are around 407 kt from 1947 to 2000 (Li and Macdonald 2005).

2.2.2.3. Polychlorinated biphenyls (PCBs)

A global inventory of PCB usage and emission has been developed by Breivik et al. (Breivik et al. 2002a, Breivik et al. 2002b, Breivik et al. 2007). The estimates account for a reported historical global production of approximately 1,300 kt PCBs, more than 70% of which are tri-, tetra- and pentachlorinated biphenyls. The results further suggest that almost 97% of the global historical use of PCBs have occurred in the Northern Hemisphere (Breivik et al. 2002b).

Major inventories of PCBs are still maintained in Canada (Environment Canada 2005) and in the US (USEPA 2010c), and use continues in closed systems. Under the Commission for Environmental Cooperation, the PCB Task Force is developing and promoting PCB management strategies for North America (CEC 2011). Emissions from in-use and waste inventories in urban areas has been estimated at between 0.01–0.3% annually of the total documented stocks (Diamond et al. 2010).

Figure 2.4 lists the top 10 countries with the largest usage of 22 PCB congeners (CB-5, -8, -18, -28, -31, -52, -70, -90, -101, -105, -110, -118, -123, -132, -138, -149, -153, -158, -160, -180, -194, -199). According to (Breivik et al. 2002b), the total global usage of these 22 PCB (Σ_{22}PCB) congeners was approximately 570 kt, among which, the use in the United States was estimated as 250 kt, or about 45% of the total global use. Denier van der Gon et al. (2007) estimated the PCB emission was 133 t in the year 2000 in UNECE Europe.

TABLE 2.3. Top 10 countries using toxaphene between 1947 and 2000 (Li and Macdonald 2005)

Country	Usage (kt)	Time period
United States	490	1947–1986
Soviet Union	254	1952–1990
Nicaragua	79	1974–1990
Mexico	71	1952–2000
Egypt	54	1956-1961
Brazil	50	1955–1993
Syria	33	1952–1990
France	26	1952–1991
Columbia	23	1955–1990
Form. East Germany	22	1950-1990

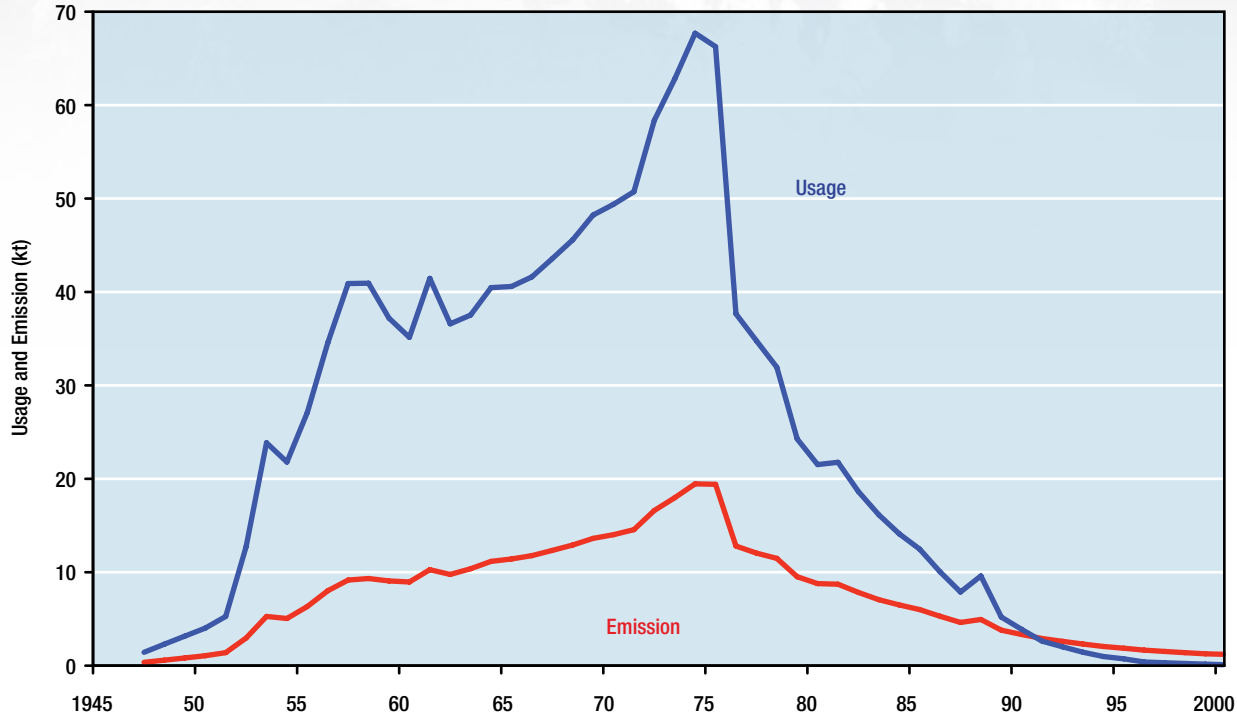


FIGURE 2.3

Temporal trends of toxaphene usage and emission from 1947 to 2000 (Li and Macdonald 2005).

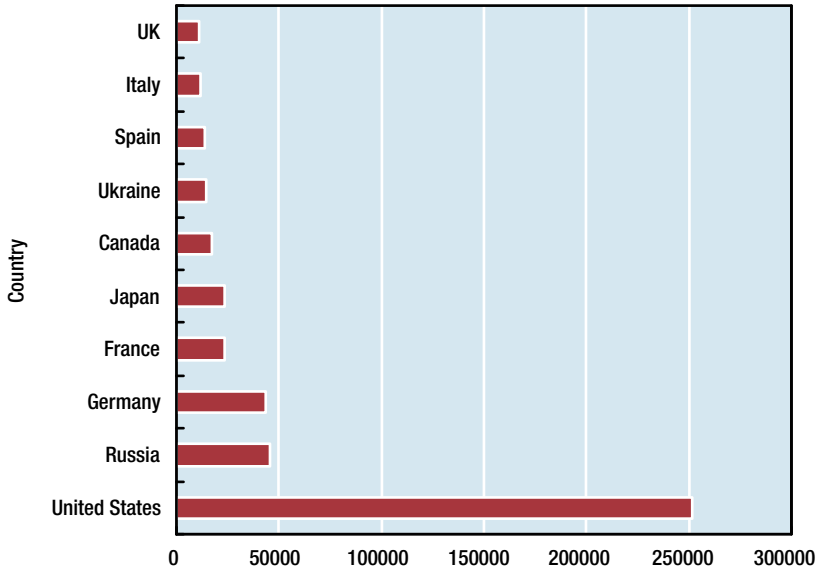


FIGURE 2.4

Top 10 countries using 22 PCB congeners (CB-5, -8, -18, -28, -31, -52, -70, -90, -101, -105, -110, -118, -123, -132, -138, -149, -153, -158, -160, -180, -194, -199) (data from Breivik et al. 2002b).

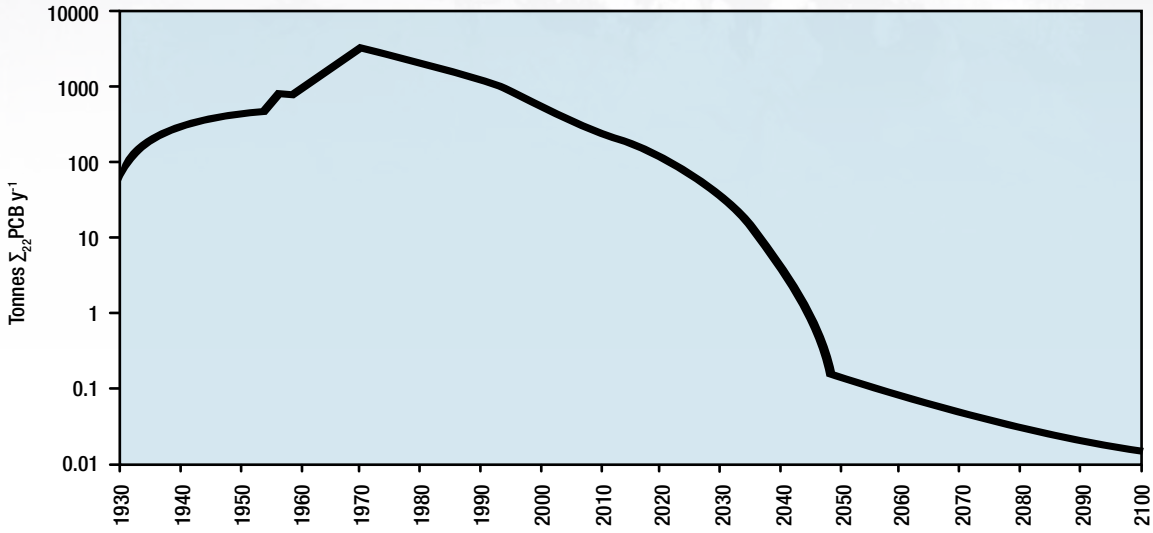


FIGURE 2.5

Estimated temporal development of global emissions of Σ_{22}PCB (in metric tons per year) from 1930 to 2100 (modified from Breivik et al. 2007).

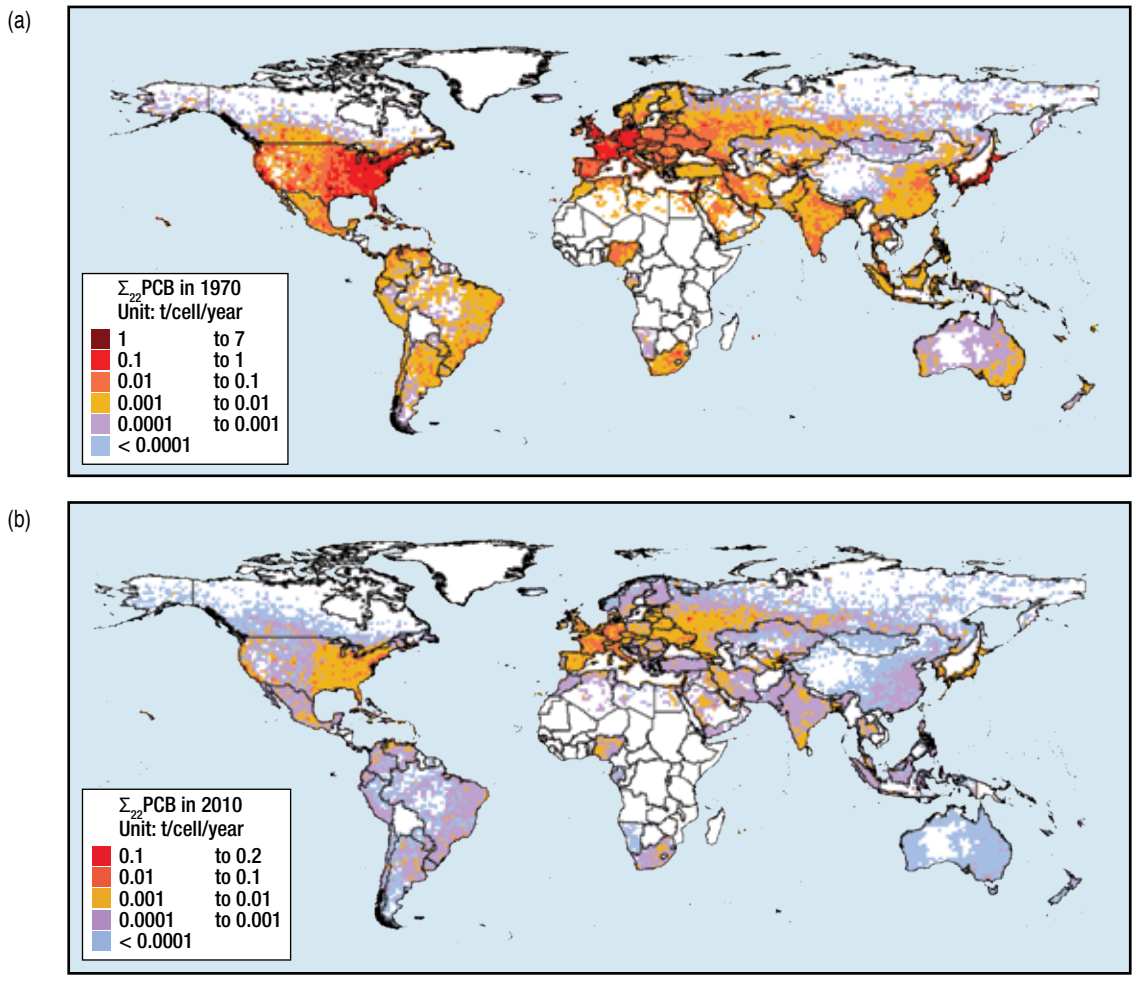


FIGURE 2.6

Emissions of Σ_{22}PCB in (a) 1970 and (b) 2010, with 1° x 1° latitude/longitude resolution. Data from Breivik et al. (2002a) and Breivik et al. (2007).

Figure 2.5 describes the estimated annual temporal trend in global emissions of Σ_{22}PCB from the start of their production in 1930 until 2100. According to this scenario, global atmospheric emissions of Σ_{22}PCB peaked with more than 3000 t emitted in 1970, and decreased continuously, reaching about 200 t in 2010. Global emissions of Σ_{22}PCB in 1970 and in 2010, with 1° x 1° latitude/longitude resolution, are shown in Figure 2.6.

2.2.2.4. Dioxins and Furans

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are "non-intentionally " produced POPs. They are ubiquitous by-products of various industrial processes and incinerators (e.g., waste incineration, iron and steel production, coal burning and some industrial processes involving chlorine) as well as of natural combustion processes (e.g., forest fires, volcanoes). Due to their pchem properties, PCDDs and PCDFs can enter into the food chain and tend to accumulate in many compartments, including adipose tissues of exposed organisms, and cause a variety of deleterious effects on biological systems.

Figure 2.7 shows the emission data of these chemicals for each region in 2004. The total global dioxin release to environment reached 77.4 kg TEQ, among which, 38.2 kg TEQ are emissions to the air. Figure 2.8 presents the total release and emissions to air of PCDD/Fs on different continents. The highest total release to all media and the emissions to air was in Asia, followed by South America.

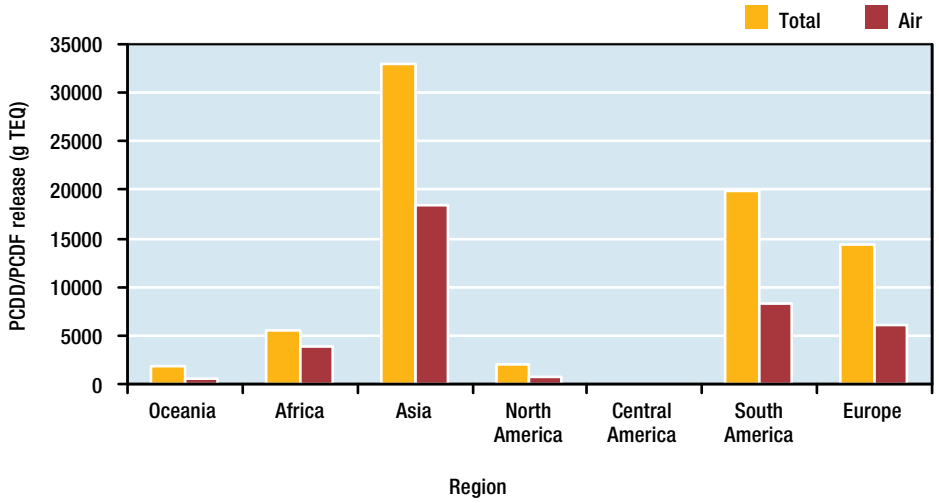


FIGURE 2.7

Global PCDD/Fs release in 2004 based on countries (a preliminary version) (Li et al. 2010).

Photo: iStock Photos

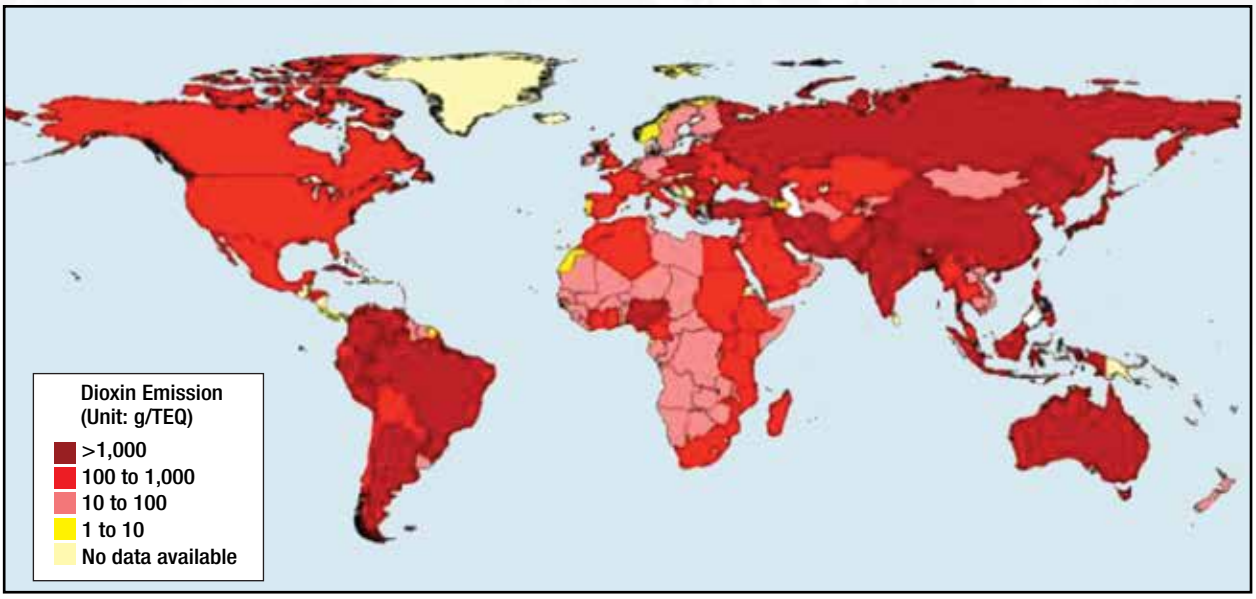


FIGURE 2.8

Total PCDD/F release and emissions to air in different continents for 2004 (Li et al. 2010).

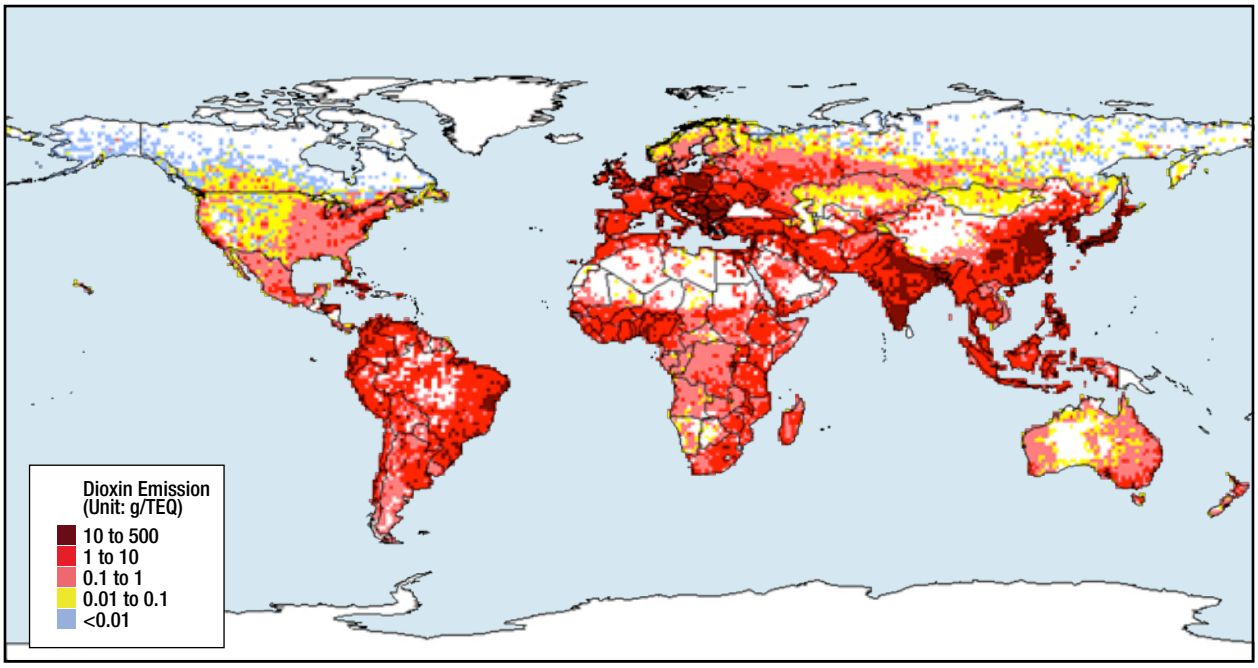


FIGURE 2.9

Gridded dioxin emission inventory for 2004 with 1° latitude by 1° longitude resolution (a preliminary version) (Li et al. 2010).

The purpose of emission gridding is to allocate the emission of pollutants to areas where the emissions actually occurred. This is very important for both policy makers and chemical fate/transport modelers. Figure 2.7 provides the total emissions for each country, but does not show the actual emission locations. It would be very useful if the emission data based on countries be distributed among proper areas. In this case, population dataset is used as a surrogate to allocate the emissions of dioxin. Figure 2.9 describes global gridded PCDD/F emission inventories, with 1° x 1° latitude/longitude resolution, showing that the emission of PCDD/F in 2004 was heavy in central Europe, India, China, South Korea, and Japan.

Denier van der Gon et al. (2007) estimated the PCDD/Fs emission to air was 11.7 kg TEQ in 2000 in UNECE Europe, almost 2 times higher than in 2004 in Europe (6.0 kg TEQ) as described in Figure 2.8.

2.2.3. CUPs including lindane and endosulfan

2.2.3.1. Global lindane soil residue inventory

Lindane, also known as γ-HCH is an organochlorine chemical that has been used as an agricultural insecticide (Geldmacher-v Mallinckrodt and Machbert 1997).

The global γ-HCH soil residue inventory for 2005, illustrated in Figure 2.10, is adapted from Li and Ren (2008). As shown in Figure 2.10, the major sources of γ-HCH across the world in 2005 were in central Europe, India, China, and the Canadian Prairie provinces. The total soil residues of γ-HCH in 2005 were estimated to be 13,600 t in the world—3,700 t in Europe, 3000 t in India, 2200 t in North America (NA), 1900 t in China, and 1200 t in the Former Soviet Union (FSU). The total amount of γ-HCH in soils of these five regions is 88% of total global residues.

2.2.3.2. Endosulfan

Endosulfan, an organochlorine pesticide used by many countries but being phased out, was first introduced in the 1950s by Hoechst AG and FMC Corporation as a non-systemic and ingested insecticide and miticide. Endosulfan has been used to control insects on food crops such as grains, tea, fruits and vegetables, as a wood preservative, and on non-food crops such as tobacco and cotton, worldwide. It is also used for public health applications such as the control of the tsetse fly. Endosulfan, consists of 70% α-endosulfan and 30% β-endosulfan (Maier-Bode 1968, Rice et al. 1997). It is extremely toxic to fish (UNEP 2010).

Global usage

Because of its toxicity to human health and the environment, endosulfan was included in the Stockholm Convention in April 2011 and the ban took effect in mid-2012, with certain uses exempted for 5 additional years. More than 80 countries, including the European Union, many West African countries, Australia, New Zealand, Canada, the United States and Brazil, have already banned it or announced phase outs. However, it is still used extensively in India, China and a few other countries (UNEP 2009). In completing revised assessments, the US EPA has concluded that endosulfan's significant risks to wildlife, the environment as well as to agricultural workers, outweigh its limited benefits and therefore US EPA is taking action to end all uses of endosulfan in the United States (USEPA 2010a) and phasing it out completely as of 2016.

According to the International Stewardship Centre (ISC) (cited in UNEP 2010), the total average annual use quantity of endosulfan in the past years is estimated at approximately 15,000 t of active ingredient. Brazil, India, China, Argentina, the US, Pakistan, Australia and Mexico represent the major markets. Also according to ISC, the use in Latin America and Asia has been growing consistently (cited in UNEP

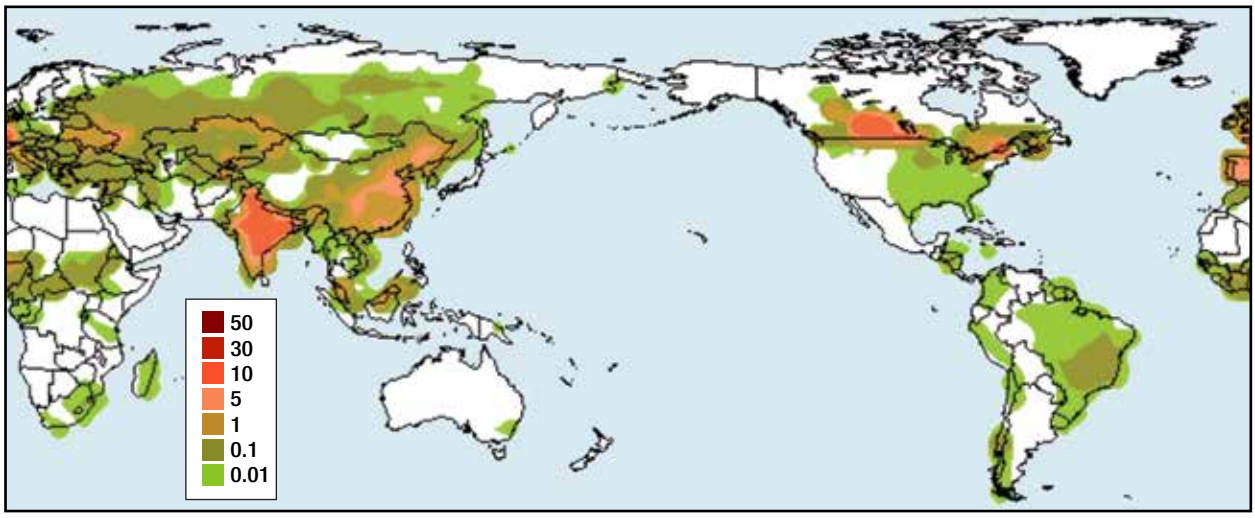


FIGURE 2.10

Gridded global γ-HCH soil residues (tonnes cell^{-1}) in 2005 with 1°×1° latitude/longitude resolution (Li and Ren 2008).

2010). Endosulfan has been one of the most widely used insecticides in India and it is the world's largest manufacturer of this insecticide as well as the major user. Of an estimated annual production of 9,500 t, 4,500–5,000 t are consumed domestically (UNEP 2010, BiPRO GmbH 2010). The endosulfan phase-out commitment under the Stockholm Convention is often loosely referred to as a "ban" thereby clearing it for elimination. However, India made use of the provision for "exception" which will allow it to manufacture and use the substance until a safer, cost-effective alternative is found. India agreed to decrease endosulfan use in five years which is extendable by another five years. Consequently, the country will have 11 years to wean away from endosulfan use altogether.

A total annual use of 15,400 tonnes was distributed in Argentina (1,500 t), Brazil (4,400 t), India (5,000 t), China (4,100 t) and the US (400 t). If the production amount of 18,000 to 20,000 tonnes per year is assumed to be used, then the remaining 3,000 to 5,000 t are used by other countries (BiPRO GmbH 2010).

Figure 2.11 (top panel) presents the temporal trend of endosulfan usage (and also its emissions) from 1954 to 2005, indicating that the general trend of total global endosulfan use has increased continuously since the first year this pesticide was applied. The total usage and emissions of endosulfan from 1954 to 2005 were 420 kt and 190 kt, respectively. The average annual endosulfan consumption in the world was estimated to be 10.5 kt from 1980 to 1989 and 12.8 kt from 1990 to 1999 (Li and Macdonald

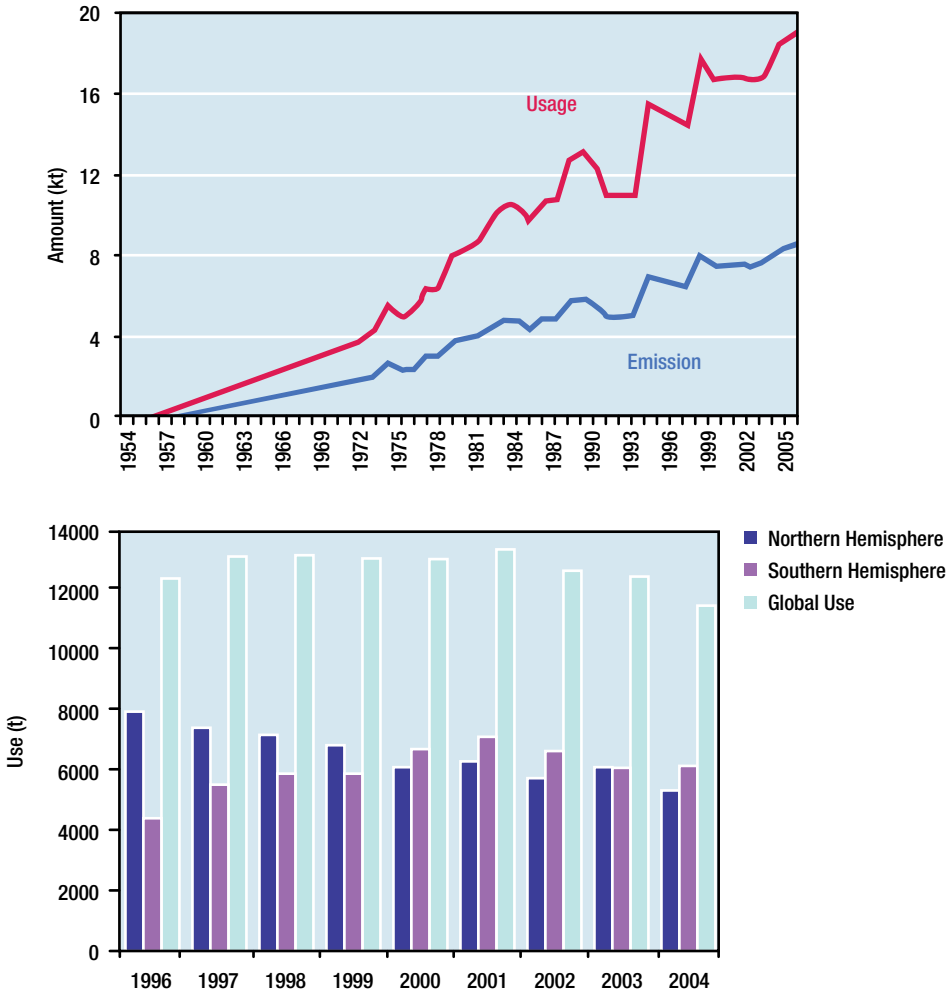


FIGURE 2.11

Temporal trend of endosulfan in usage and emissions from 1954 to 2005 (top panel) (Li and Macdonald 2005), and summary of global endosulfan use (bottom panel) (Mackay and Arnold 2005).

2005). These data correspond to the World Health Organization (WHO) report of worldwide annual production at 10 kt in the 1980s (WHO 1984) and also agree with the 12 to 13 kt reported annual production in the 1990s (Li and Macdonald 2005).

Global use of endosulfan for the period 1996–2004 is displayed in Figure 2.11 (bottom panel). While endosulfan use appears to have declined in the northern hemisphere over this period, use in the southern hemisphere has increased (e.g., South America, Australia), maintaining an annual average global use of 12.45 kt for the period 2000 to 2004 (Mackay and Arnold 2005). UNEP (2010) estimated global production of 18 to 20 kt per year as of the late 2000s with India accounting for 50-60% of global production.

Cumulative global use of endosulfan is estimated to be 450 kt from 1954 to 2010, and gridded global endosulfan usage (t cell^{-1}) for 1954–2010, with 1° x 1° latitude/longitude resolution, is presented in Figure 2.12.

Global emission

It was reported that endosulfan emissions in UNECE-Europe in 2000 was 775 t (Denier van der Gon et al. 2007). Total global endosulfan (α- plus β-endosulfan) emissions have also increased continuously since the year when this pesticide was first applied (Figure 2.11, top panel), amounting to a total emission close to 150 kt at present (Li and Macdonald 2005). Cumulative global emission of endosulfan (α- plus β-endosulfan) for 1954–2010 is estimated to be 215 kt, around 48% of the total global usage.

Figure 2.12 presents the distribution of total endosulfan emissions from 1954 to 2010 with 1° x 1° latitude/longitude resolution (Jia and Li 2010).

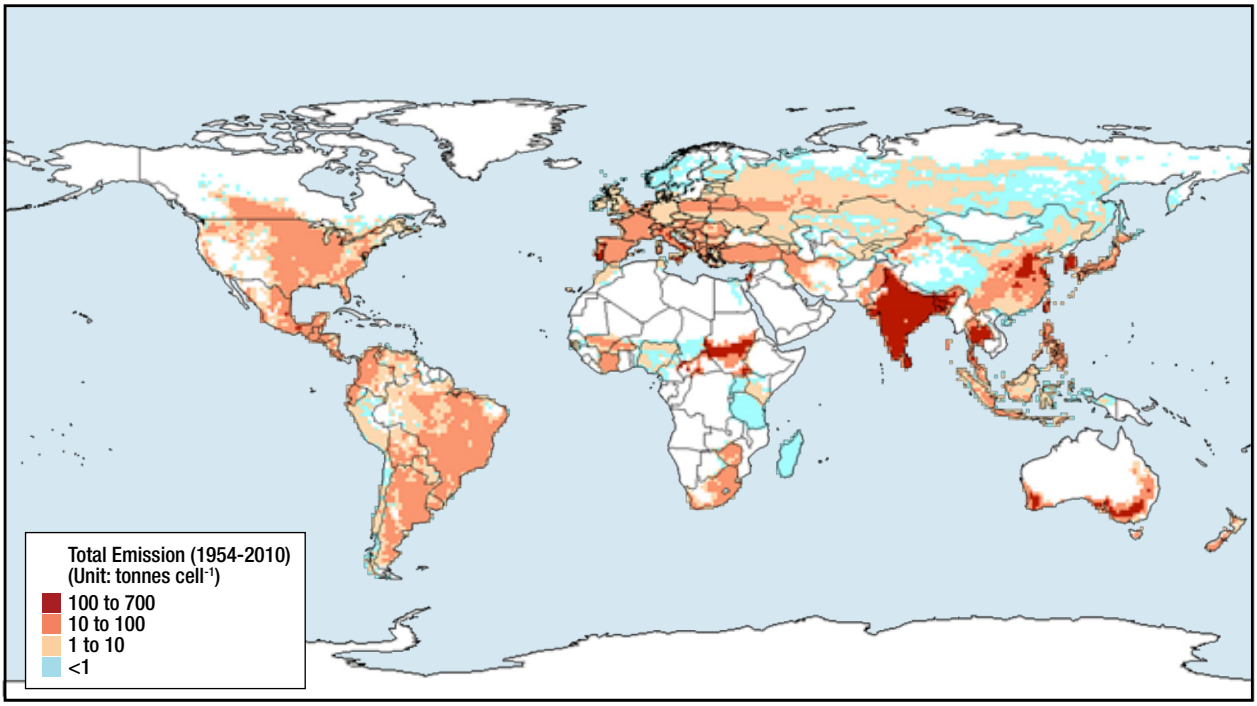


FIGURE 2.12

Distribution of total endosulfan emissions from 1954 to 2010 with 1° x 1° longitude and latitude resolution (a preliminary version). The total endosulfan emission is 215 kt, almost half of the total global usage (Jia and Li 2010).

2.2.4. PBDEs, PCNs, DP, HCB

2.2.4.1. Polybrominated diphenyl ethers (PBDEs)

PBDEs comprise a class of substances consisting of 209 possible congeners with 1–10 bromine atoms. PBDEs are found in three commercial mixtures, typically referred to as pentabromodiphenyl ether (Penta-BDE mixture), octabromodiphenyl ether (Octa-BDE mixture) and decabromodiphenyl ether (Deca-BDE mixture). Penta-BDE mixture is predominantly a mixture of penta-BDE, tetra-BDE and hexa-BDE congeners, but may also contain trace levels of hepta-BDE and tri-BDE congeners. Octa-BDE is a mixture composed mainly of hepta-BDE, octa-BDE and hexa-BDE, but may also contain small amounts of nona-BDE and deca-BDE. Current formulations of Deca-BDE are almost completely composed of deca-BDE and a very small amount of nona-BDE. Tetra-, penta-, hexa- and octa-BDEs are listed in the Stockholm Convention.

PBDEs may be released to the environment during manufacturing and polymer processing operations, throughout the service life of articles containing them, and at the end of article service life during disposal operations. With their low vapour pressures, low water solubility and high log K_{ow} values, it is expected that PBDEs entering the environment will tend to bind to the organic fraction of particulate matter, notably in sediment and soils, with only small amounts partitioning into water and air.

The commercial production of PBDEs began in the late 1970s (WHO 1994a; Hardy 2002). Historically, production of the PBDE commercial mixtures was focused in the United States, Israel, Europe and Japan. According to reports by WHO (1994a) and IARC (1990) there may have been as many as 12 major manufacturers of PBDEs in the world before 1990: 2 manufacturers in the United States (BFRIP 1990), 2 manufacturers in Belgium, 1 each in Switzerland, the United Kingdom and Israel (IARC 1990), and 2 in Japan (WHO 1994a). The total market demand for PBDE increased during later years from 204,325 tons in 1999 to 223,482 tons in 2003 (BSEF 2003).

Schenker et al. (2008b) estimated the global usage for PBDEs (as Penta-, Octa- and Deca- mixtures), with results shown in Figure 2.13. These estimates, however, are much lower than other estimates of PBDE usage. For example, according to (BSEF 2003),

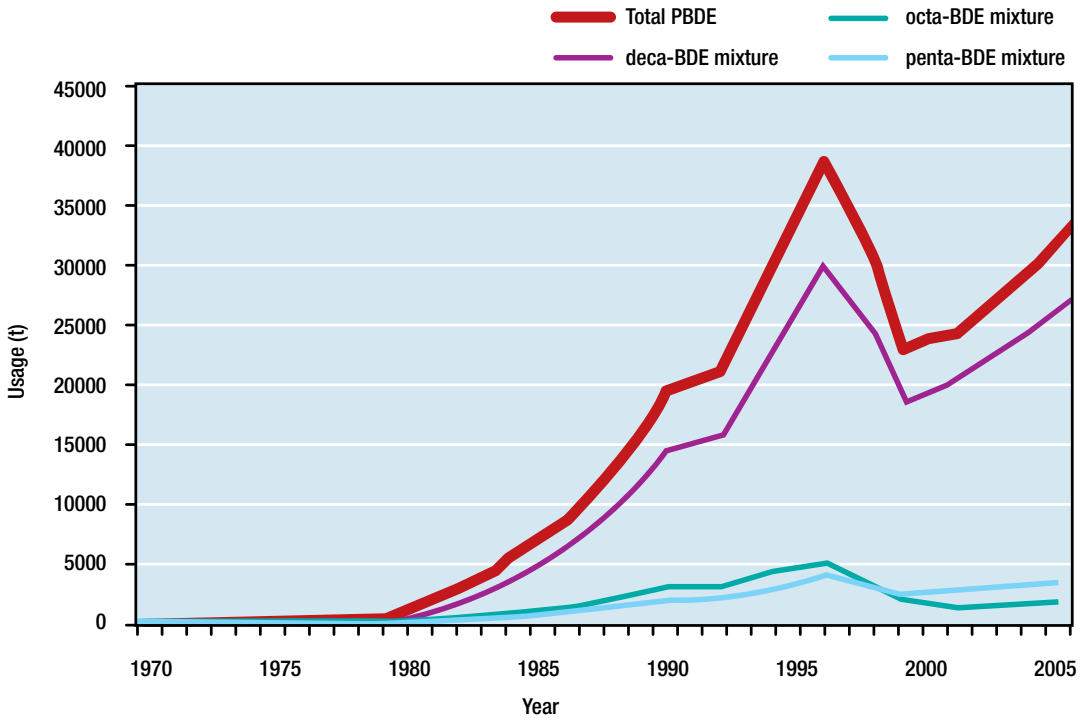


FIGURE 2.13

Estimated global PBDE usage for 1970-2005. The total usage was estimated to be 510 kt (Schenker et al. 2008b).

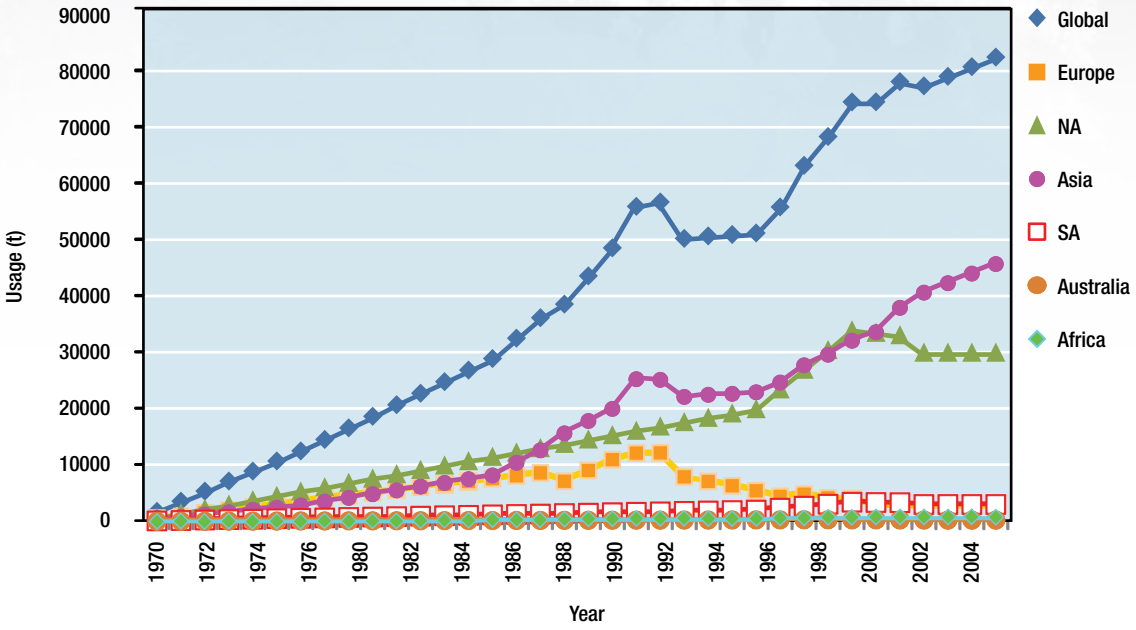


FIGURE 2.14

PBDE usage (tonnes) in different continents for 1970-2005 (Li 2009).

global demand for PBDEs rose to 67,390 tonnes for the year 2001 including 7,500 t of Penta-BDE; 3,790 t of Octa-BDE; and about 56,100 t of Deca-BDE. The global usage estimated by Schenker et al. (2008b) for the same year were 2,700 t of Penta-BDE; 1,500 t of Octa- BDE; and 20,000 t of Deca-BDE.

Another approach was carried out by Li (2009), and the results are presented in Figure 2.14. The total global usage of PBDE for 1970–2005 was estimated to be 1,218 kt, for which, 410 kt in NA, 590 kt in Asia, 160 kt in Europe, and 58 kt in other continents. This estimate over 2 -fold higher than that given by Schenker et al. (2008b) (Figure 2.13).

A preliminary version of a global grid of Penta-BDE emissions in 2005, with a 1° x 1° latitude/longitude resolution, was developed and is shown in Figure 2.15. Total Penta-BDE emissions in that year were 820 t.

2.2.4.2. Polychlorinated naphthalenes (PCNs)

Based on their high toxicity, persistence, bio-accumulation, and long-range transport, PCNs were selected as a candidate POP by the UNECE LRTAP POP protocol (Lerche et al. 2002). In 2011, the European Union proposed PCNs for addition to the Stockholm Convention. Due to their structural similarity to dioxins, PCNs exhibit toxicological properties similar to dioxins, with the ability to bind to and activate the aryl hydrocarbon receptor (Olivero-Verbel et al. 2004). In addition, studies have suggested that PCNs contribute a greater proportion of the dioxin-like activity than PCBs and PCDD/Fs in some locations (Kannan et al. 1998, Kannan et al. 2001).

PCNs were produced commercially as complex technical mixtures with trade names that included Halowaxes (US), Seekay Waxes (UK), Nibren Waxes (Germany), and Clonacire Waxes (France). PCNs started to be produced for high-volume uses around 1910 in both Europe and the United States (Puzyn and Falandysz 2004), and until the 1970s, PCNs were high volume chemicals. Production of PCNs has decreased significantly since 1977 (van de Plassche and Schwegler 2002).

Production volumes are not well known. It was reported that PCN production volumes are unlikely to have exceeded 10% of total PCB production (Beland and Geer 1973), and are estimated at 50–150 kt (Falandysz 1998, Hayward 1998).

The production of PCNs in the US stopped in 1980 (van de Plassche and Schwegler 2002). In the US, annual production was approximately 3.2 kt (around one third of the total global production if production

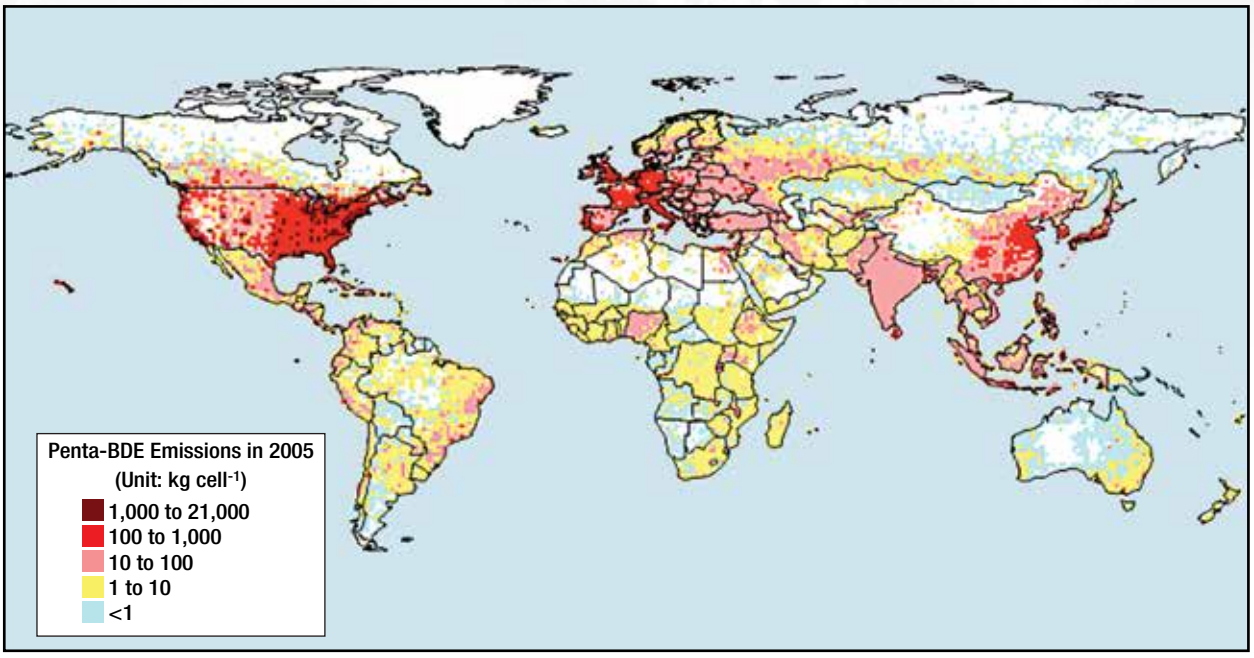


FIGURE 2.15

Global gridded penta-BDE emission (kg per cell) in 2005 on a 1° latitude by 1° longitude resolution (Li 2009).

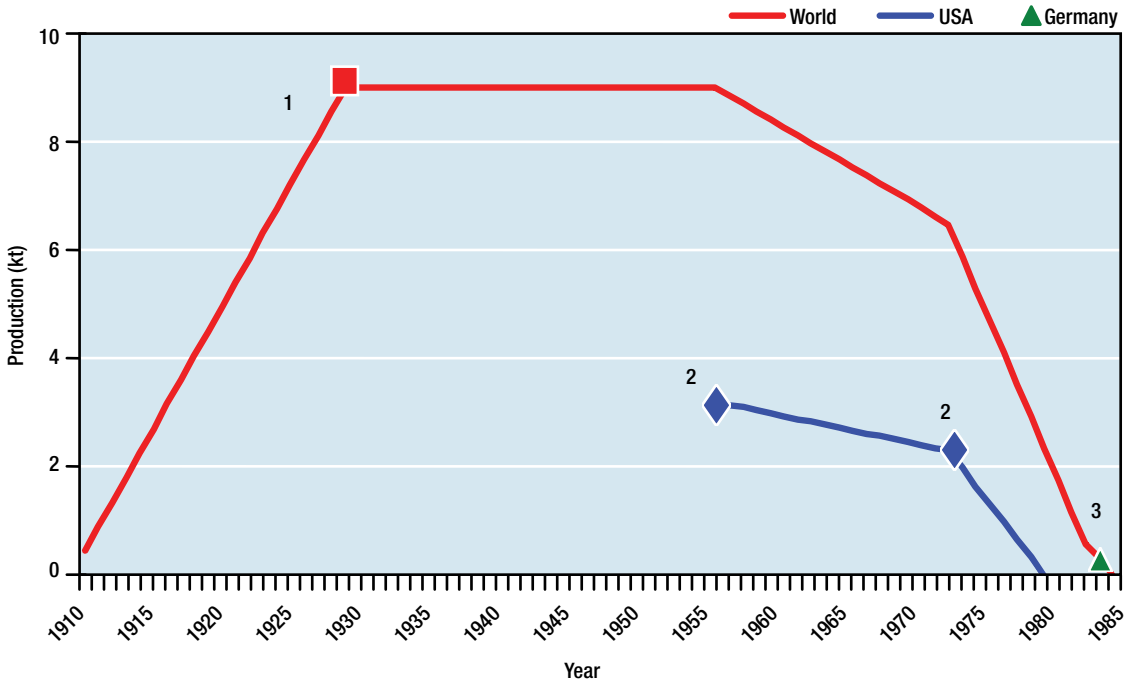


FIGURE 2.16

Global production of PCN (kilotonnes) from 1925 to 1985. The total production is estimated to be 450 kt (Li 2011). Data sources: 1. van de Plassche and Schwegler (2002); 2. Kover (1975); 3. Crookes and Howe (1993).

of 9 kt per year is used) in 1956 declining to nearly 2.3 kt by 1973 (Kover 1975). Koppers Company (Pittsburgh, USA), the main US manufacturer, ended production in 1977, and the remaining US production ended by 1980 (Crookes and Howe 1993). In the UK, production stopped in the mid-60s, although Crookes and Howe (1993) report that in 1970, small amounts of PCNs were still being produced. In Germany, around 300 t were produced in 1984, mainly for use as dye intermediates.

A linear interpolation was made to calculate the total PCN production by using the data reported above, and the results are shown in Figure 2.16. Based on the interpolation, the total global PCN production would be 450 kt, much higher than the previously estimated 50–150 kt (Falandysz 1998, Hayward 1998).

The use and application of PCNs was rather diverse. The most important uses, in terms of volume, were in cable insulation, wood preservation, engine oil additives, electroplating masking compounds, feed-stocks for dye production, dye carriers, capacitors and refracting index testing oils (van de Plassche and Schwegler 2002).

In the US, only small amounts of PCNs—approximately 15 t per year—were used in 1981, mainly as refractive index testing oils and capacitor dielectrics. The estimated annual toxic emissions of PCNs from the global coking industry vary from 430 mg to 692 mg TEQs. Characteristics of the PCN profiles were dominated by the lower chlorinated homologues, with mono-CN being the most abundant homologue (Liu et al. 2010a). It was reported that PCN emissions in UNECE-Europe in 2000 were 1 t (Denier van der Gon et al. 2007), and emissions in the United States and Asia should be much higher. The data, however, are not available at the present time. Falandysz (1998) reports the use of PCNs as casting materials until 1989 in Germany and the former Yugoslavia.

Figure 2.17 presents global, gridded PCN usage for 1920–1985, with a 1° x 1° latitude/longitude resolution, displaying the heavy use of PCNs in the United States, Europe, and Japan.

2.2.4.3. Dechlorane Plus

Dechlorane Plus (DP) is produced by combining hexachlorocyclopentadiene and 1,5-cyclooctadiene in a 2:1 mole ratio, respectively, to produce technical DP, which consists of the *syn* and *anti* isomers (Figure 2.18):

These isomers are present in the technical product in a ratio of about 1:3; that is, the *anti* isomer is about 75% of the total. Although exact synthesis procedures used in the industrial production of DP, both historical and current, are not known, patent information suggests the starting materials are also

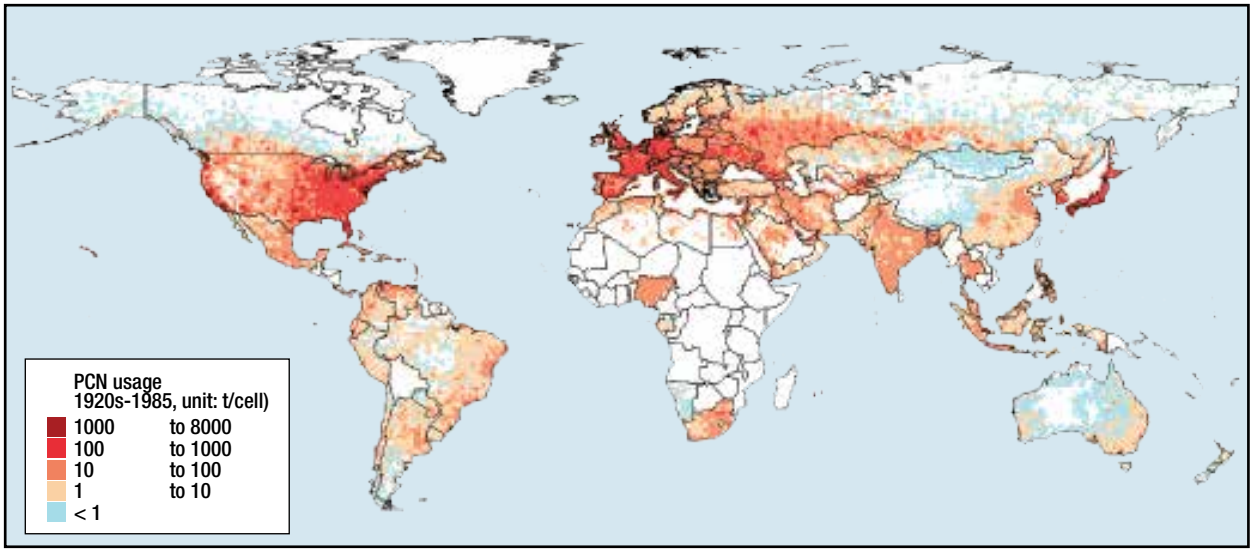


FIGURE 2.17

Global gridded PCN usage (kilotonnes) for 1920s-1985 on a 1° latitude by 1° longitude resolution (a preliminary version) (Li 2011).

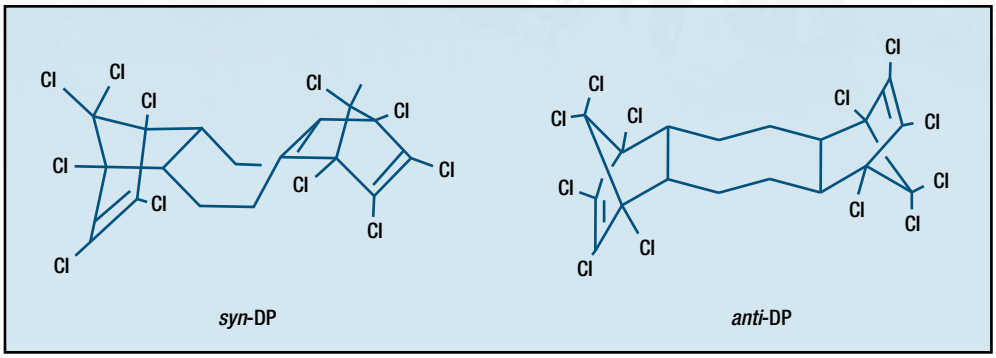


FIGURE 2.18

Structures of syn and anti isomers of Dechlorane Plus.

exposed to elevated temperatures. Current worldwide production volumes are estimated to be 5,000–6,000 tons annually (Sverko et al. 2011).

A DP manufacturing plant, Jiangsu Anpon Electrochemical Company, in Huai'an, China, was reported recently (Ren et al. 2008, Wang et al. 2010a) as operating since 2003 (ANPON 2011). Annual DP production amounts are estimated to be 300-1000 tons totaling 2100-7000 tons to date (Wang et al. 2010a).

2.2.5. Poly- and perfluorinated alkyl substances (PFASs)

PFASs are organofluorine compounds that consist of a hydrophobic alkyl chain of varying length (typically C4 to C16) and a hydrophilic end group with the general formula $F(CF_2)_n$-R (Buck et al. 2011, Parsons et al. 2008). In this assessment, we have adopted the terminology recommended by Buck et al. (2011) who suggest the abbreviation "PFAS" rather than the frequently used "perfluorinated chemicals or compounds; PFCs" because the latter refers to a much broader group of perfluorinated hydrocarbons. The PFAS have unique properties to make materials stain, oil, and water resistant, and are widely used in diverse applications. Perfluorinated alkyl acids, such as PFOS, are terminal breakdown products of PFASs that are highly persistent in the environment. PFOS (and its salts) have been identified as POPs and have been added to the LRTAP POPs protocol and the Stockholm Convention as of 2010.

From 1947 to 2002, the electrochemical fluorination (ECF) process, which is one of four distinct synthesis routes of perfluorooctanoic acid (PFOA) manufacture, was used worldwide to manufacture approximately 80–90% of total global production. The largest production sites were in the US, Belgium, Italy and Japan. The remaining 10–20% of PFOA was manufactured from 1975 to 2006 by direct oxidation of perfluorooctyl iodide in Germany and Japan. Global historical PFOA production was reported to be 4,400–8,000 tonnes whereas the estimated total global historical emissions was between 470–900 tonnes between 1951 and 2004 (Prevedouros et al. 2006).

There are many PFASs, but the most commonly studied compounds are (Guo et al. 2009):

- PFOA or perfluorooctanoic acid, used as a processing aid to make fluoropolymers such as Teflon®, among other applications. It is also a degradation product of a wide range of PFASs including the polyfluoro telomer alcohols.
- PFOS or perfluorooctanesulfonic acid, used in the semiconductor industry. Its precursors were used in stain repellents, and in aqueous foam forming firefighting products. It is also still used in other firefighting foams and this application is an acceptable use under the Stockholm Convention.
- PFNA or perfluorononanoic acid, used as surfactant in the emulsion polymerization of fluoropolymers (i.e., similar use as PFOA).
- PFBS or perfluorobutanesulfonic acid, used as a replacement for PFOS
- POSF or perfluorooctanesulfonyl fluoride, used to make PFOS-based compounds.
- PFOSA or perfluorooctanesulfonamide, formerly used as an intermediate for production of sulfonamide based stain repellents.

PFOS and POSF are included in Annex B of the Stockholm Convention on Persistent Organic Pollutants (Table 1.3).

Paul et al. (2009) published a new estimate of the global historical production for perfluorooctane sulfonyl fluoride (POSF), and then focused on producing a first estimate of the global historical

environmental releases of perfluorooctane sulfonate (PFOS). The total historical worldwide production of POSF was estimated to be 96,000 t (or 122,500 t, including unusable wastes) between 1970–2002 with an estimated global release of 6,800–45,250 t to air and water from direct (manufacture, use, and consumer products) and indirect (PFOS precursors and/or impurities) sources. The detailed information on different sectors is shown in Figure 2.19, and the temporal trends of global POSF production volumes for 1970–2005 are presented in Figure 2.20.

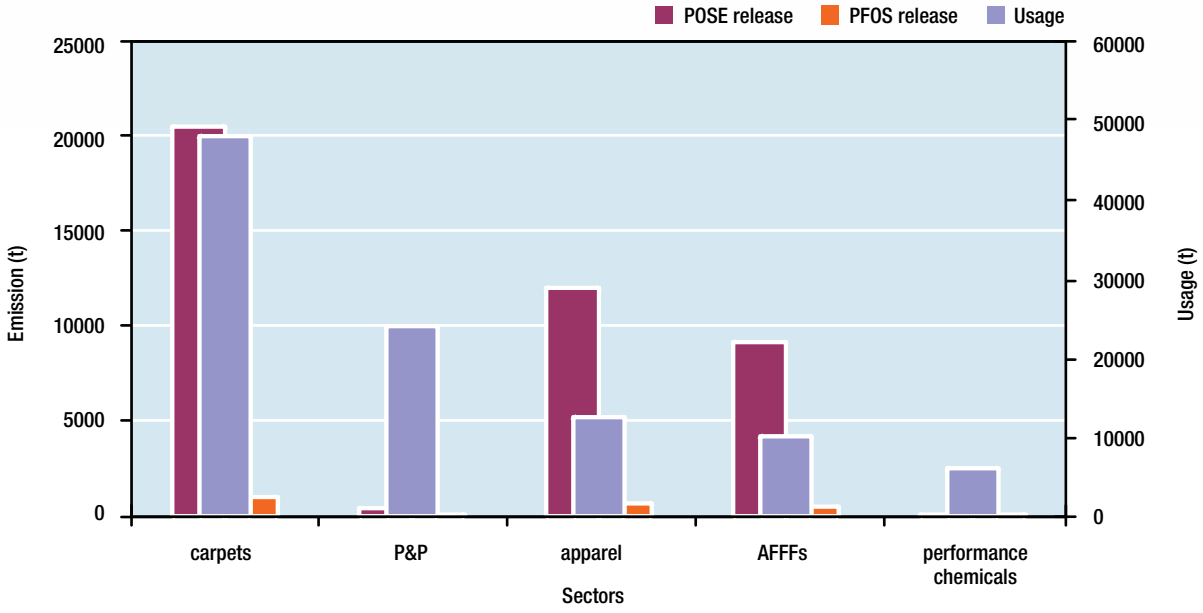


FIGURE 2.19

Global historical POSE and PFOS usage and emissions for 1970 – 2002 (Data from Paul et al. 2009). (P&P = Paper and Packaging).

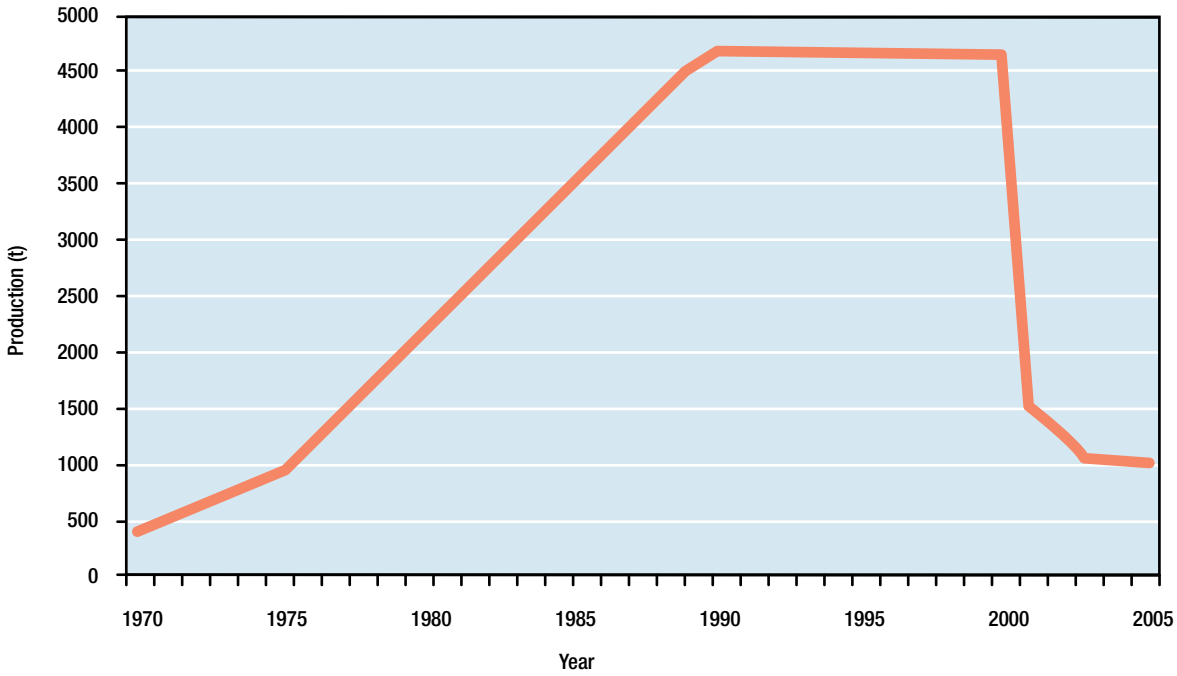


FIGURE 2.20

Estimated total global POSF production volumes for 1970-2005. The total historical worldwide production of POSF was estimated to be 100 675 t (Data from Paul et al. 2009).

Estimates indicate that direct emissions from POSF-derived products are the major source of emissions to the environment resulting in releases of 450–2,700 t PFOS into wastewater streams, primarily through losses from stain repellent treated carpets, waterproof apparel, and aqueous firefighting foams. Figure 2.21 depicts global gridded POSF emissions to air and water between 1970–2002, with a 1° x 1° latitude/longitude resolution.

The properties of PFOS (high water solubility, negligible vapour pressure, and limited sorption to particles) imply it will reside in surface waters, predominantly in oceans. It was suggested that around 235–1,770 t of PFOS currently reside in ocean surface waters, similar to the estimated values of PFOS releases (Paul et al. 2009).

2.2.6. Siloxanes

Siloxanes are organosilicons consisting of a backbone of alternating silicon-oxygen [Si–O] units with organic side chains attached to each silicon atom (Hobson et al. 1997). Over the last three decades, organosilicons (silicones), like cyclic siloxanes and polydimethylsiloxane (PDMS linear siloxane), have been widely used in consumer products such as electronics, furniture, health-care products, cosmetics, cookware, and medical devices because silicones have low surface tension, high thermal stability, and smooth texture and are believed to be inert. Annual production of octamethylcyclotetrasiloxane (D4, where D refers primarily to the dimethylsiloxane unit and the number 4 refers to the number of Si–O bonds that make up the chain), used as a base material for the production of polymeric silicones, is 45–230 kt per year (Horii and Kannan 2008). Howard and Muir (2010) and Brown and Wania (2008) identified the cyclic and linear methyl siloxanes with 3 to 6 siloxane groups as persistent and bioaccumulative chemicals with long range transport potential. McLachlan et al. (2010) showed that decamethylcyclopentasiloxane (D5) was subject to long-range atmospheric transport based on a study at a rural site in southern Sweden, but that it is was also effectively removed from the atmosphere via phototransformation. MacLeod et al. (2011) modeled the global fate of using the BETR world model (see section 2.3.4.1 for further details). They noted that the fate and transport of D5 was dominated by atmospheric processes due to its volatility. At steady-state, greater than 75% of the global inventory of D5 was predicted to be in the atmosphere, with most of the remainder in soils. Recent measurements of cyclic siloxanes have been made in arctic air (Table 2. 4) using passive sampling (Genualdi et al. 2011). Consult Chapter 3, section 3.1.5.1 for more information.

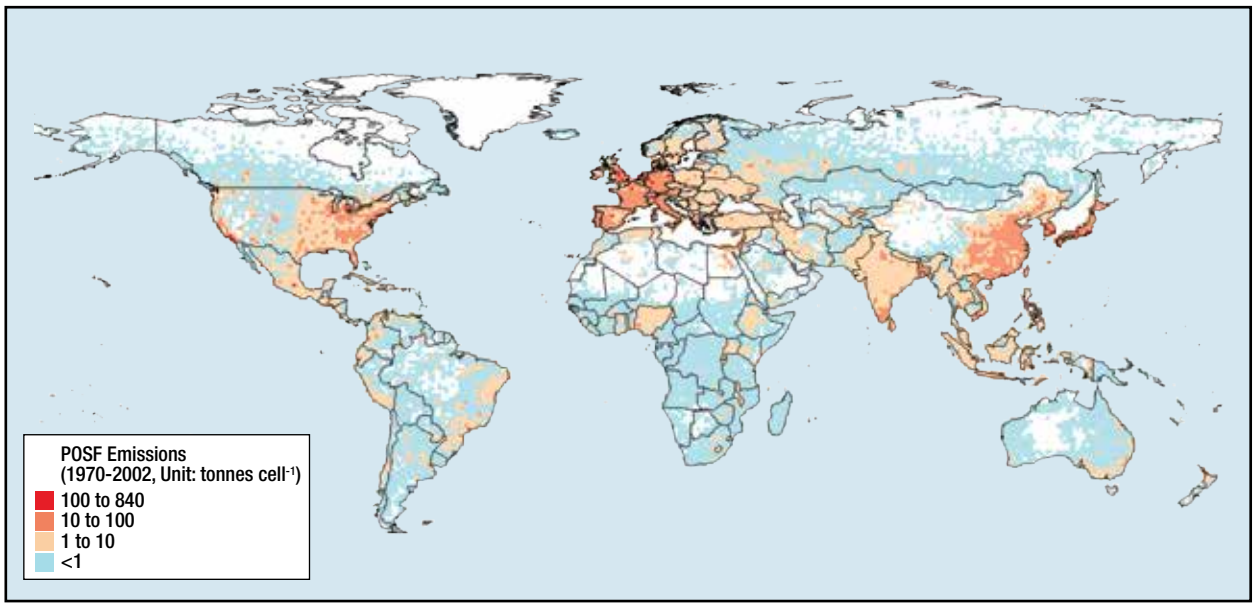


FIGURE 2.21

Global gridded POSF emissions to air and water between 1970–2002, with a 1° x 1° latitude/longitude resolution, a preliminary version. Total estimated global release is 45,250 t. Produced by using data from Paul et al. (2009).

TABLE 2.4. Names and structures of major volatile methyl siloxane compounds determined in arctic samples

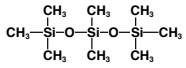
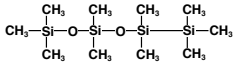
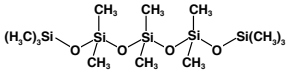
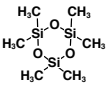
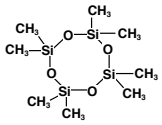
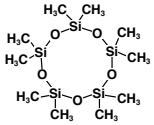
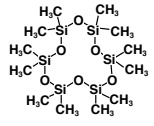
Name	Abbreviation	Formula	Structure
Octamethyltrisiloxane	L3	$C_8H_{24}O_3Si_2$	
Decamethyltetrasiloxane	L4	$C_{10}H_{30}O_3Si_4$	
Dodecamethylpentasiloxane	L5	$C_{12}H_{36}O_5Si_4$	
Hexamethylcyclotrisiloxane	D3	$C_6H_{18}O_3Si_3$	
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	
Decamethylcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	
Dodecamethylcyclohexasiloxane	D6	$C_{12}H_{36}O_6Si_6$	

Photo: Rodd Laing

2.3. Processes Controlling Transport of POPs to and Within the Arctic

Coordinating authors: Perihan Kurt-Karakus, Hayley Hung, Jianmin Ma

2.3.1. Introduction

The Arctic is surrounded by populated continents and is well connected to the currents of the atmosphere and oceans that carry various contaminants, including persistent organic substances, heavy metals, acids or radionuclides. Previous assessment reports of CACAR (Bidleman et al. 2003, Fisk et al. 2003) and AMAP (2004, 2009) confirmed the presence of POPs in all environmental compartments of the Arctic. Yet most of these contaminants originate from transboundary pollution in the atmosphere or via oceans from source areas outside of the Arctic, in particular, the industrialised and populated areas of Europe, North America and Asia. However, a few primary local sources, e.g., Distant Early Warning (DEW) line sites, and community settlement areas, have also been identified as sources contributing to the contamination of this region.

Pollution can be transported to the Arctic by the air, oceans and by rivers (Figure 2.22), as well as by migrating animals (Section 2.3.8.6 and Chapter 3, section 3.6). Atmospheric transport is the main pathway bringing certain POPs to the Arctic. Wind currents provide a fast transport route for contaminants within a matter of days. It is particularly important in the winter, when arctic haze occurs and air masses from Europe travel up into the Arctic and become either trapped by the stable conditions of the long arctic winter, or move down into northern

FIGURE 2.22

POPs transport pathways to the Arctic (adapted from Macdonald et al. 2005).

North America. Contaminants carried by these air currents are deposited along the route.

Most contaminants of interest to the Canadian Arctic generally are from outside of the polar region; however, there are some local sources to consider as well (see section 2.3.7 and Chapter 3, section 3.4). As discussed in section 2.1 and 2.2, long-range transport is governed by certain properties such as air-water partition and air-particle partition coeffcients, by atmospheric residence times and the influence of proximity of source areas. Persistence, characterized by resistance to bio-transformation and to chemical hydrolysis, is an additional characteristic for such chemicals with respect to long-range riverine and ocean transport.

Three major environmental compartments receiving contaminants in the Arctic are the atmosphere, terrestrial/freshwater and marine compartments. This chapter summarizes both physical processes and the nature of the main pathways for each of these three compartments. General concepts on transport mechanisms and processes affecting the inter- and intra-compartmental interactions of POPs are outlined. The arctic region has a total land area of 13.4×10^6 km^2 and ocean area of 20×10^6 km^2 (Gloersen et al. 1992). Canada's arctic and sub-arctic, the region north of 60º latitude, encompasses the Beaufort Sea in the west to Baffin Bay and Davis Strait in the east, Ellesmere Island to the north and Hudson Bay in the south. Although the focus of this assessment report is on the Canadian Arctic, the discussions on transport pathways and processes affecting the fate of the contaminants within the environmental compartments must be assessed for the entire Arctic. Clearly, there is a large degree of variability across this huge area. To provide a framework for this discussion, a simple box model has been used to illustrate the dominant processes and pathways of contaminants for the arctic region in the previous NCP (Bidleman et al. 2003) and AMAP (2004) assessments. In the current evaluation, we follow a similar method and the principal physical contaminant pathways into and within the Arctic are schematically summarized in Figure 2.23. The four types of pathways of contaminant transport to the Arctic are (see Figure 2.23):

- through air and water
- chemical or biological transformation within the system
- anthropogenic sources of contaminants within the system
- exchange between compartments within the system

Atmosphere, terrestrial/freshwater environment and ocean are the main components of complex transport pathways and reservoirs in the Arctic system. Snowpack, ice formations, and sea-ice are the seasonally variable sub-compartments. Estuary and deltas are also key interfaces between the terrestrial/freshwater and ocean compartments, although they are smaller spatially compared to the three main compartments as large amounts of sediment transported by rivers are deposited in deltas and estuaries. In this box model, the exchange processes involve transport and chemical/physical reactions during the movement of the chemical across the interface.

Building on this brief introduction, this section and its subsections further discuss the transport of contaminants to the Arctic by the pathways shown in Figure 2.22 and the inter-compartmental processes involved in the Arctic summarized in Figure 2.23. Section 2.3.3 explores the atmospheric compartment and its direct exchange with snowpack, surface ice of lakes and sea, and the surface ocean. Additionally, indirect exchanges of POPs between the atmosphere and the terrestrial/freshwater environments via wet and dry deposition as well as the direct exchange of POPs between the atmosphere and rivers, lakes, soil and vegetation are considered. Section 2.3.5 focuses on oceanic transport of POPs to the Arctic, with special attention on POPs with high water solubilities such as HCHs and perfluorinated chemicals. Section 2.3.6 discusses enantiomer fractions and isomer ratios as tracers of source and air-surface exchange from the point of view of arctic pollution. This section briefly discusses how chiral compounds are used as tracers of surface-air (soil-air and water-air) gas exchange, followed by information on how isomer ratios are used for source and pathway apportionment with a focus on HCHs, DDTs, chlordane and toxaphene compounds and PCNs. In general, POPs pollution in the Arctic cannot be related to any known use and/or releases in the region and is generally explained by long-range transport; nonetheless, a few local sources of organochlorines have been disclosed. Military "DEW Line" sites used DDT mixtures, as well as PCB-containing devices, widely and following disposal, vandalism and natural processes, resulted in the release of some of the PCBs into the environment. More recently, leachate from waste disposal areas has been documented as a local source of PBDE contamination in the Canadian Arctic. Such local sources of POPs are discussed in Chapter 3, section 3.4. Finally, effects of climate change on the transport of POPs to the Arctic and the fate of contaminants are discussed in section 2.3.8.

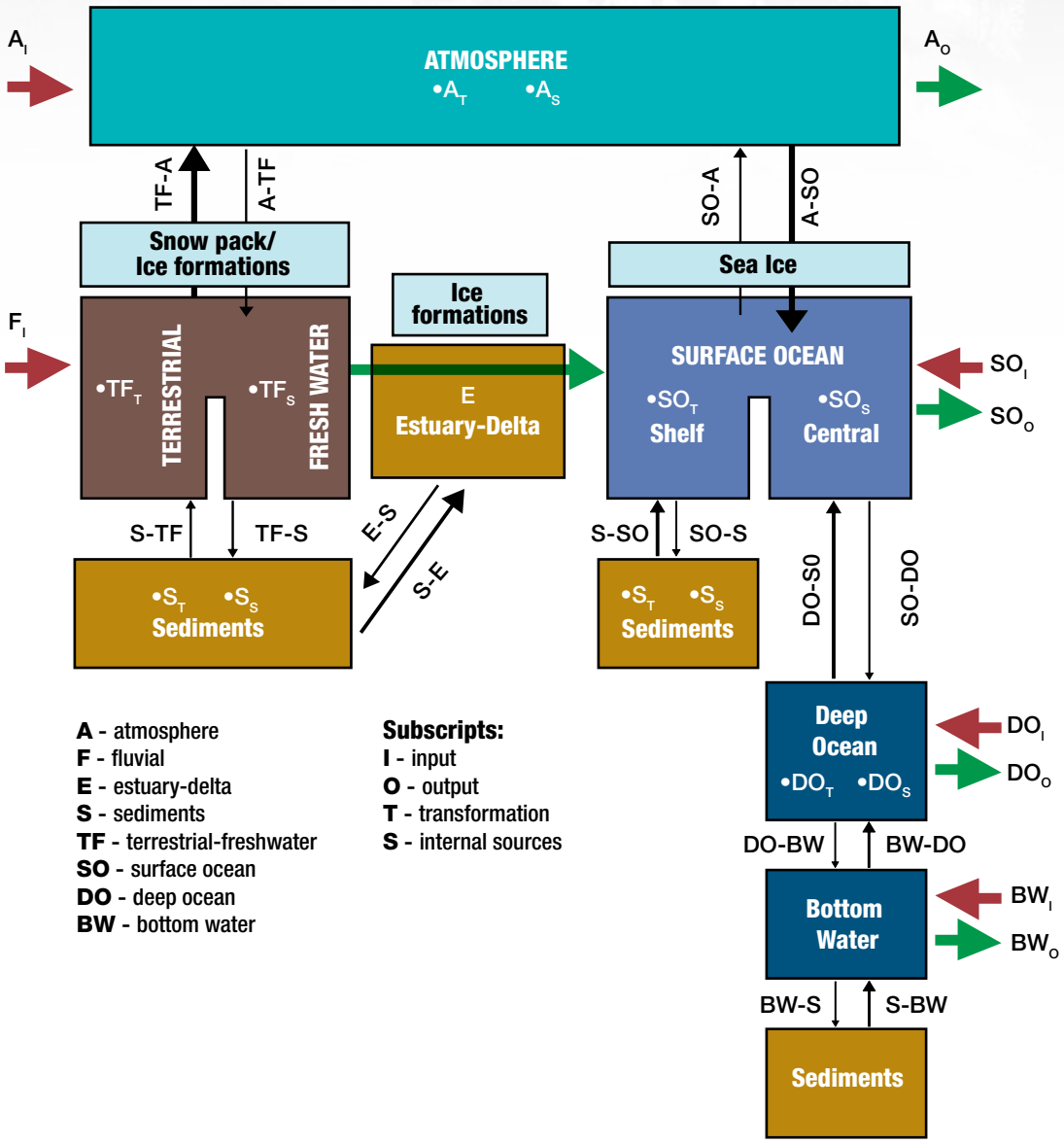


FIGURE 2.23

Arctic system components and major pathways of contaminants into and within the arctic environment. Boxes represent reservoirs, arrows represent processes and bullets within the boxes represent transformations as loss or gains (modified from Macdonald et al. 2000 and Macdonald et al 2003a).

2.3.2. Long-range atmospheric transport

Contributors: Hayley Hung, Perihan Kurt-Karakus, Jianmin Ma

The role the atmosphere plays on the transport and circulation of contaminants has been discussed in detail in earlier publications (Barrie et al. 1992, Iversen 1989a, b, 1996) and further discussions have been made in AMAP POPs assessments (2004, 2009). Contaminants are delivered to the north by atmospheric transport. Briefly, the mean flow in winter is out of Eurasia into the Arctic and out of the Arctic into North America. Northward transport from mid-latitudes decreases in summer. Three types of flow regimes involved in the exchange of mass or heat between polar and extrapolar regions are (i) mean meridional circulation, (ii) stationary planetary waves (such as the wavenumber 1–3 eddies in the Northern Hemisphere), and (iii) transient eddies. Given that stationary planetary waves are stronger in winter than in summer, in low atmosphere, Siberian high-pressure systems tend to play a more prominent role in the northern hemispheric winter than in summer. Total eddy exchange is stronger than mean meridional circulation at all times in the Northern

Hemisphere, but not during winter in the Southern Hemisphere when mean meridional circulation dominates (Macdonald et al. 2000).

Long-range atmospheric transport events can move polluted air masses within a short period of time from source regions into the central arctic region. Eckhardt et al. (2007) have reported PCBs released from biomass burning observed in air at the Zeppelin arctic station (Ny-Ålesund, Norway) after a travel time of a few days (from agricultural fires in Eastern Europe) to a few weeks (from boreal forest fires in North America).

Reductions in global emissions of certain POPs may be reflected in their atmospheric concentrations in the Arctic. Li and Bidleman (2003) have observed rapid declines in arctic air concentrations of α-hexachlorocyclohexane (α-HCH) in 1983 and 1990 as a result of usage controls in China, India and the former Soviet Union, respectively. However, such declines may not be obvious for other chemicals since the transport of POPs to the Arctic is influenced by various local and seasonal factors, as well as the lifetime of the chemicals in different environmental matrices and re-emissions of previously deposited POPs in sinks, such as soil, vegetation, oceans and ice. The long-term trends of POPs measured in Canadian arctic air will be discussed further in Chapter 3, Section 3.1.

Levels and patterns of most POPs in arctic air also show spatial variability, which is typically explained by differences in proximity to suspected key source regions and long-range atmospheric transport potentials. For instance, PCB air concentrations at Ny-Ålesund and Storhofdi in the European Arctic have always been higher than those found at the Alert station in the Canadian High Arctic. Also, the air concentrations at Alert were statistically significantly different from the other two stations between 1998 and 2005 (Hung et al. 2010). The proportion of γ-HCH (i.e., 100*[γ /(γ+α)]) is generally lower at Ny-Ålesund than at Alert (Becker et al. 2008). These observations indicate that Ny-Ålesund and Storhofdi are more affected by European sources due to their close proximity while Alert is further away from its source. Other observed spatial diversities of POPs in the Arctic will be discussed in Chapter 3, section 3.1.

In a special study of atmospheric dioxins and furans at Alert during the winter of 2000–2001, Hung et al. (2002) have shown that the air concentrations of PCDD/Fs peaked at Alert when the air mass originated from Russia and Eurasia 5 days before. In spite of the remoteness of the site, congener profiles in most samples were enriched with PCDD/Fs, corresponding to ''source'' profiles as suggested by Wagrowski and Hites (2000). Similar profiles were observed in air and tree bark at other arctic locations. These profiles were probably the result of: (1) more effective transport of PCDD/Fs to receptors in Nunavut from sources relatively close (Canada and the US) than from those further away in Mexico (Commoner et al. 2000); (2) a greater chance for less volatile congeners to deposit out of the atmosphere before they reach the Arctic; and (3) the generally low temperature in the Arctic, coupled with low levels of solar radiation during winter, curbs the degradation/reaction processes. Therefore, the ''source'' and ''sink'' homologue profiles generally applicable to samples collected at temperate sites cannot be applied to those collected in the Arctic.

With a wide range of vapour pressures, the more volatile POPs (such as HCB and HCHs) exist primarily in the gas-phase in the atmosphere, while other less volatile POPs exist primarily in the particle- or aerosol-phase (e.g., dioxins and furans). Still other POPs, with intermediate vapour pressures (many organochlorine pesticides and many PCBs), are distributed between both the gas and particle phases. As a result, POPs are subject to both gas and particle phase removal mechanisms in the atmosphere, including wet and dry deposition, gas exchange and direct and indirect photolysis.

Atmospheric transport of contaminants can comprise "half-a-hop", "one-hop" or "multi-hop" processes. In half-a-hop pathways, less volatile contaminants are emitted to the atmosphere, transported and deposited to the Earth's surface and never return to the atmosphere. In "one-hop" pathways, molecules of a substance experience a complete deposition/volatilization cycle (if emitted to air) or a complete volatilization/deposition cycle (if emitted to soil) whereas multiple cycles are present in the case of "multi-hop" processes (Gouin et al. 2004). The distribution of such a contaminant could be determined by knowledge of its initial source distribution, atmospheric circulation and its lifetime in the atmosphere. One-hop or single-hop contaminants are marked by their longer atmospheric residence times in winter (approximately 20–30 days) when precipitation is at a minimum compared to summer when precipitation is at a maximum. Their input to the Arctic is additionally enhanced in the winter with a stronger south-to-north transport from Eurasia in comparison with the summer. Unlike half-a-hop chemicals, one-hop and multi-hop chemicals re-enter the atmosphere after initial deposition to the Earth's surface and can

move through the environment in multiple atmospheric hops (grasshopper effect) (Wania and Mackay 1996). Multi-hop transport processes can include volatilization from the terrestrial and aquatic surfaces in warmer temperatures, the re-release of previously deposited contaminants from ocean water following ice break up, or re-suspension of dust or snow by winds. Most POPs are multi-hop contaminants and complex multi-compartmental environmental models accounting for all system components are necessary to understand the complex pathways of these contaminants.

Several recent modeling studies have demonstrated that the free troposphere (approximately 1,000 m above the Earth's surface) is a more efficient pathway for atmospheric transport of POPs to the Arctic due to stronger winds and weaker dilution/dispersion of chemicals induced by turbulence (Eckhardt et al. 2009, Ma 2010, Zhang et al. 2010a, Zhang et al. 2008b).

Under both mean meridional atmospheric circulation and synoptic weather conditions, the long-range atmospheric transport of modeled HCHs and HCB from warm latitudes to the Arctic occurs primarily in the mid-troposphere. Although major sources of these chemicals are in low and mid-latitude soils, the modeled air concentration of HCHs in the mid-troposphere is of the same order as, or higher than, that near the surface, demonstrating that the mid-troposphere is an important pathway and reservoir of POPs. The cold trapping effect of HCHs is also likely to take place in the mid-troposphere, where lower air temperatures are observed, over a source region of POPs in warm, low latitudes. Frequent occurrence of atmospheric ascending motion and convection over warm latitudes carry the chemicals to a higher altitude where some of these chemicals may partition onto solid or aqueous phases through interaction with atmospheric aerosols, and cloud water droplets or ice particles, and become more persistent at lower temperatures. Stronger winds in the mid-troposphere then convey solid and aqueous phase chemicals to the Arctic where they sink by large-scale descending motion and wet deposition.

Processes involved in the exchange of contaminants between the atmosphere and the Earth's surface are dry deposition of particles, gas exchange and scavenging by precipitation. Airborne particles get into the near-surface layer from the free atmosphere mostly by synoptic-scale atmospheric descending motion, wet deposition, and turbulent activities including dry deposition (only when particles reach the atmospheric boundary-layer), and are finally trapped on or in the surface layer as a result of chemical-physical and molecular diffusion processes (Voldner et al. 1986). The type of surface, physical-chemical properties of the contaminant, and the state of the atmosphere are factors controlling the rate of particle transfer.

Considerable quantities of desert soils (Barrie 1995, 1996, Welch et al. 1991) and of snow associated with dispersed soil can be suspended freely in the atmospheric boundary layer and transported long distances. The High Arctic receives little precipitation in winter, thus soils which are not covered by snow in this region are directly exposed to wind events hence soil dust gets mobilized and mixed with surface snow throughout the year. Snow transport and entrainment into the atmosphere occurs by two primary modes: saltation and suspension. Saltation occurs at low wind speeds whereas suspension occurs at higher wind speeds and can cause dispersion of snow to heights of several meters.

Association of contaminants into rain or snow result in wet deposition of contaminants which includes in-cloud and below-cloud removal processes (Barrie 1991). With in-cloud removal, particles diffuse into liquid cloud droplets that are converted to precipitation (rain or snow) in complex ways. This process may be efficient or inefficient in removing contaminants, depending on the precipitation formation and physical-chemical properties of the substance. Under stable atmospheric stratification (e.g., atmospheric inversion), the contaminants accumulate within the atmospheric boundary layer, thus below-cloud scavenging may contribute significantly to wet deposition. However, below-cloud scavenging is reported to be generally of lesser importance compared to in-cloud scavenging under unstable atmospheric conditions (Murakami et al., 1983) and also in northern regions (Murakami et al. 1983, Rehkopf et al. 1984, Schumann et al. 1988, Scott 1981). The hygroscopic nature of the particles, the size distribution of atmospheric particles, precipitation intensity and cloud-based height are the factors affecting the efficiency of the particle scavenging process (Mitra et al. 1990, Sparmacher et al. 1993).

Clearly, a precise estimate of in-cloud scavenging for POPs requires a good understanding of POPs behaviour in clouds. Unfortunately, the knowledge of the interaction between the environmental fate of POPs and clouds is still poor. Ma (2010) has recently proposed that clouds are likely an important sorbing medium of POPs for the cold condensation effect and pole-ward atmospheric transport of POPs. In particular, the zonal mean cloud covers, averaged over the Northern

Photo: Martin Fortier/ArcticNet

Hemisphere, increase towards the Arctic and are associated with decreasing temperature (Ma 2010), favouring condensation of moist air mass. Clouds likely exert an influence on atmospheric distribution of POPs through two pathways: (i) gas-aqueous phase partitioning of POPs in clouds; and (ii) the sorption of POPs onto cloud condensation nuclei formed by organic aerosols. A modeling study has revealed that the cloud liquid water contents greater than 2 g m^{-3} could lead to over 50% of α-HCH to be sorbed onto cloud water droplets. Sorption of other POPs such as PCBs, PAHs and OCPs to cloud water droplets and ice particles was also found. Because of weak convections and the large scale of cloud cover over the far north, a large portion of clouds over the sub-Arctic and Arctic was likely advected from the south or formed by condensation of warm, moist air masses when they approach the Arctic on their way to the north. In the mean time, these clouds also provide a sorbing medium for the POPs and carry contaminants to the Arctic where they then sink by descending motion and rain or snow.

Snow is very efficient in scavenging of both vapour and particle-bound POPs from the atmosphere (Halsall 2004, Lei and Wania 2004, Wania et al. 1999b). Field studies showed that snow may be five times more efficient than rain at below-cloud scavenging due to the larger size and surface area of the snowflakes (Murakami et al. 1983, Sparmacher et al. 1993, Leuenberger et al. 1988, Nicholson et al. 1991, Schumann et al. 1988). Due to the potential for chemical scavenging and exchange with the lower atmosphere, snow influences the transport dynamics of POPs in the Northern Hemisphere. Vapour scavenging is a function of the air temperature and the specific surface area (SSA) of the snow and is predicted to be most pronounced for snow possessing high SSA (e.g., 1 $m^2 g^{-1}$) and at cold temperatures (less than -10°C), resulting in scavenging ratios for semi-volatile chemicals that are generally higher than rain by over one order of magnitude (Lei and Wania 2004). The seasonal snowpack, thus, serves as a sink for chemicals transported to higher latitudes with observed concentrations reported for a variety of POPs in arctic snow (Herbert et al. 2006). Contaminants stored in reservoirs such as snowpack, lake/sea ice and glaciers at colder conditions are delivered to terrestrial, freshwater and ocean environments by runoff from melted snowpack and ice formations. In the warmer season, terrestrial and fluvial processes such as runoff, hydrology, infiltration, and permafrost are also dominant pathways for the delivery of contaminants between arctic system compartments.

Gas exchange is a process that removes chemicals from the snowpack. The potential for exchange is determined by the partial vapour pressure of a compound between ambient air and air in the pore spaces in snowpack or ice. Moreover, the process is strongly affected by the temperature. Compounds with higher vapour pressures such as HCB and α- and γ-HCH can volatilize to a great extent whereas semi-volatile compounds with lower vapour pressures, like highly chlorinated PCB congeners, may not. The snowpack is a highly dynamic chemical exchange compartment, with substantial re-emission of POPs observed during snow ageing and compaction following fresh snowfall (Herbert et al. 2006). Furthermore, fresh snowfall and diffusive vapour exchange are processes that will add or remove chemicals to the standing snowpack.

To predict vapour exchange between the snowpack and air, knowledge of a chemical's snow-air partition coefficient ($K_{Snow\text{-}Air}$) and mass transfer coefficient (in snow) are required along with the physical properties of the snowpack (e.g., depth, density and SSA). The availability of a chemical for atmosphere-snow exchange is determined by the chemical's partitioning between snow grain surfaces and interstitial air. The associated $K_{Snow\text{-}Air}$ value is proportional to the product of snow density (ρ), SSA, and the temperature dependent equilibrium snow surface-air sorption coefficient $K_{IA} = C_I / C_A$, where C_I and C_A are the chemical concentrations in each of the two phases. Snow packs in sub-arctic and arctic regions are likely to be the most influential to the fate of POPs in the Northern Hemisphere because of their large areal coverage and duration. The chemical fraction available for atmosphere-snow exchange is expected to be larger in sub-arctic snow packs because K_{IA}, SSA, and ρ are usually smaller there than in arctic snow (Dominé et al. 2007, Taillandier et al. 2006). Wind pumping significantly increases the extent of chemical mass transfer within snow (Albert et al. 2002, Albert and Shultz 2002), which is in most cases the limiting factor for atmosphere-snow exchange. Wind induced advective transport in snow increases with higher wind speed above the snow pack, larger snow permeability, and more pronounced snow surface roughness characteristics. Whereas permeability is usually one order of magnitude larger in sub-arctic snow (Dominé et al. 2008), wind speed is generally higher above arctic snow packs. A case study related to atmosphere-snow exchange of the semi-volatile pesticide PCB 28 revealed that chemical mass transfer coefficients in snow packs that exhibit relatively large surface roughness, are two to three orders of magnitudes larger under the influence of moderately strong winds than under still wind conditions (Meyer and Wania 2010).

Gas exchange of contaminants, which is commonly a reversible process, may occur between the atmosphere and liquid water (freshwater or sea water), vegetation, or soil. However, gas exchange is not the only process that exchanges mass, i.e., there are wind speed and other types of depositions and degradations that make the net flux zero, but the relative magnitudes of volatilization and absorption (pertaining to gas exchange) are different, i.e., net gas exchange flux not equal to zero resulting in larger mass transfer of materials than is apparent from their net fluxes. As long as vapour phase and dissolved phase of contaminants are present, volatilization and deposition are continually occurring. Therefore, it is suggested that gas exchange should be calculated as two separate terms: one for "volatilization" and the other for "[vapour] deposition" (Murphy et al. 1995). Gas exchange with water, soils and vegetation is a controlling factor in determining a chemical's characteristic travel distance (CTD), LRTP, and overall persistence (P_{OV}) (Gouin and Wania 2007, Scheringer et al. 2010, Wegmann et al. 2004).

As the oceans are large reservoirs of certain chemicals where total burdens are much greater than those reported in air, and since the Arctic Ocean covers the majority of the Arctic's surface area, air-water gas exchange could be an important source of contaminants to the arctic air. Atmospheric PCBs and HCB have shown increasing temporal trends at Ny-Ålesund in recent years (2003–2006). A similar increasing trend of HCB was also observed at Alert after 2002 (Hung et al. 2010). This increase may be the result of a combination of the following two factors: (1) increase in worldwide use of HCB-contaminated pesticides, e.g., chlorothalonil and quintozene (pentachloronitrobenzene), followed by subsequent transport to the Arctic and (2) reduction in sea ice cover where Ny-Ålesund is located, on the west coast of Spitsbergen (Svalbard, Norway) which has been ice-free including winter (2005–2008), potentially resulted in increased volatilization of previously deposited chemicals from the ocean. Although dramatic decrease in sea ice was also observed in other parts of the Arctic, a permanently ice-free state at 80°N is fairly unique. This ice-free zone signature could be interpreted as a possible influence of regional climate change on the POPs distribution in the arctic environment. On the other hand, studies have predicted both net deposition of

HCB into (Lohmann et al. 2006, Su et al. 2006, Wong et al. 2011) and near-equilibrium with, or volatilization (Hargrave et al. 1997) from the Arctic Ocean. Gioia et al. (2008b) have suggested greater atmospheric deposition of PCBs along the melting ice margin due to increased air concentrations. However, it was also noted that changes in air and ocean current flow over time can potentially increase or decrease the relative capacity in the two media, subsequently reversing the direction of chemical flux from the air to the ocean and vice versa.

Vegetation has a large capacity to sorb a range of POPs from air (Dalla Valle et al. 2005). It can effectively take up POPs from air due to large leaf surfaces per unit of ground area. High sorption by fresh foliage led to a decline in air concentrations after the burst of leaf buds (Gouin et al. 2002). Organic pollutants have been found in various types of vegetation around the globe (Bacci et al. 1986, Collins et al. 2006, Kylin and Sjödin 2003, Simonich and Hites 1995), and POPs may be intercepted by forests along the atmospheric transport pathway to the Arctic (Su and Wania 2005). The chemicals deposited from air to vegetation are further transferred to the soil along with fallen leaves, an effective transfer pathway for the transfer of chemicals through "air-vegetation-soil", leading to elevated depositions of chemicals to soil. Concurrent measurements showed higher concentrations of POPs in forest soil than in nearby non-forest soil (Meijer et al. 2002). Degradation loss is usually slower in forest soil than in air, therefore, pollutants take a longer time to be removed from the environment (Su and Wania 2005). After primary emissions are reduced around the world, chemicals stored in soils are volatilized to air from secondary sources. The volatilization can be accelerated by warmer temperatures and forest fires. Genualdi et al. (2009a) found that 34–100% of pesticides were lost from burned forest soil relative to unburned forest soil. Increased forest fire events from boreal regions and related arctic haze events may be considered as important additional mechanisms of POPs transport to the Arctic. As mentioned above, Eckhardt et al. (2007) have attributed high air concentrations of PCBs measured at Ny-Ålesund in July 2004 and spring 2006 to boreal forest fires in the Yukon/Alaska and agricultural fires in Eastern Europe, respectively. Several high air concentration episodes of *cis*-chlordane, *p,p'*-DDE and *o,p'*-DDE were also observed at Alert and Ny-Ålesund in 2004 during these forest fire events (Hung et al. 2010). It is believed that biomass burning can enhance volatilization of previously deposited organic chemicals, such as PCBs and pesticides, from soil (Eckhardt et al. 2007, Genualdi et al. 2009a). Forest fires are also emission sources of combustion by-products such as PAHs and dioxins. Using positive matrix factorization and potential source contribution function, Sofowote et al. (2011) associated PAHs observed at the Little Fox Lake station in the Yukon with wildfires over British Columbia and western United States in the fall of 2008.

Soils are a vast reservoir for POPs that are atmospherically deposited or contaminated through direct application. A global survey of PCBs (sum of 22 congeners) in background soils estimated a burden of 21,000 t in the upper 5 cm layer (Meijer et al. 2003a), which is about 1.6% of the known production volume and about 30% of the 66,000 t estimated to have been cumulatively emitted to the atmosphere (Breivik et al. 2007). Global models for DDT suggest that 50–95% of the total mass in the environment is contained in soils (Guglielmo et al. 2009, Schenker et al. 2008a, Stemmler and Lammel 2009). Soils act as a source and exchange medium with the atmosphere through primary emissions (e.g., volatilization of applied pesticides in agriculture and PCBs from highly contaminated sites) and secondary emissions ('grasshopping'). Both single- and multi-hopping contribute to the transport of DDT and HCH (Semeena and Lammel 2005). Multi-hopping is thought to be responsible for the slow build-up of a number of semi-volatile organic compounds (SOCs) that are persistent in air and surface media in the Arctic once emissions have ceased (Gouin and Wania 2007). For some SOCs, (e.g., HCH), accumulation in the Arctic may be explained by single-hop atmospheric transport alone (Semeena and Lammel 2005). Secondary sources may be particularly important in the context of climate interactions and possible remobilization of POPs from soil reservoirs with a warming climate.

Last but not the least, POPs react with photochemically generated OH radical in the atmosphere and this has been shown to be the most significant environmental transformation reaction for some POPs (Anderson and Hites 1996). Such transformation processes are important in removing pollutants along the atmospheric transport pathway to the Arctic, affecting its atmospheric lifetime and, subsequently, influencing its Arctic Contamination Potential (ACP). However, for pollutants entering the Arctic during the winter, photodegradation is expected to be low due to the extended duration of darkness.

2.3.3. Air-water gas exchange

Contributors: Terry Bidleman and Liisa Jantunen

2.3.3.1. Air-sea exchange and secondary sources

International regulations as well as country-specific initiatives have banned the use and production of several POPs, which has successfully led to reductions in primary emission sources and declining ambient atmospheric levels, as documented in air monitoring programs (Chapter 3, section 3.1). Consequently, secondary emissions from water bodies and soil are becoming increasingly important as sources to the atmosphere (Nizzetto et al. 2010b). Oceans, seas and large lakes play a major role in the global cycling of POPs and other semi-volatile chemicals, either acting as a sink or a source to the atmosphere. Exchanges with oceans act to buffer the atmospheric declines brought about by emission reductions. For example, PCBs in air are declining more slowly over the Atlantic Ocean than over land (Nizzetto et al. 2010a). Modeling suggests that after their phase-out in 2000–2002, atmospheric levels of volatile precursors to perfluorooctane sulfonate (PFOS) have declined and air-sea exchange has reversed from deposition to volatilization (Armitage et al. 2009d). Air-water gas exchange dominates over other loading processes in oceans and seas for chemicals with a significant proportion in the gas-phase (Breivik and Wania 2002a, Breivik and Wania 2002b, Jurado et al. 2004). Gas exchange with water, as well as with soils and vegetation, is a controlling factor in determining the CTD, LRTP, and overall persistence (P_{OV}) of the chemical (Gouin and Wania 2007, Matthies et al. 2009, Scheringer et al. 2010, Wegmann et al. 2009).

The oceans play a critical role in determining the lag time for chemicals to reach the Arctic, either by transporting dissolved contaminants slowly to higher latitudes, or by providing a relatively non-sticky temporary storage reservoir which is in constant exchange with the atmosphere. Persistent multimedia chemicals which exchange with the oceans, such as short-chain perfluorinated alcohols, low molecular weight PCBs and HCB, experience a greater number of "hops" during atmospheric transport over the oceans compared to terrestrial surfaces (Gouin and Wania 2007). Single and multiple hopping each contribute about equally to the transport of DDT and HCHs to the Arctic (Semeena and Lammel 2005). A model of DDT in the global environment from 1950–2002 suggests that the world's oceans absorbed DDT until 1977 and since then have been losing DDT, although DDT is still accumulating in large sea areas. Volatilization is the main sink to the atmosphere, with the western North Atlantic being the most significant secondary source. Large parts of the tropical oceans and southern mid-latitude oceans underwent flux reversal from deposition to volatilization in the 1980s (Stemmler and Lammel 2009).

2.3.3.2. Gas exchange processes

The direction of diffusive exchange of gaseous chemicals across the air-water interface depends primarily on chemical concentrations in air and water and the temperature. Rates of transfer are controlled by wind speed. Fluxes are constantly readjusting seasonally, daily and even diurnally due to changes in temperature and air concentrations, and over the longer term, to changes in water concentrations. The net flux direction can be assessed by comparing fugacities (Pa) of the chemical in water and air (f_W, f_A), estimated from gaseous concentrations in air (C_A, mol m^{-3}), dissolved concentrations in water (C_W, mol m^{-3}) and the Henry's law constant (H, Pa m^3 mol^{-1}) at the water temperature:

$$f_w = C_W H \qquad \text{Eq.10}$$

$$f_A = C_A R T_A \qquad \text{Eq. 11}$$

$$FR = f_W/f_A = C_W H/C_A RT \qquad \text{Eq.12}$$

R is the gas constant (Pa m^3 mol^{-1} K^{-1}) and T_A is air temperature. Water/air fugacity ratios ($FR = f_W/f_A$) of less than 1.0, 1.0 and greater than 1.0 imply net deposition, equilibrium, and volatilization respectively.

The Whitman two-film model is the most common for estimating the rate of air-water gas exchange. Deposition, volatilization and net fluxes (F_D, F_V, F_N, mol m^{-2} d^{-1}) are calculated from the individual air and water fugacities and the mass transfer coefficient, which is mainly a function of wind speed. Relationships for calculating fluxes are presented in Bidleman and McConnell (1995) and Jantunen and Bidleman (2003). For simplicity, the net flux directions in the rest of this section are referred to as "deposition", "volatilization" and "near equilibrium".

2.3.3.3. Complications and uncertainties in gas exchange calculations

C_A and C_W specifically refer to gaseous chemicals in air and dissolved chemicals in water, respectively. These are usually measured as the fraction of the total chemical which passes through an air or water filter and is retained in a solid adsorbent trap. The particle/gas distribution can also be predicted through models based on the compound's liquid-phase vapour pressure or octanol-air partition coefficient, and soot-

Photo: Shelly Carpenter/ArcticNet

air partition coefficient for PAHs (Lohmann and Lammel 2004). Such models do not capture the complex interactions that occur between compounds of differing polarity and aerosols of varying composition. Polyparameter linear free energy relationships (pp-LFERs) have been proposed as an alternate approach, especially for polar compounds. Compounds sorbed to dissolved/colloidal organic matter in water are not retained by filters, which leads to overestimation of C_W and artificially inflates the volatilization component. Corrections can be estimated using partition coefficients of the chemical to dissolved/colloidal and particulate organic matter (Garcia-Flor et al. 2005, Rowe et al. 2007, Sobek et al. 2004, Zarnadze and Rodenburg 2008). Processes in the water column, such as plankton activity, dissolved-particle phase partitioning followed by sequestering to deep-water, chemical and biological degradation (Gioia et al. 2008b), and the salting-out effect on the Henry's law constant in saline waters (Cetin et al. 2006) also influence the rate of gas exchange. If particle sinking fluxes are faster than air-water exchange fluxes, then the system will not be at equilibrium (Gioia et al. 2008b). Concentration of POPs tend to be higher in the surface microlayer than in underlying water (Garcia-Flor et al. 2005, Guitart et al. 2010, Wurl and Obbard 2004) and modify the direction and magnitude of the flux (Guitart et al. 2010).

Uncertainty calculations using propagation of errors are an important consideration when estimating FRs and fluxes (Bamford et al. 2002, Bruhn et al. 2003, Gioia et al. 2008a, Gioia et al. 2008b, Jantunen et al. 2008a, Jantunen et al. 2008b, Wong et al. 2011, Xie et al. 2005). The largest uncertainties lie in the Henry's law constants and the air-water mass transfer coefficients, although in some cases variations in air concentrations are also a limiting factor (Cincinelli et al. 2009, Jantunen et al. 2008b, Jaward et al. 2004a). Short-term changes in wind speed lead to uncertainties in mass transfer coefficients, and using a Weibull distribution to describe cumulative frequency distribution of wind speed helps to reduce this uncertainty (Zhang et al. 1999, Wanninkhof et al. 2009). Accurate Henry's law constants are crucial in assessing gas exchange, and literature values are often in poor agreement. Progress has been made to achieve thermodynamic consistency among literature values of physicochemical properties, thereby reducing uncertainty in Henry's law constants and other properties (section 2.1).

2.3.3.4. Air-water gas exchange in the Arctic

The state of gas exchange for HCHs depends on location and time. Concentrations of α-HCH in the arctic atmosphere declined 10-fold between the 1980s and 1990s due to emission reductions in Asia (Li and Macdonald 2005, Li and Bidleman 2003), and concentrations of both γ-and α-HCH are continuing to decline (Becker et al. 2008, Hung et al. 2010). This decline forced a reversal of exchange in the Bering-Chukchi seas, from deposition in 1988 to near equilibrium or volatilization in 1993 (Jantunen and Bidleman 1995, Sahsuvar et al. 2003). A global model of α-HCH fate also predicted reversal of its exchange direction in the Arctic Ocean in the early 1990s (Wania and Mackay 1999, Wania et al. 1999a). Equilibrium or volatilization continues in the Archipelago and southern Beaufort Sea (Jantunen et al. 2008b, Su et al. 2006, Weber et al. 2006, Wong et al. 2011). In the eastern Arctic Ocean where water concentrations are lower, near-equilibrium or deposition was found for both HCHs (Harner et al. 1999b, Lakaschus et al. 2002, Lohmann et al. 2009).

Fewer measurements have been made of β-HCH in arctic-subarctic air and water. Reported concentrations in air of β-HCH at arctic monitoring stations are less than 1 pg m^{-3} (Annex Table A2-6), but higher concentrations have been reported from shipboard measurements over the North Pacific, Bering-Chukchi seas and Beaufort Sea (Wu et al. 2010). These authors suggested that volatilization from seawater may have contributed to the elevated β-HCH in air, despite its low Henry's law constant. Su et al. (2006) suggested that emissions from seawater may have contributed to atmospheric β-HCH concentrations at Point Barrow, AK, which

in 2002–2003 were approximately 2–3 times higher than those at Kinngait and Little Fox Lake (Annex Table A2-6). See also the modeling of β-HCH in the Arctic Ocean (Section 2.3.5.4).

Gas exchange of chemicals other than HCHs has been less well studied in arctic and subarctic waters. Phthalate esters were near equilibrium from 60–85°N (Xie et al. 2007b), while the polycyclic musk fragrances Galaxolide® and Tonilide® were depositing (Xie et al. 2007a). Air-water fluxes of PCBs 28, 52, 118 and 138 were estimated from paired air and water samples in the Norwegian and Greenland seas and the eastern Arctic Ocean (EAO) from 78–85°N (Gioia et al. 2008b). *FRs* depended on the choice of Henry's law constants, but in general indicated deposition. Deposition of Σ_{36}PCBs was reported for the Bering Sea in 1990 (Iwata et al. 1993a). Deposition of HCB was estimated in the Archipelago in 2007–2008 (Wong et al. 2011) (Figure 2.24 A). Measurements in the EAO-Greenland Sea region in 2004 indicated near-equilibrium of HCB, equilibrium of *trans*-chlordane and deposition of *cis*-chlordane (Lohmann et al. 2009). Concentrations of HCB in air at Svalbard had been declining since 1994, but then underwent an increase from 2003–2006. One factor may be an increase in ice-free conditions around Svalbard, which would facilitate sea-to-air exchange. Another factor may be use of HCB-contaminated pesticides such as chlorothalonil (Becker et al. 2009). Occurrence and air-water exchange of PBDEs 47, 99 and the non-BDE flame retardant DPTE (2,3-dibromopropyl-2,4,6-tribromophenyl ether) was investigated in the Greenland Sea by Möller et al. (2011) (Möller et al. 2011),with the result that all three compounds were undergoing net deposition, with fluxes ranging from -13 to -492 pg m^{-2} d^{-1} (BDE-47), -7 to -272 pg m^{-2} d^{-1} (BDE-99) and up to -1044 pg m^{-2} d^{-1} for DPTE.

Expeditions were made in the Canadian Arctic to investigate air-sea exchange of the legacy OCPs chlordane, heptachlor epoxide and dieldrin, and the CUPs dacthal, chlorothalonil and endosulfan (Jantunen et al. 2009a, b). Paired water and air samples were collected in summer and early fall across the Archipelago on Tundra Northwest 1999 (TNW-99), in the Labrador Sea, Hudson Strait and Hudson Bay on ArcticNet-2007, and off Banks Island in 2008 during the International Polar Year (IPY) Circumpolar Flaw Lead (CFL) study (collective referred to as ANIPY-2007/08). Water/air *FR*s are summarized in Figure 2.24. Chlordane compounds (*cis*-chlordane, *trans*-chlordane and *trans*-nonachlor) and dieldrin approached air-water equilibrium within a factor of two. A strong potential for volatilization was estimated for heptachlor epoxide in the ANIPY-2007/08 study, with *FRs* of approximately 3.

Total toxaphene concentrations in the surface water of the eastern Archipelago on TNW-99 averaged 114 ± 31 pg L^{-1}. Concentrations of 150 and 253 pg L^{-1} were reported at Holman Island and Baffin Bay in 1999–2000 (Hoekstra et al. 2002), and 45–85 pg L^{-1} at Resolute Bay in 1992 and 1993 (Bidleman et al. 1995, Hargrave et al. 1997). Air concentrations were unusually high on TNW-99 (mean 20 ± 8 pg m^{-3}) and similar levels were found at Resolute Bay (mean 19 ± 9 pg m^{-3}) in that summer. The *FR* = 0.15 (deposition), estimated using 114 pg L^{-1}, 19 pg m^{-3} and the appropriate temperature-adjusted Henry's Law constant (Jantunen and Bidleman 2000) (Figure 2.24). No explanation was found for the high air concentrations during that time, which otherwise had averaged 7 pg m^{-3} at Resolute Bay in 1992 (Bidleman et al. 1995), 4 pg m^{-3} over the Bering-Chukchi Sea in 1993 (Liisa Jantunen, Environment Canada, unpublished data), 11 pg m^{-3} at Alert in 1993 (Hargrave et al. 1997) and 3–7 pg m^{-3} at Alert in 1998 (Braekevelt et al. 2001). Combining the ranges of reported toxaphene concentrations in water (45–253 pg L^{-1}) and air (3–20 pg m^{-3}) yields a range of *FRs* of 0.06 to 2.1, while the *FR* = 0.37 using the averaged concentrations (133 pg L^{-1} water, 9 pg m^{-3} air). Overall, toxaphene exchange has varied throughout the 1990s from deposition to volatilization, with a tendency toward deposition. Toxaphene concentrations were below detection in air and water during 2007–2008.

FRs of α-endosulfan and dacthal were less than 1 across the Archipelago in 1999 and for 2007–2008, indicating deposition (Figure 2.24). A previous assessment also estimated deposition of α-endosulfan in all arctic regions, with lowest FRs in the Archipelago (Weber et al. 2006). Chlorothalonil was measured in water across the Archipelago during 1999, but due to technical difficulties was only measured off Banks Island during 2008. Exchanges were in deposition in both years (Figure 2.24). Chlorpyrifos was only sought in 2007–2008 and was undergoing deposition (Figure 2.4).

The accuracy of these *FR* estimates depends on the reliability of the Henry's law constants selected for calculation. Henry's law constants for the chlordanes, heptachlor epoxide, dieldrin and α-endosulfan were thermodynamically consistent "final adjusted values" (FAVs) at 25 °C (Shen and Wania 2005) (see section 2.1.3). FAVs at 25 °C were also used for chlorpyrifos and dacthal (Muir et al. 2004). The Henry's law constant of chlorothalonil at 25 °C was taken from

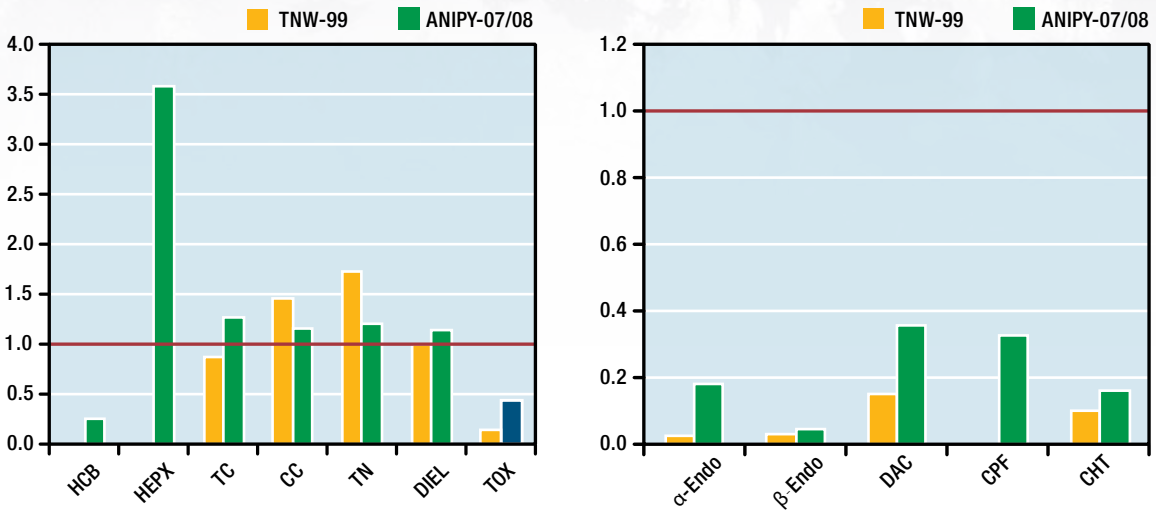


FIGURE 2.24

Water/air fugacity ratios (FRs) calculated from averaged air and water concentrations across the Archipelago. Measurements were carried out on expeditions in the east, central and west Archipelago and southern Beaufort Sea on TNW-99 and ANIPY-2007/08. Values of FR <1, = 1 and >1 indicate net deposition, equilibrium (solid red line) and net volatilization, respectively (Jantunen et al. 2009a, b). A) legacy OCPs. HCB, metabolite heptachlor exo-epoxide (HEPX), chlordane components *trans*-chlordane (TC), *cis*-chlordane (CC), and *trans*-nonachlor (TN), dieldrin (DIEL) and toxaphene. FRs of toxaphene are shown for the TNW-99 expedition when air concentrations were unusually high and also calculated from averaged air and water concentrations throughout the 1990s (blue bar). B) FRs of the CUPs endosulfan (α-Endo and β-Endo), dacthal (DAC), chlorpyrifos (CPF) and chlorothalonil (CHT).

a European Commission review (European Commission 2006). Adjustments to surface water temperature were made using $\log H = m/T + b$. Experimental temperature-dependent Henry's law constants were used for toxaphene (Jantunen and Bidleman 2000) and HCB (Jantunen and Bidleman 2006). Henry's law constants available only at 25 ºC were adjusted using the following procedures. Temperature slopes of Jantunen and Bidleman (2006) and Cetin et al. (2006) were averaged for chlordanes, while the Cetin et al. (2006) slopes were used for dieldrin, heptachlor epoxide chlorpyrifos and endosulfans. Averages of these slopes were assumed for dacthal and chlorothalonil. All Henry's law constants were raised by 20% to account for the salting-out effect in seawater (Jantunen et al. 2008a).

2.3.3.5. Effect of sea ice on gas exchange in arctic regions

The "lid" of ice cover in the Arctic Ocean and its regional seas provides an effective barrier to gas exchange of POPs (Jantunen and Bidleman 1996, Lohmann et al. 2009). Each summer, the ice pack in the low-mid Arctic Ocean and subarctic seas recedes, thereby enabling air-water gas exchange to resume. The ice edge is a region of intense biological activity, opening the possibility of greater metabolism and sinking fluxes of particulate POPs (Gioia et al. 2008b, Lohmann et al. 2009). Snow and ice are temporary storage reservoirs for POPs and losses take place upon melting and aging, which may increase air concentrations (Daly and Wania 2004). Both processes would lead to increased potential for air-to-sea transfer (Gioia et al. 2008b).

Climate change in the Arctic will lead to reduced ice cover and generally warmer surfaces. Less ice cover will increase the release of HCHs (Ding et al. 2007, Jantunen et al. 2008a, Wong et al. 2011, Wu et al. 2010) and possibly other POPs from the Arctic Ocean, remobilizing them into the atmosphere for redistribution. In the case of chemicals that are predicted to undergo gas-phase deposition to the Arctic Ocean, loss of ice cover will provide more open water for such deposition to occur. Precipitation is expected to increase in the Arctic, which will increase loadings of chemicals to the Arctic Ocean directly through washout over the ocean and indirectly through river runoff. Melting ice can also impact the nutrients in the water column, affecting primary productivity. With higher temperatures, more wintertime polynyas will be present which will lead to an increase in sea fog, which scavenges and deposits POPs in areas known to be important for biota (Macdonald et al. 2005).

The evasion of α-HCH predicted by fugacity calculations has been confirmed by measurements of higher α-HCH concentrations in air over the Bering-Chukchi

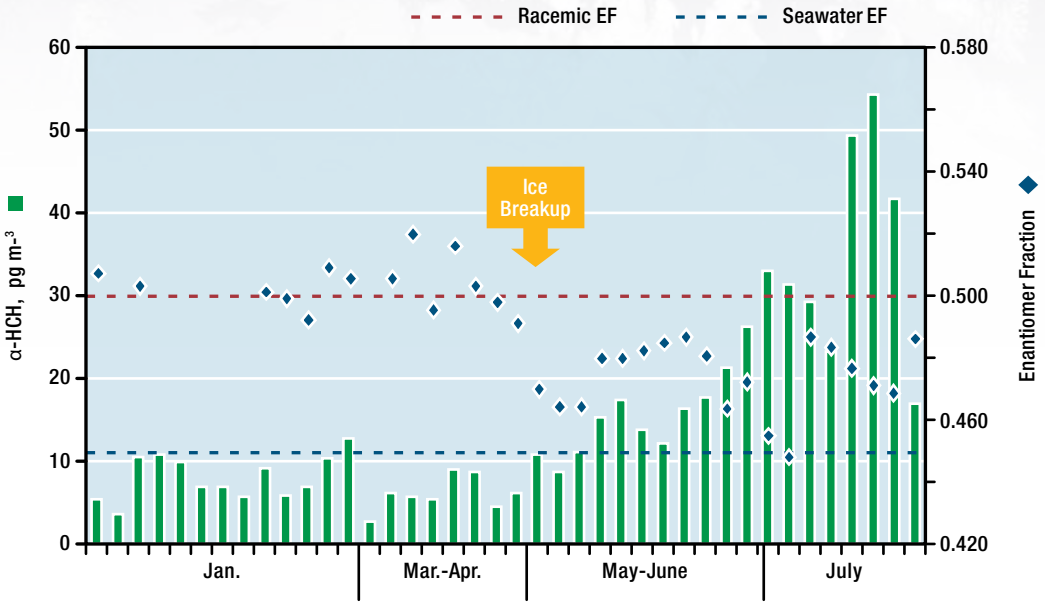


FIGURE 2.25

Increase in air concentrations of α-HCH with onset of ice breakup at Banks Island during May, 2008 and continuing throughout the summer. The concentration increase was accompanied by drop in the enantiomer fraction α-HCH, EF = (+)/[(+) + (–)], an indicator of evasion from the ocean. The racemic EF of 0.5 is typical of α-HCH from long-range air transport, while α-HCH in seawater at Banks Island had an EF = 0.455 due to preferential degradation of the (+) enantiomer by microbes (modified from Wong et al. 2011).

and Greenland seas during the ice-free period (Jantunen and Bidleman 1995, Jantunen and Bidleman 1996). Air concentrations of α-HCH in the "floating sea ice" region of the high arctic were higher than those measured over pack ice (Wu et al. 2010). An abrupt increase in α-HCH concentration in air accompanied the ice breakup in the central Archipelago during the Tundra Northwest 1999 (TNW-99) expedition (Jantunen et al. 2008b) (Figure 2.57). Similar observations were made during the 2008 Circumpolar Flaw Lead (CFL) study off Banks Island (Figure 2.25). Air concentrations of α-HCH increased 3–4 fold between winter-early spring and late spring-summer as the transition occurred from ice cover to open water (Wong et al. 2011). In both of these studies, sea-to-air transfer was traced by the appearance of non-racemic α-HCH from seawater in the air boundary layer (see Figure 2.57 and also Figure 2.58).

In the Greenland Sea-EAO region, HCHs, chlordanes and HCB in surface water were about twice as high under ice as in ice-free areas, whereas no significant difference was seen for these POPs in air (Lohmann et al. 2009). This contrasts with a clear increase in α-HCH air concentration over open water in the Archipelago and southern Beaufort Sea (Jantunen et al. 2008b, Wong et al. 2011) and is probably due to higher levels of α-HCH in surface water of the latter regions.

On the 2007 ArcticNet expedition in Hudson Bay and the 2008 CFL study off Banks Island, Wong et al. (2011) conducted an experiment to simultaneously measure air concentrations of α-HCH, HCB and bromoanisoles at 1 m (C_1) and 15 m (C_{15}) above the surface. *FRs* indicated volatilization of α-HCH, deposition of HCB and volatilization or near equilibrium of di- and tri-bromoanisole. The C_1/C_{15} ratio of α-HCH was significantly higher when samples were collected over water (C_1/C_{15} = 1.14) than over sea ice (C_1/C_{15} = 0.99) with $p < 0.05$. Other chemicals did not show significant air concentration differences between 1 m and 15 m. In principle, the air gradient for α-HCH over water can be used to estimate volatilization fluxes when coupled with micrometeorological measurements. Fluxes of α-HCH and HCB over Lake Superior were estimated from shipboard by coupling measurements of C_A at two heights with Bowen Ratio measurements of heat flux (Perlinger et al. 2005). Such measurements require constancy of meteorological conditions over the sampling period, which should be restricted to a few hours or less. The measurements of Wong et al. (2011) were conducted over 8–12 hours, which was too long an integration time for the estimation of fluxes by micrometeorological methods. Nevertheless, such estimates were made and compared with fluxes calculated using the two-film method.

Fluxes of α-HCH were estimated by using (a) micrometeorological flux (FM) approach in which micrometeorological measurements were made from a 10m tower at the bow of the ship, and (b) two-film model (FTF; based on fugacities in air and water) (Jantunen and Bidleman 2003).

The comparison of fluxes was done for eight sampling events over open water off Banks Island in July 2008. The micrometeorological method could not be used for one event because of unstable atmospheric conditions. Both approaches estimated net volatilization (positive flux) of α-HCH for six out of the seven other events, the exception being event 5 when FTF was positive and FM was negative. The range of FM for the seven events was -3.5 to 18 (mean 7.4) ng m^{-2} d^{-1}, compared to the estimated FTF range for eight events 3.5 to 14 (mean 7.5) ng m^{-2} d^{-1} (Wong et al. 2012). Results are encouraging and show the feasibility of making real-time flux estimates based on micro-meteorology, but improvements to reduce the sampling time are needed.

2.3.4. Modeling studies on long-range transport of POPs

Contributors: Jianmin Ma, Don Mackay and Liisa Reid

In this section we discuss the possible roles of dynamic models and mass balance models to assess fate and transport of POPs, and models as contributors to international negotiations and regulations.

2.3.4.1. BETR-World model and Distant Residence Time concept

As shown in the previous sections, long-range transport of contaminants to the Arctic occurs via air, oceans and even on a local scale by biovectors. Models are usually developed for single vectors and they often use large datasets to parameterize complex flow patterns of air, water or biotic migration patterns. Due to the complexity of these models, computation times can be long, especially for decades-long simulations. Verifying the results becomes challenging because of the vast spatial scales of the North. Monitoring projects provide valuable information on spatial and temporal trends, and they can be used to verify modeling efforts, which in turn can predict future temporal and spatial trends of contamination or decontamination with changes in global and/or local emissions. Models can also be used to determine the likely fate of emerging contaminants and can thus guide the spatial extents and patterns of demanding and expensive monitoring programs.

Increasingly, it is recognized that the combination of monitoring and complementary modeling is the optimal path forward. Not only do the model results have to be credible to the scientific community, they must also be conveyed in relatively simple, direct and understandable form to those responsible for international negotiations leading to the global regulation of chemical usage.

No single model is likely to satisfy all demands. Indeed, global scale modeling is still in an evolutionary phase in which various approaches are being tested, accepted or rejected, and modified in the light of tests, to achieve scientific credibility and meeting regulatory needs. It is likely that development of a suite of models will prove to be the optimal approach.

This suite would include a series of simple to complex models of varying temporal and spatial scale. A simple one-compartment steady-state model such as the EQC model (Mackay, 2001) can indicate, based on the physical-chemical properties (as described in section 2.1) whether a chemical is likely to partition to a mobile phase such as air or water. It can also provide insights into the extent that the chemical is persistent and if it is likely to be bioaccumulative. Many chemicals of concern are multi-media in nature. They partition into mobile phases in sufficient quantities to be transported long distances from the point of emission, but they also partition into organic phases that can pose a risk to the ecosystem and ultimately human health in contaminated regions. Based on these findings, using a minimum of input data, a more complex and site-specific model can then be used to assess a realistic scenario of chemical fate and transport.

Notable among the global circulation models are those by Dastoor and Larocque (2004), Gong et al., (2007), Li et al., (2004) and Ma (2010). Of particular interest in the arctic context is the Arctic Mass Balance Box Model (AMBBM) model of Li et al. (2004) that addresses the fate of hexachorocyclohexanes in the Beaufort Sea. Among the global segmented models are BETR-World (Toose et al. 2004), BETR-Global (MacLeod et al. 2005), GloboPOP (Wania 2003) and CliMoChem (Schenker et al. 2008a). Here we focus on the BETR-World model, but the same general conclusions can be reached by applying other models. Indeed, there is merit in applying different models to the same scenarios with a view to identifying common strengths and any inconsistencies.

The BETR-World model originally included 25 regions with only one representing the Arctic. This was found to be insufficiently detailed for the Arctic because of observed differences in oceanic and biotic concentrations between, for example, the Eastern and Western Canadian Arctic. Consequently,

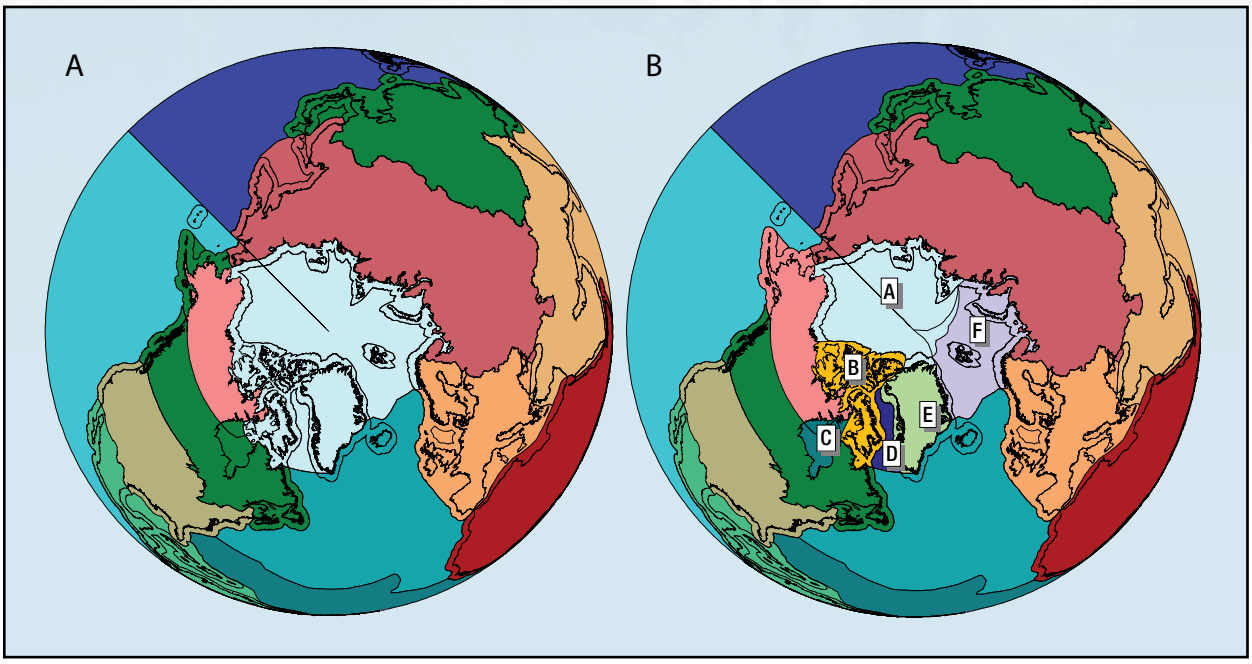


FIGURE 2.26

(a) Original Arctic segmentation of the BETR-World model; (b): Improved Arctic segmentation of the BETR-World model.

a more detailed segmentation was developed. The original Arctic segmentation and the more detailed segmentation are shown in Figure 2.26 a and b.

The quantity of data generated by even the relatively simple BETR-World model can be significant and even overwhelming, especially when treating time-varying conditions over decades. As a result, effort has been devoted to presenting the results of such models in a more readily understood matrix form by devising the Distant Residence Time concept (Mackay and Reid 2008, Reid and Mackay 2008).

The concept has been used to rank contaminants by their long-range transport potential (Mackay and Reid 2008, Reid and Mackay 2008). By linking a series of multi-media environments by atmospheric or marine/freshwater exchanges in either a linear (as a tunnel) or non-linear (as in the BETR-World model in Reid and Mackay (2008), the potential for contamination of a selected region (such as the Arctic) by emissions from other distant, yet connected regions, can be assessed (Figure 2.27 a and b).

Figure 2.27 shows that at steady-state, the mass in environment 1 is M_1, thus the residence time in that environment is M_1/E_1. The total mass in the system, M_T, is $M_1 + M_2 + M_3 + M_4$, and thus the total residence time of the system is M_T/E_1 which comprises the sum of individual residence times M_i/E_1. We refer to M_1/E_1 as a local residence time and M_2/E_1, M_3/E_1 etc. as Distant Residence Times (DRTs), thus the Distant Residence Time, DRT_4 is M_4/E_1. The DRTs are therefore the mass in each receptor region divided by the emission rate in the source region. These Distant Residence Times (e.g., 0.1 years) are proportional to the quantity in the region at steady-state attributable to a specific source region. If the model used to estimate them is linear, the DRTs are independent of the emission rate. Results from any suitable steady state model can be used to calculate a set of DRTs for each source region. For a set of source regions, the results can be presented in a DRT source-receptor matrix that quantifies the relative contributions of each source to the contamination of each receptor region.

Complex models

The 25 region BETR-World model with a single arctic compartment has been used to illustrate the potential of a well-studied chemical, α-HCH to contaminate various regions in the Arctic (Reid and Mackay 2008). This simulation has been extended to include a segmented arctic region in which circulation patterns, atmospheric, riverine and oceanic influences can be deduced. The physical-chemical properties of α-HCH were taken from Schenker et al. (2007) with only a few changes to enthalpies of phase change and activation energies from the properties used in Reid and Mackay (2008).

Using this adapted model, there is potentially a 31 x 31 "efficiency of transfer" matrix illustrating the probability

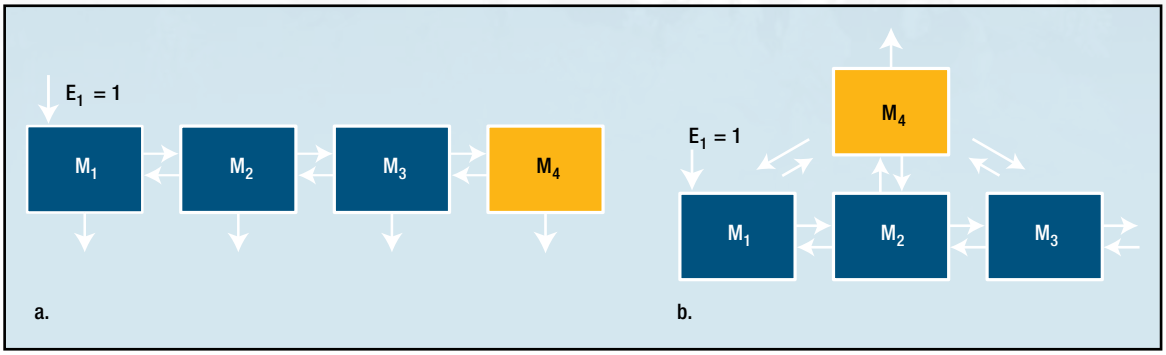


FIGURE 2.27

Linear (a) and non-linear (b) arrangements of linked environments. E_1 indicates an emission rate to environment 1, $M_{1\text{-}4}$ is the mass of chemical resulting in each environment. The orange is the "target" environment, which is selected to be region 4 here, but could realistically be any of the environments which would be of interest to the researcher or policy-maker (adapted from Mackay and Reid 2008).

of emissions in each region to reach all the other regions. This can be simplified by addressing only terrestrial regions as sources and arctic regions as sinks, giving a 15 x 7 matrix. This can be further simplified by focusing only on the influence of regions in the Northern Hemisphere, outside of the Arctic and including an adjacent oceanic region for illustrative purposes using a 7 x 7 matrix (Table 2.5). The diagonal in the matrix in this case is not the local residence time as the source and target regions differ. Table 2.5, using the total regional DRT (i.e., including mass in all receptor region media divided by emission in the source region) shows that transport from the Canadian Provinces region to the Canadian Archipelago (DRT_{Total} = 0.0494 years) is more efficient than from Europe (DRT_{Total} = 0.0058 years) as indicated by the higher DRT_{Total} resulting from a unit emission in those respective regions. The efficiency of transfer matrix is useful in determining the risk each region poses to other regions for a particular chemical, but it does not take into account the quantities emitted.

Table 2. 5 also shows that the Eastern and Western Arctic Ocean regions are potentially dominant sinks for contaminants released into the global environment because their DRT_{Total} values are relatively high. It also shows that the transport from the Continental Arctic (including the Canadian Northwest Territories, Yukon and the US state of Alaska) and Russia is efficient due to their proximity. The implication is that emissions from these regions should be closely monitored and may be a high priority for regulatation. The DRT_{Total} calculated from a unit emission in the North Atlantic is included in Table 2.5 to illustrate that chemicals can be efficiently transported from this oceanic region.

TABLE 2.5. Efficiency of transfer DRT matrix for α-HCH transported to arctic regions, all media, using the BETR-World model. In the interests of brevity, each region is assigned a one-word identifier. For example, "East Asia" includes China and much of South-East Asia.

		DRT_{Total} (years) Receptor Regions						
Source Region	Emisson kg y^{-1}	Hudson Bay	East Arctic Ocean	Davis Strait	Greenland	Canadian Archipelago	Barents-Greenland Seas	West Arctic Ocean
Continental Arctic	1	0.0585	0.1056	0.0261	0.0345	0.1355	0.0694	0.1896
Canadian Provinces	1	0.0318	0.0313	0.0086	0.0111	0.0494	0.0256	0.0494
Russia	1	0.0061	0.0696	0.0064	0.0104	0.0250	0.0628	0.0502
Europe	1	0.0014	0.0129	0.0016	0.0035	0.0058	0.0149	0.0104
USA	1	0.0020	0.0049	0.0011	0.0020	0.0052	0.0052	0.0057
East Asia	1	0.0006	0.0046	0.0006	0.0013	0.0024	0.0038	0.0043
North Atlantic	1	0.0055	0.0518	0.0080	0.0093	0.0213	0.0723	0.0389
Other*	17	0.0019	0.0103	0.0016	0.0035	0.0067	0.0106	0.0099
Total	**24**	**0.1077**	**0.2911**	**0.0539**	**0.0755**	**0.2513**	**0.2646**	**0.3584**

*emission in regions within the Arctic was not considered

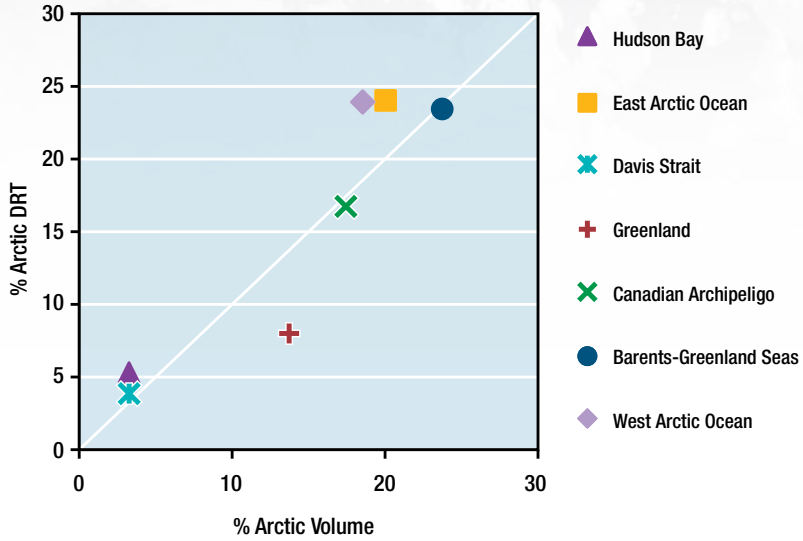


FIGURE 2.28

Average proportion of DRT_{Total} for α-HCH among arctic regions as a function of regional volume/total arctic volume.

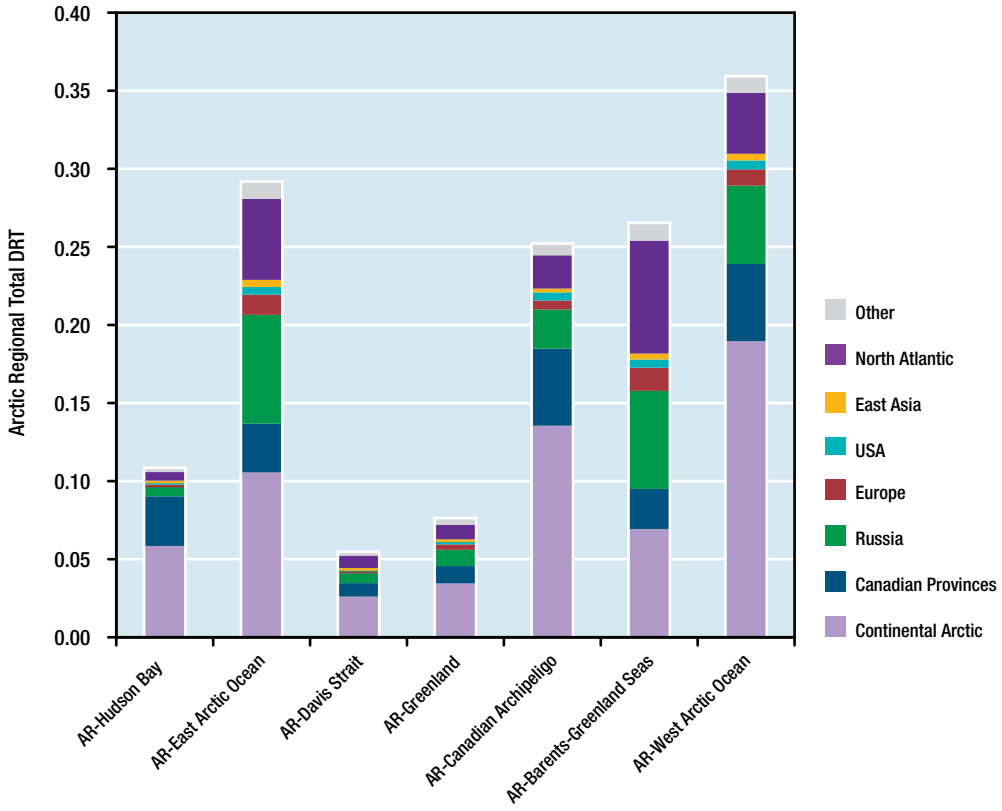


FIGURE 2.29

Contribution to arctic regional DRT for α-HCH by global source regions.

Regional DRT is proportional to the mass of chemical in that region. A larger mass in a larger region can be expected. The "vulnerability" of some regions related to others can be deduced. If the inventory, thus DRT_{Total}, is higher than the proportional volume or area for the Arctic, this indicates that the region is an area more susceptible to contamination. For the seven arctic regions, the proportion of total arctic DRT_{Total} (or mass) vs. the proportion of arctic volume can be plotted (Figure 2.28).

In Figure 2.28, the three points above the 1:1 line (starting at the low end) are Hudson Bay, and the Western and Eastern Arctic Oceans. These regions are primarily marine in nature, thus indicating the importance of marine ecosystems as sinks for α-HCH in the Arctic. The region that is well below the 1:1 line is Greenland, a primarily barren terrestrial region. The BETR-World model does not account for glaciers and sea ice.

The quantity of the emissions in each region is also important. The efficiency of transfer may be high, but if little or no chemical is used within that region, it poses no hazard to the target region. Li et al. (2000, 2003b) have carried out extensive work in assessing emission patterns of HCHs, including the α-isomer. Using Li's total global estimates of α-HCH usage between 1940 and 2000, a "steady-state" emission can be estimated by using an average annual emission in each region. If an emission pattern is applied to the matrix values in Table 2.5, the resulting masses in each of the regions in the system can be determined, creating a "responsibility matrix" (Figure 2.29 and Figure 2.30). It becomes evident that the East Asian region (mainly China and South-East Asia) and Russia have comparable contributions to the inventories in the receptor regions; Russia having a relatively low rate of emission but a high efficiency of transfer value and East Asia having a high rate of emission but a low efficiency of transfer. Both factors are clearly important.

This gives an estimate of the contribution of various global regions to arctic contamination. Figure 2.29 clearly suggests that the Continental Arctic, Russia and the North Atlantic, as in Table 2. 5, provide the largest proportion of the DRT in each arctic region. Figure 2.30 shows that East Asia has the largest emission of α-HCH and that the continental Arctic and the North Atlantic have none. The responsibility

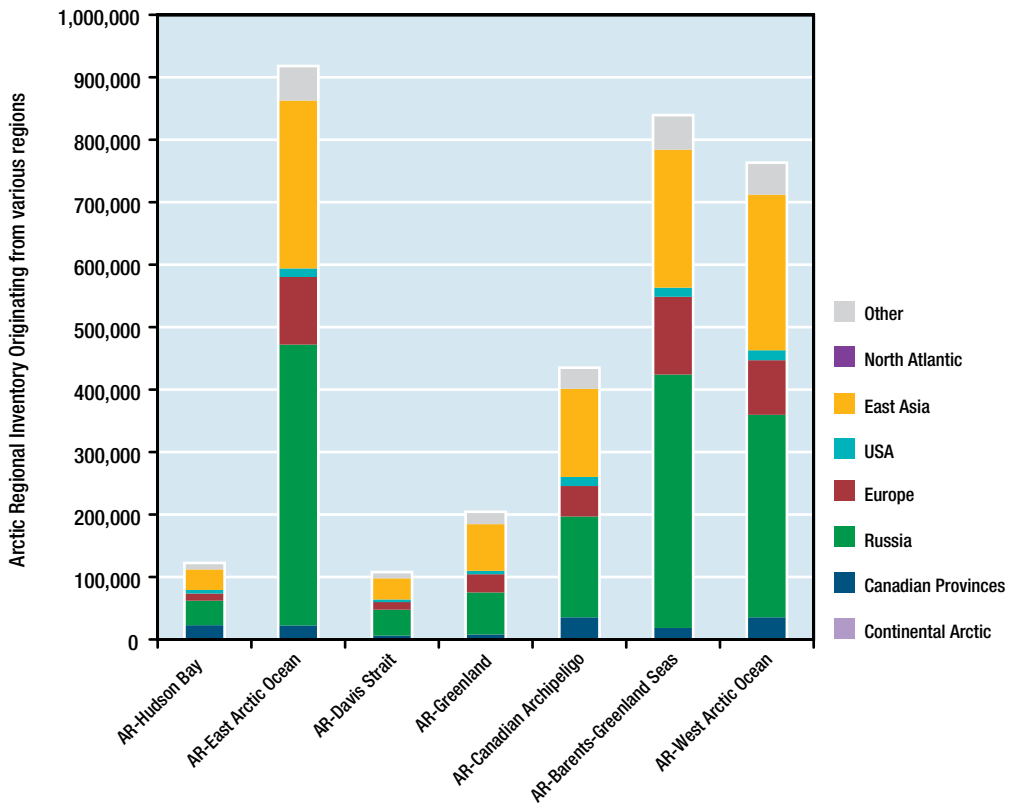


FIGURE 2.30

Contribution of α-HCH to arctic regional inventory by global source regions.

matrix as Figure 2.30 shows that sources in Russia, Europe and East Asia dominate the contamination of the arctic regions by α-HCH.

This approach effectively separates the two factors that control long-range transport, namely (1) the efficiency of transport which is a function of chemical properties and geographic factors such as atmospheric or marine circulation patterns and (2) the quantity of emission. The efficiency matrix addresses the first factor and the responsibility matrix addresses both factors. The aim here has been to demonstrate the concept using the available data. These numerical results should therefore be regarded as tentative, not definitive. One useful approach would be to apply other independent models to this example.

Regional Influences

By examining the DRT and steady-state inventory of select media in the arctic regions, a comparison can be made between receptor regions and the level of influence of the source regions. In the Canadian Archipelago (Figure 2.31) and the East Arctic Ocean (Figure 2.32), Upper air is dominated by α-HCH from distant sources (from East Asia 44%, 53% respectively for the Canadian Archipelago and EAO, and from "Other", 12%, 11% respectively). Marine water in both regions is dominated by α-HCH from Russian emissions (37% and 49% respectively). The total load in each region is dominated by Russian and East Asian emissions with emission from Europe and the Canadian Provinces contributing more to the total load in the Canadian Archipelago (8%) than to the Eastern Arctic Ocean (2.5%).

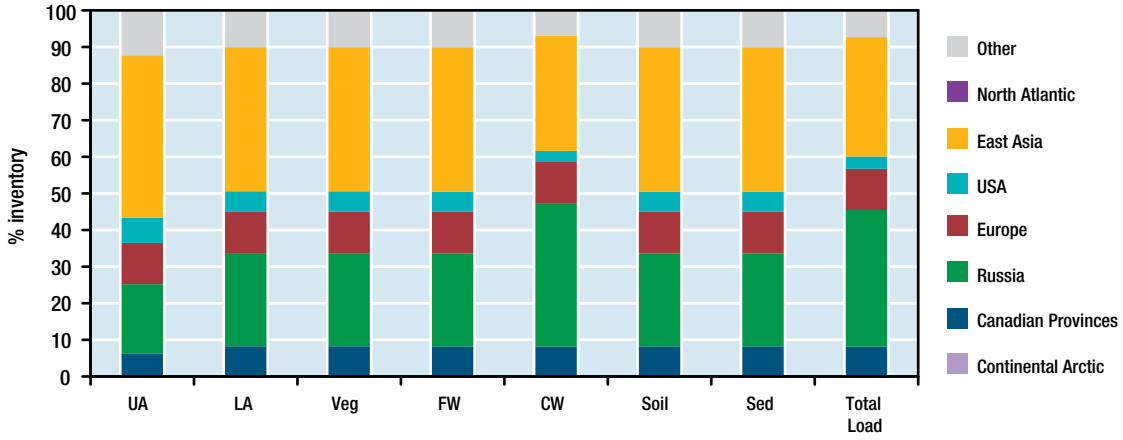


FIGURE 2.31

Proportional "responsibility" assigned to the Canadian Archipelago region as sourced from estimated emissions of α-HCH in individual source regions.

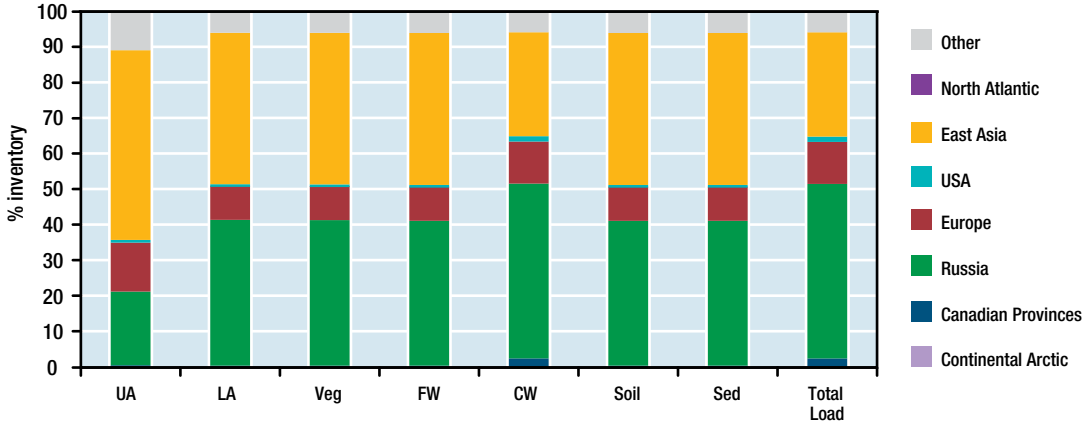


FIGURE 2.32

Proportional "responsibility" assigned to the East Arctic Ocean region as sourced from estimated emissions of α-HCH in individual source regions. The media included in the model are Upper Air (UA), Lower Air (LA), Vegetation (Veg), Freshwater (FW), Coastal/oceanic water (CW), soil and freshwater sediment (Sed).

Decontamination of the arctic region

Emission reduction strategies can be guided using global models. Several scenarios can be compiled with a view to guiding international actions regarding the reduction or elimination of emissions. How long a reduction in concentration will take depends on the rates of loss processes such as transport, reaction, volatilization and transfer to deep oceanic waters. These processes are believed to be slower in cold, polar regions, thus the arctic environment is expected to take longer to respond to reductions in emissions. To estimate the response time of the arctic regions, a dynamic (time-variable) model can be used. To illustrate the response time of the arctic regions, a hypothetical scenario of a complete reduction of emissions (i.e., total global emissions = 0 kg y^{-1}) of α-HCH after reaching a steady-state condition was considered. An arbitrary endpoint of 1 µg m^{-3} in marine water is being used to illustrate the response times of an arctic region vs. a temperate one.

Figure 2.33 shows that the marine water in the Canadian Archipelago would take more than 13 years to decrease the concentration to less than 1 µg m^{-3}. It also shows that in the region with the highest emissions, East Asia, the steady-state marine concentration is 7 µg m^{-3}, but the predicted time to decrease to less than 1 µg m^{-3} is only 4.2 years. This pattern shows both the vulnerability in arctic regions and the necessity for ongoing, long-term monitoring programs. In practice, the total cessation of emissions of commercial chemicals is unlikely. Even chemicals such as DDT are still in use today because of its value in reducing malaria rates in tropical countries. As discussed in Chapter 1, usage may actually increase.

DRT and emission reduction strategies

Chemicals of commerce, like those used in industry and agriculture, are a necessary and often beneficial part of business or of health and safety. Taking information such as no-effect or defined effect concentrations into account, it is possible to use a global model to suggest a cap on the annual emissions in various parts of the world, depending on the efficiency of transport to a vulnerable area. This can be illustrated using the Canadian Archipelago as an example of a vulnerable region given the human and wildlife population living there.

Selecting an endpoint or a maximum concentration is detailed in other publications (Arnot et al. 2006) and is beyond the present scope of this discussion. Here, for purely illustrative purposes, an endpoint of 1 µg m^{-3} α-HCH in marine water in the Canadian Archipelago is selected. The existing usage data indicate that 13 BETR-World regions historically use/produce this chemical (Toose et al. 2004). Using a unit emission from each of these 13 regions, a concentration in the marine water is expected to be 4.44 x 10^{-7} µg m^{-3}. Assuming that regions take on equal responsibilities in arctic contamination (though this point is clearly open to debate), each region is assigned a contribution of a maximum of 1/13 of 1 µg m^{-3} in concentration or 13,800 kg in the marine waters of the Canadian Archipelago (volume = 1.797 x 10^{14} m^3).

Table 2. 6 shows that for a target region in the Canadian North, the maximum target emission in East Asia is calculated to be about 20 times that of the Canadian Provinces and 2 times that of the United States (column 4). The actual average

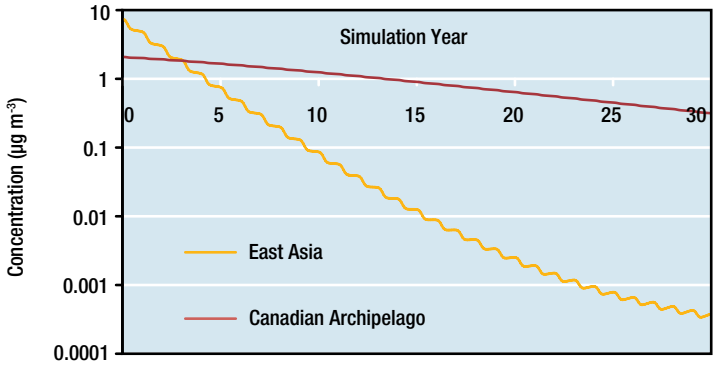


FIGURE 2.33

Predicted marine water decontamination concentrations of α-HCH in the Canadian Archipelago and East Asia from steady-state with no global emissions.

emission rate in East Asia is 80 times higher than the Canadian Provinces and 20 times higher than the United States (column 5).

To limit the concentration in arctic marine waters, international actions could be taken to achieve a redistribution of global emissions, but the nature of this redistribution would presumably be the subject of international negotiations and would include consideration of local effects. This example of α-HCH is, of course, largely irrelevant to the real current situation because it is an unwanted by-product of lindane production. A more realistic example would be for DDT, which has value for malaria control. Any redistribution would presumably take into account the relative needs for this substance in source regions.

This approach of assigning acceptable emissions or loadings on a global scale is entirely analogous to the Total Maximum Daily Loading (TMDL) concept that is routinely applied by the United States Environmental Protection Agency's Clean Water Act (USEPA 2010b) when regulating water quality as it is impacted by a number of sources. The Clean Water Act also provides a framework for stakeholders to trade unused contributions to the maximum loading. Whether or not this concept can be applied globally remains to be seen. What is certain is that regardless of whether total bans or more selective partial bans are to be implemented, global scale mass balance models describing chemical sources fate and transport in all relevant media can support the development of such proposals and the justifications for such actions.

In this section we have argued that global scale mass balance models can play a significant role in developing an improved understanding of the fate and transport of the wide variety of chemicals of actual and emerging concern. This quantitative understanding can contribute to international negotiations to reduce the impacts of long-range transport. Models are most valuable when applied with complementary monitoring programs, i.e., modeling and monitoring should be viewed as mutually supportive. We assert that no single model can satisfy all present demands, thus an optimal strategy is to foster a suite of models in the expectation that the most useful will emerge by a process of "natural selection". The Distant Residence Time concept can, we believe, play a valuable role in guiding global modeling efforts and presenting findings in a relatively simple and understandable manner. Models can thus encourage the international regulation of contaminants in a globally transparent framework. The results can be used to assess the efficiency of transport, responsibilities for region to region contamination,

TABLE 2.6. Calculation of maximum emissions by region, based on the efficiency of transfer of α-HCH to the Canadian Archipelago using an endpoint of 1 μg m^{-3} in marine water, compared to average annual emissions.

	Unit emission	Total Marine Load	Target Marine Load	Target Max emission	50 year average emission*	AvgE TargetE
	Kg y^{-1}	Kg	Kg	Kg y^{-1}	Kg y^{-1}	
Canadian Provinces	1	$4.26x10^{-2}$	$1.38x10^{4}$	$3.25 x10^{5}$	$7.18 x10^{5}$	2.21
United States	1	$4.04 x10^{-3}$	$1.38x10^{4}$	$3.42 x10^{6}$	$2.79 x10^{6}$	0.82
Caribbean	1	$7.91 x10^{-4}$	$1.38x10^{4}$	$1.75 x10^{7}$	$5.99 x10^{6}$	0.34
Central America	1	$6.61 x10^{-5}$	$1.38x10^{4}$	$2.09 x10^{8}$	$2.67 x10^{6}$	0.01
Argentina Chile	1	$2.09 x10^{-5}$	$1.38x10^{4}$	$6.62 x10^{8}$	$1.49 x10^{5}$	0.0002
Europe	1	$5.02 x10^{-3}$	$1.38x10^{4}$	$2.75 x10^{6}$	$8.37 x10^{6}$	3.04
Middle East	1	$1.02 x10^{-3}$	$1.38x10^{4}$	$1.36 x10^{7}$	$8.98 x10^{6}$	0.66
Russia	1	$2.27 x10^{-2}$	$1.38x10^{4}$	$6.10 x10^{5}$	$6.46 x10^{6}$	10.59
East Asia	1	$2.01 x10^{-3}$	$1.38x10^{4}$	$6.87 x10^{6}$	$5.85 x10^{7}$	8.52
Oceania	1	$4.01 x10^{-5}$	$1.38x10^{4}$	$3.45 x10^{8}$	$7.43 x10^{4}$	0.0002
Northern Africa	1	$1.05 x10^{-3}$	$1.38x10^{4}$	$1.32 x10^{7}$	$1.08 x10^{7}$	0.82
Southern Africa	1	$3.95 x10^{-5}$	$1.38x10^{4}$	$3.50 x10^{8}$	$7.43 x10^{4}$	0.0002
Asian North Pacific	1	$4.77 x10^{-4}$	$1.38x10^{4}$	$2.90 x10^{7}$	$5.68 x10^{5}$	0.02
Total	**1**	**$7.98 x10^{-2}$**	**$1.80x10^{5}$**	**$1.65 x10^{9}$**	**$1.06 x10^{8}$**	**0.06**
Marine Conc. μg m^{-3}		$4.44 x10^{-7}$	1			

* from Li et al. (2000)

assign vulnerabilities and possibly design a global scale strategy to assign tolerable rates of chemical usage and emission.

2.3.4.2. Dynamic models

Dynamic air quality simulation models can be broadly characterized by the manner in which the fate and transport of pollutants within the air are simulated. Models of physical processes whose equations are stated relative to a volume of air that follows the dispersing material during transport downwind can be referred to as Lagrangian models. Those whose equations are stated relative to a volume of air fixed in space, through which the air moves, can be referred to as Eulerian models. Both types of models are powerful tools to mathematically describe the environmental behaviour of POPs in multi-compartments (atmosphere, oceans, lake waters, soils etc.), through physics, chemistry and dynamics, and provide numerical assessments of POPs transport and their budget in environments.

Lagrangian models describe atmospheric transport by calculating the transformation of a chemical-laden air parcel during its movement in the atmosphere over time. These models can be run both forward and backward in time. The Lagrangian type models that have been used to simulate POPs atmospheric transport and source-receptor relationships include FLEXPART (Eckhardt et al. 2009), developed by the Norwegian Institute for Air Research, and HYSPLIT-POPs (Hybrid Single Particle Lagrangian Integrated Trajectory model) (Cohen et al. 2002), developed by the National Oceanic and Atmospheric Administration (NOAA) of the USA. The atmospheric dispersion model, Modèle Lagrangien de Dispersion de Particules d'ordre zéro (MLDP0), was developed and has been in use at the Canadian Meteorological Centre (CMC) of Environment Canada for several years. The model was initially designated to support environmental emergency response activities. An effort is currently underway in Environment Canada to upgrade the MLDP0 to enable it to be applied in modeling atmospheric transport of toxic chemicals and other air pollutants.

Lagrangian models are suitable for examining the dispersion from a single source, which it represents as a large number of parcels that are advected with the wind field. The main advantage of Lagrangian models is that unlike with Eulerian models, there is no numerical diffusion. Furthermore, in Eulerian models, a tracer released from a point source is instantaneously mixed within a grid box, whereas Lagrangian models are independent of a computational grid and have, in principle, infinitesimally small resolution. Thus, they are fast and easily manipulated. This type of model provides a framework of temporal trend and fate of toxic chemicals but it treats heterogeneous and complex atmospheric environments as a homogeneous compartment. In addition, such models do not presently cover surface exchange and, hence, do not take into account secondary sources (e.g., re-emission to air from soils, oceans).

An Eulerian model is suitable for modeling a situation with many distributed sources, as it carries concentration values at every point on a grid. Atmospheric transport in Eulerian models is considered as fluxes between grid cells. Models of this type can include dynamic evaluation of the inter-media exchange with allowance for the variability of types of underlying surface and meteorological conditions (also called multimedia chemical transport models–MCTMs). Typical examples of such models are MPI-MCTM (Lammel et al. 2001, Semeena and Lammel 2003), and MSCE-POP (Gusev et al. 2005). Environment Canada has also developed this type of model. These are the Multicompartment Environmental Diagnosis and Assessment (MEDIA) model (Koziol and Pudykiewicz 2001, Zhang et al. 2010a, Zhang et al. 2008b), GEM/POPs (Gong et al. 2003), and the Canadian Model for Environmental Transport of Organochlorine Pesticides (CanMETOP) (Ma et al. 2003, Zhang et al. 2008b). Both MEDIA and CanMETOP were coupled with air/soil, air/water, and air/snow (ice) exchange. The differences between the MEDIA and CanMETOP models are that the two were solved with different computational schemes and parameterizations, and used different soil modules. Application of the CanMETOP in numerical simulations of atmospheric transport and deposition of penta-BDE is provided in section 2.3.4.3. Figure 2.34 provides a schematic view of major atmospheric, physical, and chemical processes incorporated in atmospheric transport models for POPs, such as the CanMETOP and MEDIA.

Detailed horizontal and vertical structures of the atmosphere can be taken into consideration in a POPs atmospheric transport model. For example, the horizontal resolution of the CanMETOP spans from 5 km^2 (urban scale), 24 km^2 (regional scale), to a 1^o x 1^o latitude/longitude (global scale). In the vertical, the model separates the atmosphere as (1) the surface boundary layer (SBL, 0–100 m from the surface) where atmospheric turbulence dominates local momentum, heat, concentration fluxes and vertical mixing which are always in equilibrium with underlying surface conditions; (2) the atmospheric boundary layer (ABL, 100–1000 m from the surface)

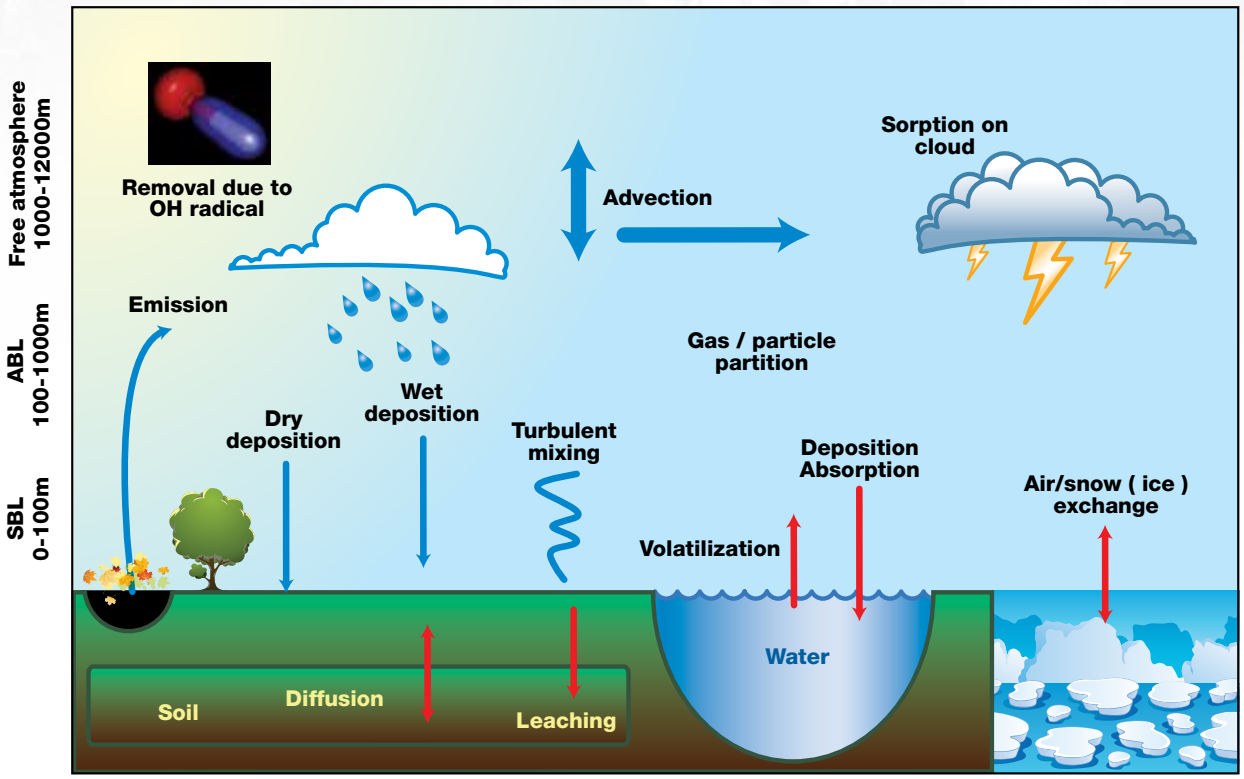


FIGURE 2.34

Schematic illustration of major atmospheric, physical, and chemical processes and features in the CanMETOP model. SBL for surface boundary layer and ABL for atmospheric boundary layer.

where both large-scale atmospheric motions and local turbulence activities act together to determine horizontal and vertical movement of a toxic chemical; and (3) the free atmosphere (above 1000 m from the surface) where large scale atmospheric motion plays a major role in the long-range atmospheric transport of POPs.

These features enable the Eulerian type of POPs atmospheric transport models to provide a sufficiently detailed overview of POP fate in the environment so as to evaluate contamination levels and source-receptor relationships as well as examine trends and projections of POP contamination. They also provide details (up to hourly and diurnal changes in air concentration) of episodic atmospheric transport events of POPs. This information is useful in the negotiation process for inclusion of POP candidates in international legislations as the models can provide information on the ability of substances to transport over long distances and as well as supportive evidence of their persistence in the environment. Figure 2.35 illustrates the superimposed snapshots of the mean daily lindane air concentration, modeled at the height of 5245 m (upper panel), once every two days during the period of an atmospheric transport event from China to the Arctic from March 30, 1997 to April 10, 1997. This is overlaid by the mean of the winds, averaged over the same period and at the same height, simulated by the MEDIA model. The lower panel of Figure 2.35 shows the vertical profiles of the daily air concentration crossing 30°N to 90°N on April 9, 1997 from the surface to 5245 m, averaged over 110°E to 140°W, which is the area covering the major East Asia source region, the North Pacific Ocean, and a large area of the Arctic. The figure is also overlaid by the vector winds, derived from the meridional wind component (v, m s^{-1}) and the vertical velocity (m s^{-1}) (Zhang et al. 2010a).

The figure shows that, although the chemical was emitted from contaminated soils, the presence of high air concentrations of this insecticide at relatively high latitudes suggests that the free atmosphere is an important pathway for atmospheric transport of toxic chemicals to the Arctic due to stronger winds and weaker dispersion of chemicals.

The nature of Eulerian models enables them to be applied to distinguish the contribution of individual sources of POPs from different locations to the

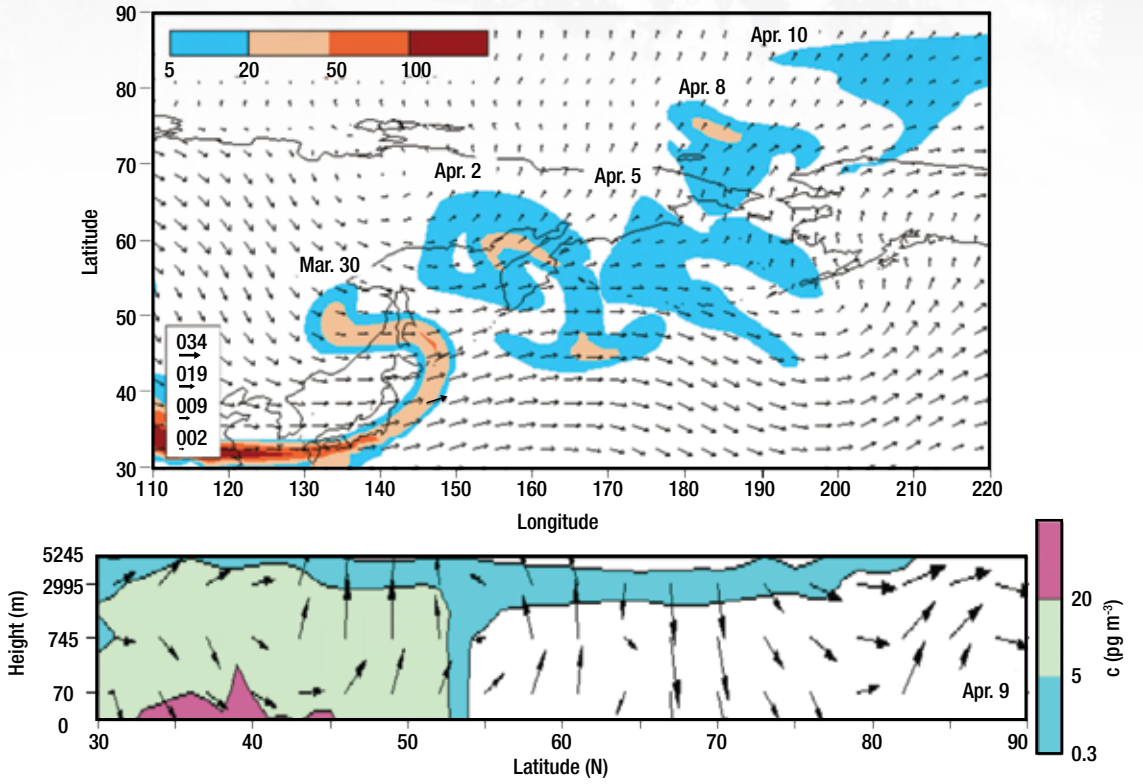


FIGURE 2.35

Modeled mean daily lindane air concentration and the vertical profiles at the height of 5245 m. *Upper panel:* modeled daily lindane air concentration (pg m^{-3}) at 5245 m height on selected days over the period March 30 – April 10, 1997. The figure also shows mean vector winds over the same period and height. The bars at the lower left give wind vectors in knots (Note that 002 means 2 knots). *Lower panel:* vertical cross section of MEDIA modeled mean daily lindane air concentration (pg m^{-3}) from the surface to 5245m height on April 9 1997, averaged over longitude 110°E to 140°W. The figure also shows cross-section of daily mean vector winds by derived from meridional wind and vertical velocity, averaged over the same region and over the same period.

environmental fate of POPs at receptors. One such example was presented in section 2.3.4.3 where the influence of penta-BDE emitted from different continental sources on PBDE contamination and loading in the Canadian Arctic was highlighted.

2.3.4.3. Modeled atmospheric transport and deposition of PBDEs to the Canadian Arctic

The presence of BFRs in the Arctic has been attributed to the long-range transport from their sources in industrialized countries, e.g., Western Europe and eastern North America (de Wit et al. 2010). It has been estimated that the lower-brominated congeners do have a long-range transport potential and can be delivered to a remote pristine region (Wania and Dugani 2003). In order to further identify the major atmospheric pathways and the sources of PBDEs to Canadian Arctic, Environment Canada's global atmospheric transport model for persistent toxic chemicals CanMETOP has been used to simulate the atmospheric transport, source receptor relationships, and multi-compartment fate of PBDEs in the Arctic. The model is driven by a recently developed global PBDEs 1° x 1° latitude/longitude gridded emission inventory with meteorological/geophysical data (winds, air temperature, sea ice concentration, precipitation, etc.) for 2005. Special attention was paid to penta-BDE because the United States (US) has become the major emission source of penta-BDE after its ban in the European Union (EU) in 2004 (de Wit et al. 2010). This section describes the main findings from this modeling study on major global emission sources contributing to PBDE contamination in the Canadian Arctic through long-range atmospheric transport.

Table 2.7 lists the penta-BDE emissions to air from 10 countries based on currently available information of penta-BDE emissions in 2005. Air emission from these 10 countries accounts for 87% of the total global amount of penta-BDE emissions (820 t y^{-1}), and the United States is the largest source of penta-BDE emissions.

TABLE 2.7. Penta-BDE air emissions for top 10 countries (Total global penta-BDE air emissions was 820 t in 2005).

Country	Emission (t)	% of total global emission
United States	540.0	65.6
Canada	58.00	7.05
China	42.18	5.12
Germany	14.27	1.73
Russia	13.35	1.62
India	10.53	1.28
Italy	10.36	1.26
United Kingdom	10.36	1.26
France	10.20	1.24
Japan	9.22	1.12
Total	**718.46**	**87.30**

To assess the impact of global sources on penta-BDE contamination to the Canadian Arctic, multiple simulations were conducted by including or excluding different penta-BDE sources. Output data from the different scenario model simulations were used to elucidate and identify major sources, atmospheric pathways, and the fate of penta-BDE in the Canadian Arctic. Preliminary results for the contribution of the air emissions from major source regions to the total deposition (dry deposition and wet deposition, ng m^{-2}) of penta-BDE to Canada are illustrated in the present case study. The modeling scenario assessments consisted of following these five model scenario simulations:

1. with all sources in the globe
2. with the US and Canada sources only
3. with China sources only
4. with India sources only
5. with European and Russian sources only

The modeled air concentration derived from scenario 1 was compared with weekly monitored data at Alert. Modeled air concentrations closely reflected the weekly changes in measured BDE-99 (correlation coefficient of r = 0.63) in 2005. However, the model underestimated air concentrations, likely due to the assumption of zero background air concentrations across the Arctic as well as the underestimation of emissions in the emission inventory (Figure 2.15 and Table 2.7).

We define the region north of 62°N as the Canadian Arctic receptor and the north of 80°N as the Canadian high Arctic receptor. To highlight the contribution of the total deposition from each of the four source regions to the two receptor regions in the Canadian Arctic, we calculated the ratio of the total deposition from each source (scenarios 2–5) to that from global emission sources (scenario 1). Figure 2.36 presents the relative contribution of different sources to the two Canadian Arctic receptors. The US and Canada sources of penta-BDE made the largest contribution at 45% towards the penta-BDE loadings to the Canadian Arctic, followed by China at 26%, Europe and Russia at 18%, and India at 11%. In the case of the Canadian high Arctic, the US and Canada emissions of penta-BDE again were the largest contributor to the toxic contamination to the Canadian high Arctic and the rest of con-tributors followed the same sequence as that to the Canadian Arctic.

Monthly total deposition (dry and wet, pg $month^{-1}$) of penta-BDE to the Canadian high Arctic are illustrated in Figure 2.37. The monthly loadings are consistent with the relative contributions of major emission sources, as shown by Figure 2.37, indicating that the US and Canada were the largest source of penta-BDE in the Arctic on a monthly basis, followed by China, Europe and Russia, and India. Largest loadings are found in the summertime, which is consistent with higher air concentration of penta-BDE at Alert in summer. These results reveal the different atmospheric pathways of the pollutants from Eastern Asia and North America entering the Canadian Arctic.

A number of atmospheric transport modeling and trajectory calculations (Bailey et al. 2000, Zhang et al. 2010a, Zhang et al. 2008b) have revealed trans-Pacific transport of toxic chemicals from Eastern Asia to the west part of the Canadian Arctic following prevailing westerly winds crossing the North Pacific Ocean, especially in the springtime. During the spring period, the atmospheric circulation

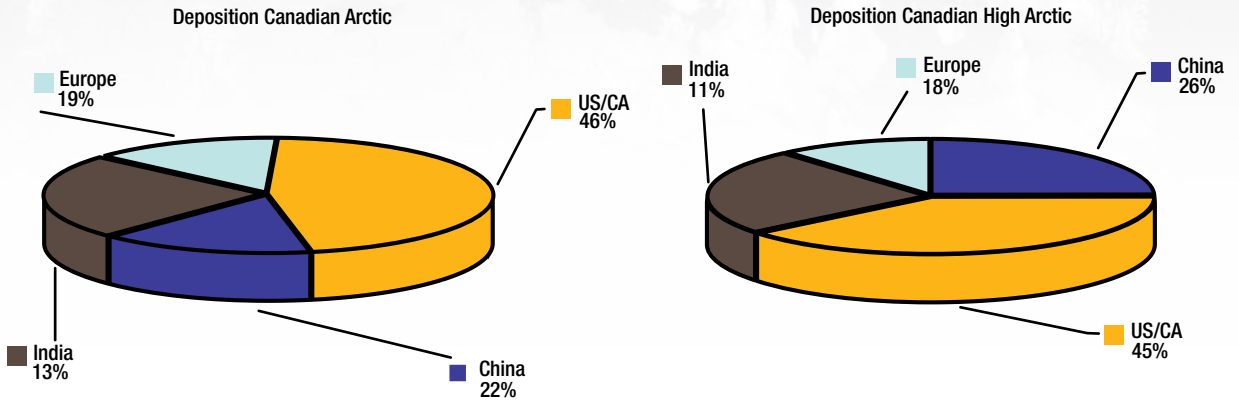


FIGURE 2.36

Relative contribution of penta-BDE from different sources to Canadian Arctic (left panel) and Canadian high Arctic (right panel). US/CA–the United States and Canada.

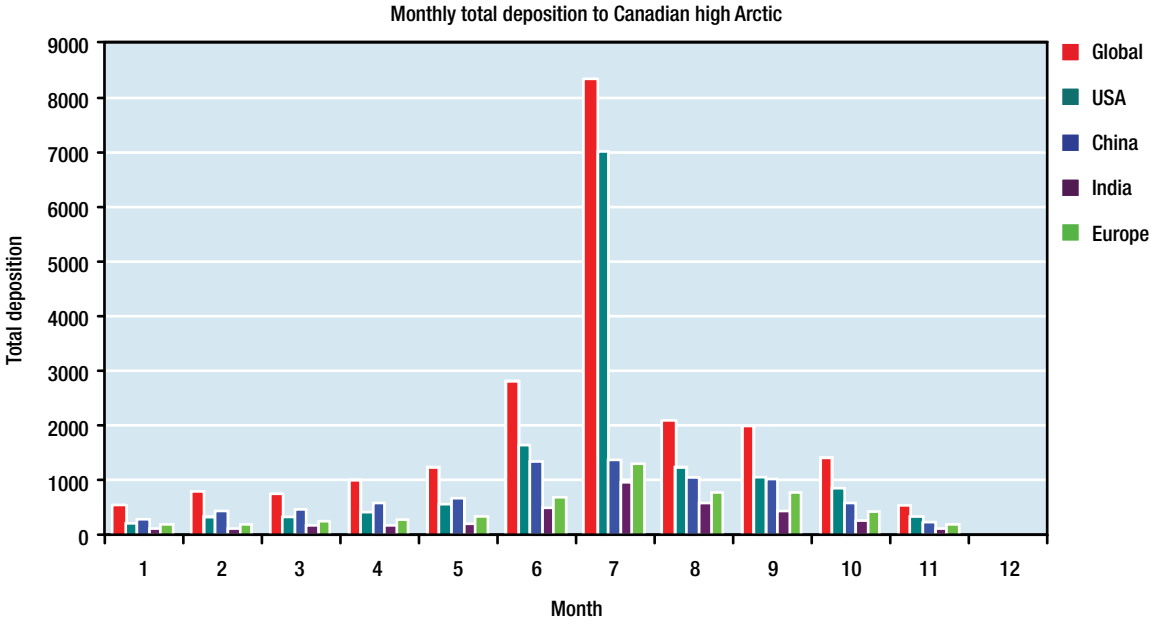


FIGURE 2.37

Monthly total (dry + wet) deposition of penta-BDE to the Canadian high Arctic (pg month^{-1}). Global emissions; US/CA–the United States and Canada; Europe including Russia.

from Northeast Asia to Northwest Canada is forced by a ridge of high pressure, known as the North Pacific high pressure (NPHP) system, centered near the Bering Sea and Alaska region (Figure 2.38). The NPHP is a semi-permanent high pressure system in the North Pacific Ocean. It becomes strongest in the Northern Hemispheric summer and is displaced towards the equator during the winter. When it becomes stronger in the springtime and moves towards the east, it directly exposes the Arctic to Asian pollutants. Given that the atmospheric high pressure circulates the air mass clockwise, the southerly winds on the west part of the NPHP then turn the air to the north during its eastwardly transport pattern across the North Pacific. However, because the southerly winds seldom extend to the high Arctic, especially the Canadian high Arctic, Asian emissions of POPs contribute less to the Canadian high Arctic.

Previous investigations have demonstrated that Europe and North America are major source regions of POPs to the Canadian high Arctic (Halsall et al. 1997, Wang et al. 2010b, Zhang et al. 2010a). In the case of the data from 2005 of penta-BDE emissions, the Eastern US was still a major source of penta-BDE, as shown by Figure 2. 28 and Table 2.7. The eastern seaboard

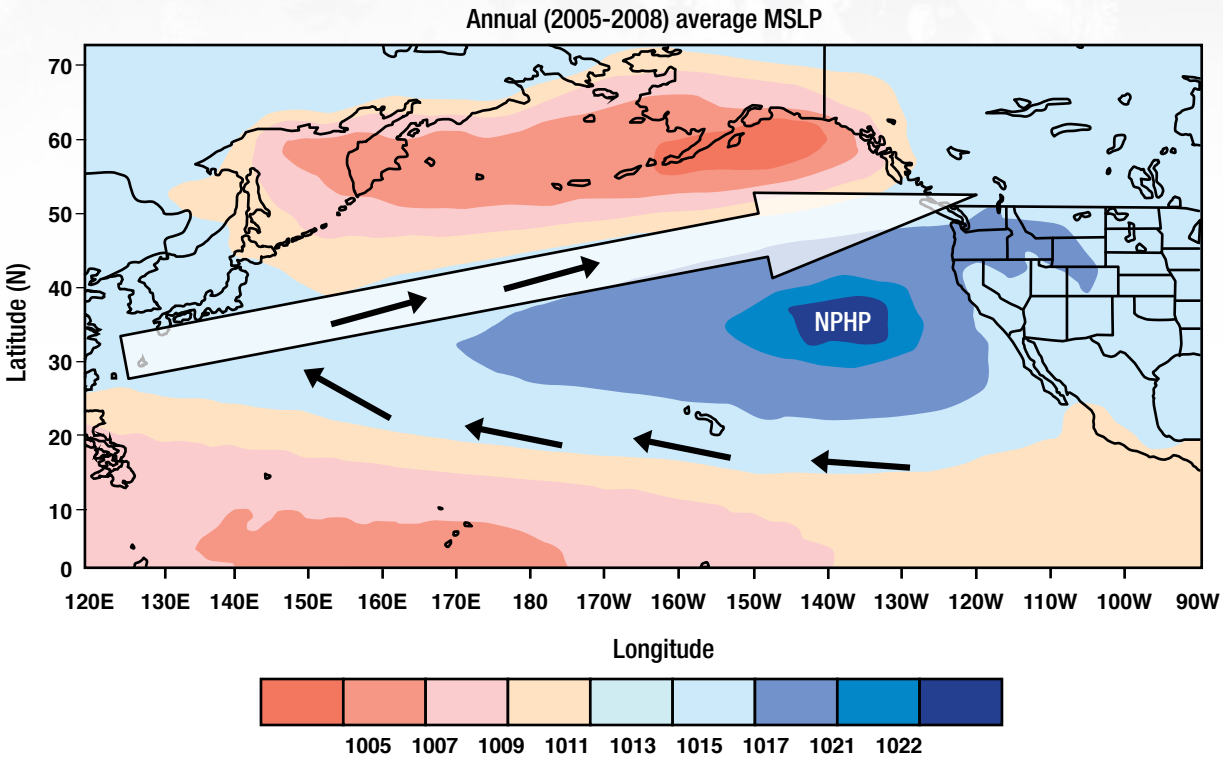


FIGURE 2.38

Schematic view of the North Pacific high pressure system illustrated by the mean sea level pressure (MSLP, hPa, averaged from 2005 through 2008). Black arrows indicate wind directions and the large arrow indicate the atmospheric pathway of toxic chemicals from Asia to the Canadian Arctic. Original image was collected from the National Oceanic and Atmospheric Administration (NOAA).

of North America, a major atmospheric transport pathway of POPs from the Eastern US to the Canadian high Arctic, is affected by southerly wind flows from the west of Azores-Bermuda high over the North Atlantic Ocean (Zhang et al. 2008b).

2.3.5. Oceanic transport of POPs

Contributors: James Armitage, Terry Bidleman, Paul Helm, Liisa Jantunen, Henrik Kylin, Yi-Fan Li, Robie Macdonald

2.3.5.1. Introduction

Long-range oceanic transport (LROT) has been studied for decades although less frequently in the context of POPs. For example, elucidation of circulation pathways from temperate oceans to the Arctic, and within the Arctic Ocean, has been followed with radionuclides (Alfimov et al. 2004, Smith et al. 1998), nutrient ratios (Carmack et al. 1997, Jones et al. 1998, Jones et al. 2003) and lead (Gobeil et al. 2001). Evidence is now accumulating to show that some persistent organic chemicals are also subject to substantial LROT. This was first demonstrated for HCHs, which over time have arrived in the Arctic Ocean by a combination of atmospheric and oceanic transport. In particular, β-HCH is more subject to oceanic transport than α-HCH because of its greater tendency to partition from air to water (Li and Macdonald 2005, Li et al. 2002, Li et al. 2004). Global-scale fate and transport models have been parameterized for other persistent and relatively water-soluble compounds; e.g., PFCAs and PFSAs (Armitage et al. 2009a, b, Armitage et al. 2009d, Prevedouros et al. 2006, Wania 2007) as well as current-use pesticides (Matthies et al. 2009). These tools can also be used to derive integrated metrics of long-range transport potential (e.g., Arctic Contamination Potential) which characterize overall contaminant delivery to the Arctic ecosystem and can also elucidate the relative importance of atmospheric and oceanic pathways e.g., (Brown and Wania 2008, Gouin and Wania 2007, Wania 2007).

This section begins with an overview of processes that limit the ability of chemicals to be transported long distances through the ocean. For example, partitioning between the particle and dissolved phases, particle sinking rates, deep-water formation and chemical/microbial stability (Section 2.3.5.2). Monitoring of perfluorinated chemicals in seawater and LROT is discussed in section 2.3.5.3. Following is a presentation of the Arctic Mass Balance Box

Model (AMBBM) of transport and fate of HCHs in the Arctic Ocean, previously applied to α-HCH (Li and Macdonald 2005, Li et al. 2004), it is updated to include β-HCH and presented in section 2.3.5.4. Finally, a detailed investigation of spatial variability of α-, β-, and γ-HCHs in the Canadian Archipelago during the summer of 1999 is discussed in section 2.3.5.5).

2.3.5.2. Potential limitations to long-range oceanic transport

Chemicals entering coastal waters in temperate latitudes are subject to various fate processes which influence the efficiency of LROT. With respect to contamination of the Arctic Ocean, the following processes are briefly discussed here.

– Degradation

– Particle settling

– Deep-water formation (vertical mixing)

– Subduction/exclusion within the Arctic Ocean

– Horizontal circulation patterns within the Arctic Ocean.

Degradation

Hydrolysis (neutral, base-catalyzed) is a key potential abiotic reaction pathway in the marine environment. Chemical classes with hydrolysable functional groups include halogenated aliphatics, organophosphate esters, carboxylic acid esters, amides, and carbamates (Larson and Weber 1994). HCHs, a relatively well-studied group of POPs are also susceptible to hydrolysis, but with degradation kinetics highly dependent on ambient conditions. For exam-ple, estimated hydrolysis degradation half-lives of α-HCH and γ-HCH at seawater pH (8.1) are 64–110 years at 0 °C and less than a year at 25 °C (Harner et al. 1999b, Ngabe et al. 1993). Thus, degradation in tropical and subtropical oceans could limit their LROT. Hydrolysis of β-HCH is much slower, and this isomer appears to be more efficiently transported via ocean circulation (section 2.3.5.4). Other potential reaction pathways include photo-chemical reactions occurring at the air-water interface, in the surface microlayer, and also in the bulk water column to the euphotic depth. Biodegradation in the water column is also possible given the presence of microbial communities in the bulk water column and the surface microlayer and may be far more effective than abiotic reaction pathways. For example, biodegradation half-lives of HCHs in the Arctic Ocean were estimated to range from 5.9–23.1 years (Harner et al. 1999b).

By definition, POPs tend to be resistant to degradation as reflected by the estimated half-lives in water summarized in Table 2.8. Lower tempera-tures can substantially reduce abiotic reaction rate constants, depending on the sensitivity of the reaction (typically characterized by an activation energy). This temperature dependence can be estimated using the Arrhenius expression, which can be used to quantify the relative change in rate constant as a function of temperature. The relationship between temperature and biodegradation rate may exhibit a similar trend (Macdonald et al. 2005) but this effect is possibly obscured by the type of microorganisms present in different ecosystems (e.g., microorganisms in cold waters may be well-adapted to these conditions and still able to maintain efficient metabolism). Note that these half-lives are applicable to the freely-dissolved (i.e., bioavailable) fraction only; the mass fraction of the chemical sorbed to particulate and dissolved organic carbon (POC and DOC respectively), are assumed to be shielded from reactions.

Based on the half-lives presented in Table 2.8, degradation in the water column is not likely to be a key fate process for most POPs entering aquatic systems with short residence times (e.g., rivers). Even in aquatic systems with long residence times (e.g., Baltic Sea), modeling studies indicate that degradation in the water column represents only a minor sink in comparison to other fate processes such as revolatilization, sediment deposition and sediment burial (Armitage et al. 2009c, Breivik and Wania 2002a). For non-volatile compounds with low affinity for suspended solids however, degradation in the water column during oceanic transport could be significant. For example, assuming an average current velocity of 1–5 cm s^{-1}, the time required to travel a distance of 1,000 km ranges from 230–1,150 days. Since a chemical released into coastal waters at 45°N must travel at least 2,000 km to reach the Arctic Circle (66°N), it is clear that degradation in the water column can act as a substantial barrier to LROT.

Particle settling

Sorption to particular organic carbon in the water column and subsequent deposition to sediments is an important fate process for many POPs due to their hydrophobic nature (e.g., high organic carbon-water partition coefficients, K_{OC}). In the context of ocean transport, this process is manifested as the transfer of contaminant mass from the mixed surface layer (0–200 m) to the deeper ocean, which is generally

TABLE 2.8. Estimated degradation half-lives in water at 25 °C for a selection of POPs[1]

Compound class	Estimated degradation half-life in water* (d)	Reference or source of information
PCBs	20–2,000; 60–10,000 at 7°C;	Mackay et al. (2006) Sinkkonen and Paasivirta (2000)
PAHs	7–70	Mackay et al. (2006)
PCDDs & PCDFs	20–2000; 170–8000 at 7°C;	Mackay et al. (2006) Sinkkonen and Paasivirta (2000)
HCB	2000	Mackay et al. (2006)
PeCBz	194–1250	Zarfl et al. (2011)
DDT, DDE	230–2,000	Mackay et al. (2006)
cis- & -*trans*-chlordane	≥180	EPI Suite; U.S. EPA (2009)[2]
chlordecone	≥180	EPI Suite; U.S. EPA (2009)[2]
dieldrin	≥180	EPI Suite; U.S. EPA (2009)
aldrin	≥180	EPI Suite;U.S. EPA (2009)
endrin	≥180	EPI Suite; U.S. EPA (2009)
heptachlor	≥180	EPI Suite; U.S. EPA (2009)
mirex	≥180	EPI Suite; U.S. EPA (2009)
α-HCH	145–710; 1,970–6,170‡	Zarfl et al. (2011) ‡ at 0°C Harner et al. (1999b)
γ-HCH	30–300	Zarfl et al. (2011)
α-endosulfan	>180	EPI Suite; U.S. EPA (2009)
Hexabromobiphenyl	>180	Zarfl et al. (2011)
Hexabromocyclododecane	60	EPI Suite; U.S. EPA (2009)
BDE47 (Br_4)	≥180	EPI Suite; U.S. EPA (2009)
BDE99 (Br_5)	~150	Zarfl et al. (2011)
PFOS	≥180	Zarfl et al. (2011)

[1] at 25 °C unless otherwise indicated

[2] Based on the Level III fugacity model output in EPI Suite V4.0

considered a permanent sink (Dachs et al. 2002, Scheringer et al. 2004). Following Lohmann et al. (2006), the flux of contaminants out of the mixed surface layer (F_{SINK}, kg m^{-2} y^{-1}) can be calculated as follows:

$$F_{SINK} = C_{i,POC} F_{POC} \quad \text{Eq. 13}$$

where $C_{i,POC}$ is the concentration of chemical in particulate organic carbon (kg *i* kg POC^{-1}) and F_{POC} is the settling rate for POC (kg POC m^{-2} y^{-1}).

Settling rates are highly variable spatially and temporally as they are strongly dependent on phytoplankton biomass (primary productivity). For example, average settling fluxes for ocean waters spanning 30–45°N and 45–60°N were estimated to be approximately 50 mg OC m^{-2} d^{-1} (range: 12–545) and 120 mg OC m^{-2} d^{-1} (range: 45–890) respectively during the fall of 1998 (Dachs et al. 2002). Using these settling rates and empirical data on concentrations of PCB 28, 52, 101, 118, 138, 153 and 180 in the water column, Lohmann et al. (2006) estimated settling fluxes ranging from 520–8,900 kg y^{-1} for these PCBs across the entire Atlantic Ocean. The impact of this settling flux on the efficiency of long-range oceanic transport is somewhat obscured by the fact that these compounds are semi-volatile and therefore multimedia chemicals. For example, particle settling in regions of high primary productivity can lead to enhanced atmospheric deposition which then compensates for the depletion of the chemical in the mixed surface layer to some extent (Dachs et al. 2002).

Assessing the influence of particle settling on LROT strictly as a function of hydrophobicity can be simplified if the chemicals are assumed to be perfectly persistent and non-volatile, i.e., degradation and air-surface exchange is neglected. Adopting this approach and applying the OECD Overall Persistence (P_{OV}) and LRTP Tool (OECD 2006, Wegmann et al. 2009), the Characteristic Travel Distance (CTD) in water and the half-life due to particle sinking and deep-water formation (see next section) as a function

of log K_{OC} were calculated and are presented in Figure 2.39. CTD represents the distance travelled from the source, at which point the concentration of chemical has fallen to 1/e (i.e., 37%) of the original value (Bennett et al. 1998, Beyer et al. 2000). The default current velocity in the OECD P_{OV} and LRTP Tool is 2 cm s^{-1} and the particulate organic carbon settling rate is 0.045 kg OC m^{-2} y^{-1} (OECD 2006), corres-ponding to 125 mg OC m^{-2} d^{-1}. This POC settling rate is similar to values in Dachs et al. (2002). Regardless, these model results that are evaluative in nature and are best interpreted in relative terms.

The CTD in water are in excess of 40,000 km for chemicals with log $K_{OC} \leq 4.0$ and decline to 160 km once the log $K_{OC} \geq 7.5$. For low log K_{OC} chemicals, the CTD is controlled by deep-water formation since the fraction of the total mass in the water column sorbed to POC is negligible. As log K_{OC} increases, the relative importance of particle sinking increases until it dominates the overall loss term. In this model, the transition between the dominance of particle sinking over deep-water formation occurs at around log K_{OC} = 4.5, dictating the shape of the curve relating CTD to log K_{OC} shown in Figure 2.39.

The results presented in Figure 2.39 can be more broadly understood if the mass fraction of chemical sorbed to POC (%) as a function of log K_{OC} as well as the concentration of POC in the water column, is also illustrated, as in Figure 2.40. This fraction can be calculated from the concentration of POC and dissolved organic carbon (DOC) in the water column and the POC-water and DOC-water partition coefficients. The range of reported values of concentrations of POC in global ocean surface waters is indicated as well (Duforêt-Gaurier et al. 2010). The concentration of DOC in the water column was assumed to be zero, equal to POC, and 5 times POC whereas the sorption capacity was assumed to be approximately one-fifth of POC (Burkhard 2000, Seth et al. 1999).

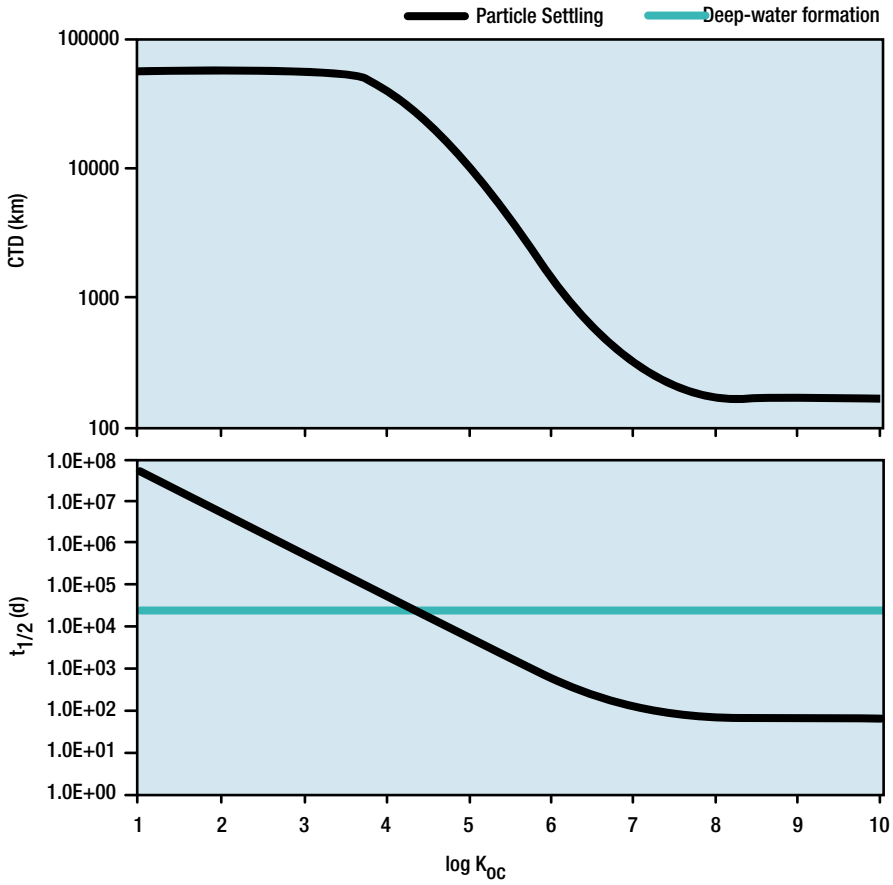


FIGURE 2.39

Characteristic travel distance (CTD) of a persistent and non-volatile chemical in water (km) (top panel) and half-life (d) due to particle sinking and deep-water formation as a function of log K_{OC} (bottom panel).

Consistent with the model output of the OECD P_{OV} and LRTP Tool, the mass fraction of chemicals sorbed to POC is low when the log $K_{OC} \leq 4.0$ at all concentrations of POC in the water column. Given that the global average concentration of POC in the water column is 0.05 mg L^{-1} (Duforêt-Gaurier et al. 2010), it is apparent that particle settling is not likely the most important process limiting LROT in most ocean regions of the world unless the affinity for POC is extremely high (e.g., log $K_{OC} > 7$). In the context of LROT to the Arctic Ocean, the North Atlantic is worth considering specifically because relatively high concentrations of POC and DOC occur in the water column of this region, averaging around 0.2–0.3 mg L^{-1} and 0.6–0.7 mg L^{-1} respectively in summer according to recent estimates (Carlson et al. 2010, Duforêt-Gaurier et al. 2010). With these water column characteristics, the estimated fraction sorbed to POC for chemicals with properties similar to highly chlorinated PCBs (i.e., log K_{OC} of approximately 5.5–7.0) ranges from approximately 10–50%. For ionizing chemicals like PFCAs and PFOS however, which have apparent log organic carbon-water distribution

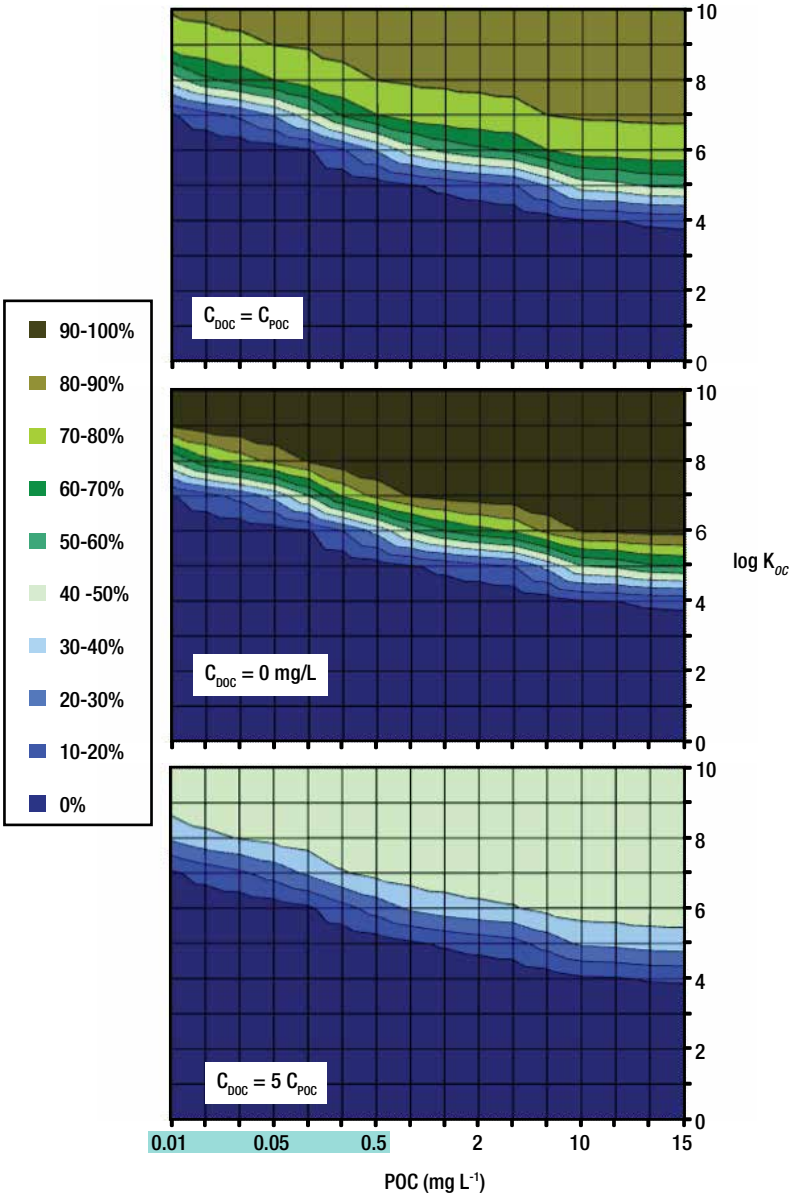


FIGURE 2.40

Mass fraction of the chemical sorbed to POC in the water column (%) as a function of log K_{OC} and concentration of POC in the water column under different assumptions about the concentration of DOC. Blue highlighting on x-axis indicates approximate range of concentrations of POC in near-surface ocean waters reported in Duforêt-Gaurier et al. (2010).

ratios (log D_{OC}) in the range of 2.0–4.5 (Higgins and Luthy 2006), particle settling is a far less efficient barrier to LROT (sorbed fraction < 1%).

Deep-water formation (vertical mixing)

Exchange between the mixed surface layer and deeper layers in the open ocean can occur due to turbulence between stratified water layers (diapycnal mixing) and also, in some regions as part of the global "conveyor belt" circulation pattern (Stewart 2008). Upwelling and downwelling events in coastal waters also promote vertical exchange. Vertical eddy diffusivities related to diapycnal mixing in the open ocean are in the range of 10^{-5} m^2 s^{-1} (Stewart 2008). The mass transfer coefficient (MTC) describing vertical exchange in the OECD P_{OV} and LRTP Tool (OECD 2006) was based on studies with inert tracers which suggest an average residence time of approximately 100 years in the mixed surface layer due to vertical mixing. This parameterization follows the approach adopted for GloboPOP, a global-scale fate and transport model (Wania and Mackay 1995). Assuming a diffusion path length half of or equal to the assumed depth of the mixed layer (200 m), the vertical diffusivities corresponding to the MTCs in GloboPOP are approximately 10^{-5} m^2 s^{-1}, consistent with the value cited above. Whereas vertical exchange due to diapycnal mixing is assumed to occur everywhere in the ocean, deep-water formation related to the global "conveyor belt" is localized to certain regions. With respect to LROT to the Arctic Ocean, the key regions are the Nordic Seas (approximately 68–80°N, 0–25°E) and the Labrador Sea (approximately 50–60°N, 60–40°W) where deep-water formation rates are an estimated 15 Sv (1 Sv = 10^6 m^3 s^{-1}) (Isachsen et al. 2007, Lohmann et al. 2006, Rahmstorf 2002). Deep water formed in these regions is assumed to move predominantly southward as opposed to continuing on into the Arctic Ocean at depth.

Following Lohmann et al. (2006), the mass flux of contaminant associated with vertical exchange/deep-water formation (F_{DWE}, kg m^{-2} y^{-1}) can be estimated similarly to particle settling, i.e.,

$$F_{DWE} = \frac{C_W R_{DWE}}{A} \qquad \text{Eq. 14}$$

where C_W is the total concentration of the chemical in the water phase (kg L^{-1}), R_{DWE} is the rate of vertical exchange in the area of interest (L y^{-1}) and A is the surface area (m^2).

This process can be important for many classes of chemicals, at least on a regional-scale. For example, deep-water formation was found to be more important than the particle settling flux for PCBs in the Norwegian and Labrador Seas; however, the particle settling flux dominated overall when considering the entire Atlantic (Lohmann et al. 2006). Based on the deep-water formation rates estimated above for areas in the North Atlantic, approximately 475 kg y^{-1} is transported to the deep ocean per pg L^{-1} of chemical in the water column. This mass flux is independent of the phase distribution of the chemical since it is assumed that particles are advected with the bulk water. For chemicals with relatively low affinity for particles such as PFCAs and PFOS, deep-water formation in these regions represents a key potential loss term and hence a barrier to LROT.

Subduction/exclusion within the Arctic Ocean

Water enters the Arctic through the Bering Strait (North Pacific origin), through the Fram Strait between Greenland and Svalbard as well as through the Barents Sea (North Atlantic origin) (Jones 2001), see Figure 2.22. Research on the stratification and composition of the water layers in the Arctic Ocean using different tracers (e.g., nitrate:phosphate ratios, radionuclides such as I-129) have greatly improved the understanding of how horizontal and vertical mixing occurs (Carmack et al. 1997, Jones et al. 1998, Rudels et al. 1996). For example, Jones et al. (1998) derived a contour map detailing the percentage of Pacific and Atlantic source water in the surface layer (upper 30 m) across the entire Arctic Ocean using empirical nitrate:phosphate ratios. These data do not support the assertion that contaminants entrained in Atlantic water are excluded from the most biologically relevant depths. Reported vertical profiles of I-129 and Cs-137 transported from Northern Europe to the Barents Sea (Smith et al. 1998) also indicate that contaminants originating from inflowing Atlantic water will be present in upper surface waters; concentrations of I-129 and Cs-137 in the Barents Sea are essentially uniform from 2–337 m deep indicating extensive mixing as opposed to permanent subduction of North Atlantic water in this region. The key conclusion with respect to LROT is that while density-driven stratification will occur to a certain extent (i.e., top few meters), as inflowing Atlantic water interacts with the Polar Mixed Layer (PML), Atlantic Water at the surface has been extensively modified during transit towards the Arctic and will continue flowing into the Arctic Ocean at biologically relevant depths (Rudels et al. 1996). As discussed above however, deep-water formation in the Norwegian Sea is likely to be an important loss term. This process, along with vertical mixing in general, should be considered a dilution effect as opposed to exclusion however.

Horizontal circulation patterns within the Arctic Ocean

While vertical distribution does not appear to be a barrier to biological exposure to contaminants in the Arctic via LROT, the general circulation patterns dictating the horizontal distribution must be considered. As discussed above, regions dominated by waters of Pacific origin can be distinguished from regions dominated by water of Atlantic origin using the nitrate:phosphate ratio (Jones et al. 1998) and indicate limited mixing in the surface layer. The Atlantic-Pacific front is generally assumed to be located above the Lomonosov Ridge (Macdonald et al. 2003). Surface waters (0–200 m) of the western Arctic (e.g., Chukchi Sea, Beaufort Sea) are therefore dominated by waters of Pacific origin whereas surface waters of the eastern Arctic (e.g., Kara Sea, Barents Sea) are dominated by waters of Atlantic origin (see also section 2.3.5.5), The western and eastern basins are termed the North American Arctic Ocean (NAAO) and the Eastern Arctic Ocean (EAO) in section 2.3.5.4 and in Macdonald et al. (2000). Although mixing across the Atlantic-Pacific front is not favoured by typical circulation patterns, the location of the front can shift under conditions associated with a high Arctic Oscillation index (Macdonald et al. 2003).

The significance of these general circulation patterns on the horizontal distribution of a contaminant in the upper surface waters can be illustrated through hypothetical tracer simulations using an ocean circulation model, in this case the ANWAP RAIG model (Layton et al. 1997). This model was developed to assess potential health impacts related to releases of radionuclides in the Arctic Ocean. It is a box model which divides the surface waters of the Arctic Ocean into 15 regions corresponding to major water bodies (e.g., Beaufort, Sea, Laptev Sea, Barents Sea). Horizontal and vertical water exchanges between the regions were estimated using model output from a three-dimensional coupled ocean-ice model. Two 100-y model scenarios were simulated, (i) constant inflow of a conservative tracer via the Bering Strait only and (ii) constant inflow of a conservative tracer via the North Atlantic only. The surface water concentrations in all regions at year 100 relative to the concentration in the highest region were then calculated and are presented in Figure 2.41 and Figure 2.42.

As shown in Figure 2.41 and Figure 2.42, the model results indicate limited mixing between the two major basins (EAO and NAAO). This transport is consistent with general circulation patterns and demonstrates the distinct domains of influence for waters of Pacific and Atlantic origin. Note that although the Canadian Archipelago is not explicitly included in the ANWAP RAIG model, this region is dominated by waters of Pacific origin (Jones et al. 2003) and will likely have concentrations one-fifth to one-tenth of the highest region in Figure 2.41. The simplified model results are broadly consistent with the empirical distribution of radionuclides released into the North Sea from nuclear processing facilities in the UK and France (Alfimov et al. 2004) and also with more spatially-resolved three-dimensional model simulations (Gao et al. 2004, Karcher et al. 2004). While the finer details of ocean circulation within the Arctic cannot be captured by this box model (e.g., rapid northerly transport and limited dispersion associated with entrainment in the Norwegian Coastal Current, and that narrow

Photo: Crispin Halsall

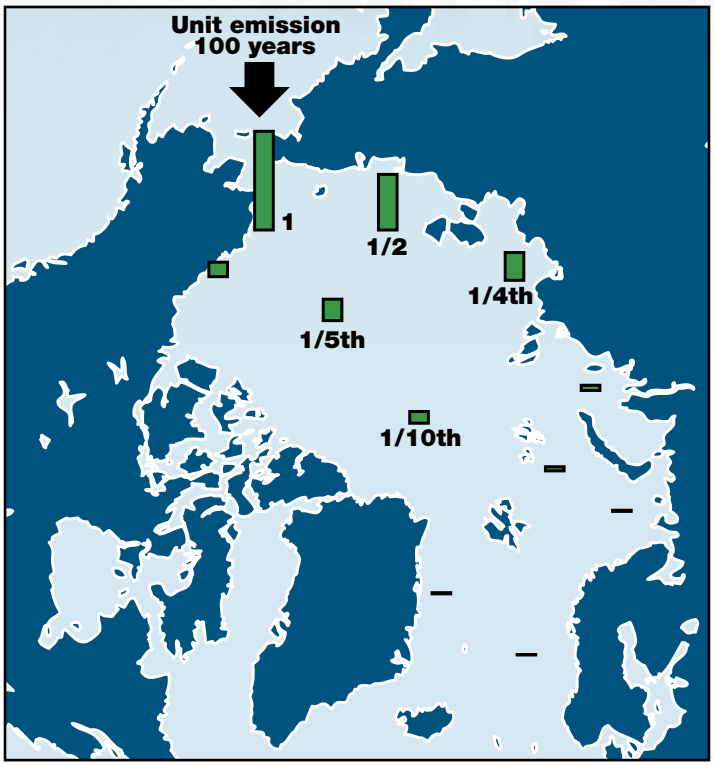


FIGURE 2.41

Relative concentrations of a conservative tracer in the Arctic Ocean following 100 years of inflow via the Bering Strait only.

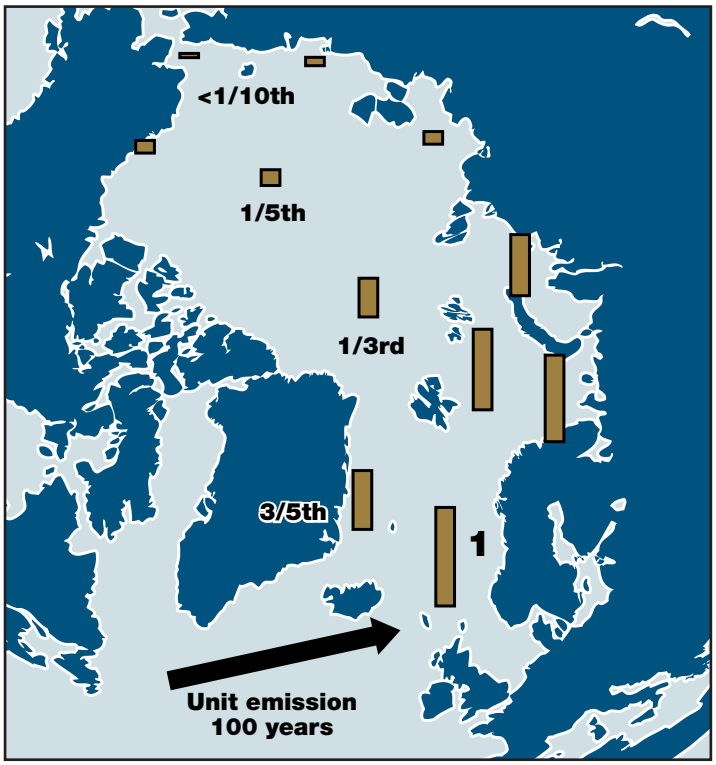


FIGURE 2.42

Relative concentrations of a conservative tracer in the Arctic Ocean following 100 years of inflow via the North Atlantic only.

coastal currents bringing Pacific water into the North Atlantic), it does provide a useful guide to the underlying patterns associated with ocean transport of persistent, water-soluble contaminants in the Arctic Ocean. Most importantly, contaminants released into the Atlantic or Pacific Ocean are not expected to approach a uniform distribution across the Arctic during the period of peak emissions and subsequent mass loading due to the transport limitation imposed by the general circulation patterns. Biological exposure related to LROT in the eastern arctic waters, for example, may be substantially different than exposure elsewhere (i.e., the pattern of exposure associated directly with LROT has a strong regional signal). This pattern of distribution is distinct from LRAT, which tends to result in more uniform deposition fluxes and therefore of concentrations/exposure in the water column.

2.3.5.3. Long-range oceanic transport of perfluorocarboxylates and perfluorosulfonates

PFCAs and PFOS remain of scientific and regulatory interest due to their high persistence in the environment, substantial historic production, wide range of uses, and detection in abiotic and biological samples in remote regions. One of the more interesting and challenging aspects of understanding the available monitoring data is that in addition to emissions related to manufacturing and use of these compounds, there are several other classes of related compounds which degrade in the atmosphere under environmentally-relevant conditions to yield these substances (Anderson et al. 2006, Ellis et al. 2004, Martin et al. 2006, Prevedouros et al. 2006, Young et al. 2007).

Regardless of the origin of PFCAs and PFOS, once these compounds enter the marine environment they will be subject to LROT to remote regions. The relative importance and efficiency of this transport pathway compared to others can be assessed in several different ways. Following Macdonald et al. (2000), one approach is to define a boundary representing the geographical extent of the Arctic Ocean and then estimate the mass flux of these compounds from measured concentrations in the water column outside the boundaries and the estimated rate of water flowing across the boundary i.e.,

$$F_{SWF} = C_W R_{SWF} \qquad \text{Eq. 15}$$

where C_W is the total water concentration (kg L^{-1}) and R_{SWF} is the surface water inflow rate (L y^{-1}). This approach was applied by Prevedouros et al. (2006) using background concentrations of PFOA from the central Pacific Ocean (15–62 pg L^{-1}) (Yamashita et al. 2005) and a total inflow rate of 4.9 ± 1.3 Sv (10^6 m^3 s^{-1}). The corresponding gross inflow is approximately 2,000–12,000 kg y^{-1}, well in excess of the gross inflow related to the atmospheric transport and degradation pathway. The main advantage of the approach outlined above is its simplicity and transparency and the ease with which updated estimates can be obtained. It is, however, hindered by data quality issues (i.e., the suitability and reliability of the empirical data used) and the lack of insight gained into the distribution of the contaminants once in the Arctic Ocean. Regardless, this type of calculation serves as a reasonable initial approximation for assessing the relative importance of oceanic transport.

Environmental fate and transport models are routinely used to assess the relative efficiency as well as relative importance of different transport pathways. CTD, for example, is a well established metric used for assessing LRTP but other metrics have also been developed (Scheringer et al. 2004). The main advantage of focusing on the estimates of the relative efficiency of different transport pathways derived by the model (i.e., LRTP metrics) as opposed to the relative importance (i.e., gross inflows) is that the inevitable uncertainties and debate regarding the quality of the emission estimates is avoided since all LRTP metrics are independent of the mass of the chemical introduced to the system. In addition, all calculations are conducted using the same model framework and so are directly comparable. Wania (2007) applied the GloboPOP model to assess the LRTP of PFCAs and a key class of precursors (perfluoroteleomer alcohols, FTOHs) using the Arctic Contamination Potential ($eACP_{10}$). This LRTP metric is defined as follows (Wania 2003).

$$eACP_{10} = \frac{M_R}{E_T} \qquad \text{Eq. 16}$$

where M_R is the total mass of contaminant in the Arctic minus the mass present in its overlying atmosphere and E_T is the total mass of contaminant emitted to the global environment after 10 years of continuous emission. According to Wania (2007), the $eACP_{10}$ of PFCAs emitted directly to coastal regions in temperate latitudes and transported in the ocean is more than 10-fold higher than the $eACP_{10}$ characterizing the long-range atmospheric transport and degradation of FTOHs. The main factor inhibiting the precursor pathway is not deposition and sequestration in lower latitudes but rather the low yield of the reaction pathway converting precursors to PFCAs in the Arctic. The relatively high transport efficiency of PFCAs via ocean transport follows from the general considerations previously discussed

Photo: Caroline Sevigny/ArcticNet

(i.e., negligible degradation and sorption to settling POC). A similar $eACP_{10}$ characterizing oceanic transport would be obtained for PFOS based on its physical-chemical properties. One caveat to the results obtained using the GloboPOP model (and also the OECD P_{OV} and LRTP Tool) is that account is not taken of the large-scale deep-water formation in the Norwegian and Labrador Seas. Furthermore, the model segments the globe based on latitudinal zones so it is not possible to distinguish between the $eACP_{10}$ of emissions originating in Asia versus North American and Europe. Interestingly, output from highly resolved ocean transport models suggest that radionuclides (Gao et al. 2004, Karcher et al. 2004) and anionic PFOA (Stemmler and Lammel 2010) entering the North Sea are predominantly transported northward in the Norwegian Coastal Current, bypassing the regions of deep-water formation identified above. The LRTP of emissions from North America are likely to be the most susceptible to attenuation by deep-water formation.

The global fate and transport of PFCAs and PFOS have also been assessed using available emission estimates (Armitage et al. 2009d, Paul et al. 2009, Prevedouros et al. 2006). Model output from these applications can therefore be used to gain insight into the relative importance of directly emitted PFCAs and PFOS in comparison to precursor sources (Armitage et al. 2006, Armitage et al. 2009a, b, Armitage et al. 2009d, Stemmler and Lammel 2010, Wania 2007). The spatial resolution of the applied models range from 10-zone latitudinal segmentation (Armitage et al. 2006, Armitage et al. 2009d, Wania 2007), to a 15 º x 15º grid (Armitage et al. 2009a, b) to a 1.5–3º x 1.5–3º grid (Stemmler and Lammel 2010).

2.3.5.3.1. Assessment of key findings on PFAS ocean transport

- Modelled concentrations of PFOA and PFOS are in reasonable agreement with currently available monitoring data (see Chapter 3, section 3.2.3.1), suggesting that available emission estimates for these two compounds are plausible (Armitage et al. 2006, Armitage et al. 2009a, Armitage et al. 2009d, Stemmler and Lammel 2010).
- Oceanic transport of directly emitted PFOA and PFOS is the dominant source of these compounds to the arctic marine environment (Armitage et al. 2006, Armitage et al. 2009d, Stemmler and Lammel 2010, Wania 2007). Particle settling and vertical mixing in the open ocean are not limiting factors on LRTP.
- Redistribution of these contaminants from lower latitudes to the Arctic Ocean is ongoing and the total mass (and average concentration) of PFOA and PFOS in the marine environment is expected to increase for the next 10–20 years (Armitage

et al. 2006, Armitage et al. 2009d, Wania 2007). Regulation of PFOS in North America and Europe as well as its inclusion in the Stockholm Convention will result in lower global average concentrations as emissions decrease.

- Deep-water formation in the North Atlantic was estimated to remove approximately 25% of the total global emissions of PFOA over the period 1950–2004, confirming its importance in the overall fate and transport of these compound classes (Armitage et al. 2009b).
- Measured concentrations of PFCAs with ≥ 9 carbons in the open ocean are frequently below detection limits preventing a more quantitative evaluation of model performance and by extension, the reliability of the emission estimates. Modeled concentration ratios between the C10:C11 homologues are not consistent with empirical data from coastal waters however (Armitage et al. 2009a).
- Sequestration in the terrestrial environment, particularly soils, is an important determinant of LRTP and becomes increasingly effective at limiting the LRTP of PFCAs as a function of chain length/hydrophobicity. The reduction in LRTP due to terrestrial sequestration is sensitive to the assumed dissociation constant (pK_a) since the neutral form of these compounds is semi-volatile and therefore counteracts the influence of sequestration in terrestrial organic carbon pools (Armitage et al. 2009a).
- Inter-annual variability in ocean current velocities and flow pathways has a substantial influence on the gross and net mass fluxes of PFOA across the arbitrarily defined boundaries of the geographical extent of the Arctic (Stemmler and Lammel 2010). While the variability associated with changes in the emission function over time ultimately drives the concentration field within the Arctic Ocean, climatology has a more important influence than previously recognized. The effect of the variability in positive net mass inflows on modeled trends in PFOA concentrations across the Arctic Ocean over time in comparison to output from other models has not been rigorously assessed.

2.3.5.4. Historical β-HCH budget in the Arctic Ocean

2.3.5.4.1. Introduction

Hexachlorocyclohexane (HCH), a cheaply produced OCP, entered into widespread use during the 1940s. Two formulations have been produced: technical HCH, which contains five stable isomers (α: 60–70%, β: 5–12%, γ: 10–12%, Δ: 96–10% (Kutz et al. 1991), and lindane (> 99% γ-HCH), which is the insecticidal form. The production and use of technical HCH increased with time following its introduction in the 1940s until it was abandoned for agricultural use by China in 1983 and by India and the former Soviet Union in 1990. Synchronous decreases in α-HCH concentrations in arctic air following these step decreases in usage and emissions (Li and Bidleman 2003, Li et al. 1998) clearly demonstrate that LRAT provides rapid dispersion of α-HCH from its source regions (mainly in Asia) into the Arctic.

Given the transient release history of HCH, the construction of mass balance budgets, especially for a sequence of years, helps develop an understanding of how this chemical loaded into the Arctic Ocean, what its fate has been, and how the Arctic Ocean responded to the withdrawal of atmospheric loadings. Furthermore, comparison of model results with time-series data collected during the past two decades helps identify knowledge gaps critical to the prediction of future trends of HCH and other chemicals.

The Arctic Mass Balance Box Model (AMBBM) (Li et al. 2004), created specifically to view the Arctic Ocean as a receptor of HCH, has three major modules—one dealing with air concentration, a second with river loadings to the Arctic Ocean, and a third that considers ocean transport and transformation. Model output at annual resolution includes air and water concentrations in the Arctic, loading and removal of HCH from the Arctic Ocean, and cumulative burden in the Arctic Ocean from the first year of entry (1945) to the present. Results for α-HCH were presented in Li et al. (2004) and Li and Macdonald (2005). The model results compared well with published data showing that the α-HCH burden in the Arctic Ocean started to accumulate in the early 1940s and reached the highest value of 6,670 t in 1982, one year before China banned the use of technical HCH. Since that time, the burden of α-HCH in arctic waters decreased quickly by approximately 270 t y^{-1} during the 1990s, and amounted to an approximate estimate of 1,550 t in 2000. The model implies that complete elimination of α-HCH from arctic waters would require another two decades. The total loading of 27,700 t between 1945 and 2000 accounts for approximately 0.6% of total global α-HCH emissions.

β-HCH is the predominant chemical form of HCH which is concern for top aquatic predators because it biomagnifies and apparently resists degradation. Surprisingly, this isomer behaves very differently

from α-HCH in terms of its distribution in the northern hemispheric surface ocean. Even though β-HCH partitions much more strongly into cold water than α-HCH, it did not accumulate in the same way under the pack ice of the Arctic Ocean, as might be expected from the similar emission histories for these two chemicals (Li et al. 2002). Instead, β-HCH was rained out or partitioned into North Pacific surface water where it subsequently entered the western Arctic Ocean via currents passing through the Bering Strait. An important lesson is that, even for seemingly similar environmental contaminants like the HCHs, the environmental pathways must be understood comprehensively for each individual compound (Li et al. 2002).

As was the case for α-HCH, a sequential historical β-HCH budget for the Arctic Ocean from its introduction in the 1940s, provides insight into the pathways taken by this chemical, identifies gaps in our knowledge, and allows for the prediction of future trends. Here, we use known chemical properties of β-HCH, together with the AMBBM, to determine the historical evolution of the budget of β-HCH in the Arctic Ocean, starting in the 1940s when technical HCH was first used.

2.3.5.4.2. Physical and chemical properties of α- and β-HCH

Properties affecting the partitioning and degradation of α- and β-HCH provide crucial input to the model and are summarized in Table 2. 9. The Henry's law constant (H, Pa m^3 mol^{-1}), liquid-phase vapour pressure (P_L, Pa) and octanol–air partition coefficient (K_{OA}) are strong functions of temperature while the octanol-water partition coefficient (K_{OW}) depends weakly on temperature. Thermodynamically consistent "Final Adjusted Values" (FAVs) (Section 2.1.3) for properties of PCBs and pesticides at 25°C are given in Annex Table A2-1, A2-2 and A2-3 (Xiao et al. 2004). Table 2.9 gives FAVs of H, P_L, K_{OA} and K_{OW} at 0°C for α- and β-HCH, and FAVs of parameters for calculating the temperature dependence from log (property) = m/T + b. Organic carbon–water partition coefficients (K_{OC}) have been reported only at 20–25°C; however, these values should not be much different from those for 0°C since K_{OW} appears to vary only slightly with temperature for organochlorines (Bahadur et al. 1997).

Temperature affects the base-catalyzed hydrolysis of α- and γ-HCHs through the second-order hydrolysis reaction and also because the dissociation of water is controlled by temperature (Ngabe et al. 1993). The estimated half-life of α-HCH in seawater at 0°C and pH 8.1 is 64 y) using the Ngabe et al. (1993) rate constant. No rate constant is available for β-HCH, but the hydrolysis is much slower than for α-HCH. Cristol (1947) reported no degradation of β-HCH in 0.005M sodium hydroxide in 72 hours, conditions that hydrolyze α-HCH in a few minutes. A hydrolysis half-life of 100 years for β-HCH was assumed in the model.

Half-lives due to microbial degradation have been estimated as 5.9 ± 1.2 years for the (+)-α-HCH, 22.8 ± 4.7 years for the (–)-α-HCH, and 18.8 ± 10.1 years for γ-HCH (Harner et al. 2000a, Harner et al. 1999b). The half-life of α-HCH in the atmosphere due to OH radical reaction is estimated as 83 days using a second-order rate constant k = 1 x 10^{-13} cm^3 s^{-1} at 4 °C and 24 hour average [OH] = 9.7 x 10^5 (Brubaker and Hites 1998). No microbial or OH radical degradation rates are available for β-HCH. A 20 year half-life for microbial degradation of β-HCH was assumed in the model, similar to microbial degradation half-lives of (-)α-HCH and γ-HCH, but it may be longer.

TABLE 2.9. Properties of α- and β-HCH affecting partitioning and fate in the Arctic[1]

Property	Log H 0°C (Pa m^3 mol^{-1})	Log P_L 0°C (Pa)	Log K_{OA} 0°C	Log K_{OW} 0°C	Log K_{OC} 20-25°C	Hydrolysis 0°C $t_{1/2}$ (y)	microbial deg. Arctic Ocean $t_{1/2}$ (y)	gas-phase OH reaction $t_{1/2}$ (d)
α-HCH	-1.09 m = -3099 b = 10.26	-1.69 m = -3497 b = 11.12	8.46 m = 3235 b = -3.39	4.02 m = 266.2 b = 3.04	3.25-4.10 (b)	64 (c)	6-23 (e)	83 (f)
β-HCH	-2.519 m = -3541 b = 10.444	-2.38 m = -3563 b = 10.67	10.10 m = 4391 b = -5.98	4.17 m = 847.5 b = 1.07	3.36-3.98 (b)	β >> α (d) 100 y used	unknown 20 y used	unknown

[1] H, P_L, K_{OW}, K_{OA}, and parameters for log (property) = m/T + b are the thermodynamically consistent "Final Adjusted Values" (Section 2.1.3), Xiao et al. (2004) ;b) Mackay et al. (2006), c) Using second-order rate constants (Ngabe et al. 1993) and seawater pH = 8.1; d) No reaction in 0.005 M sodium hydroxide in 72 hours (Cristol 1947); e) Harner et al. (2000a), Harner et al. (1999b), 6 years for (+) and 23 years for (-) enantiomer of α-HCH; f) Using second-order rate constant k = 1 x 10^{-13} cm^3 s^{-1} at 4 °C and 24 hour average [OH] = 9.7 x 10^5 (Brubaker and Hites 1998).

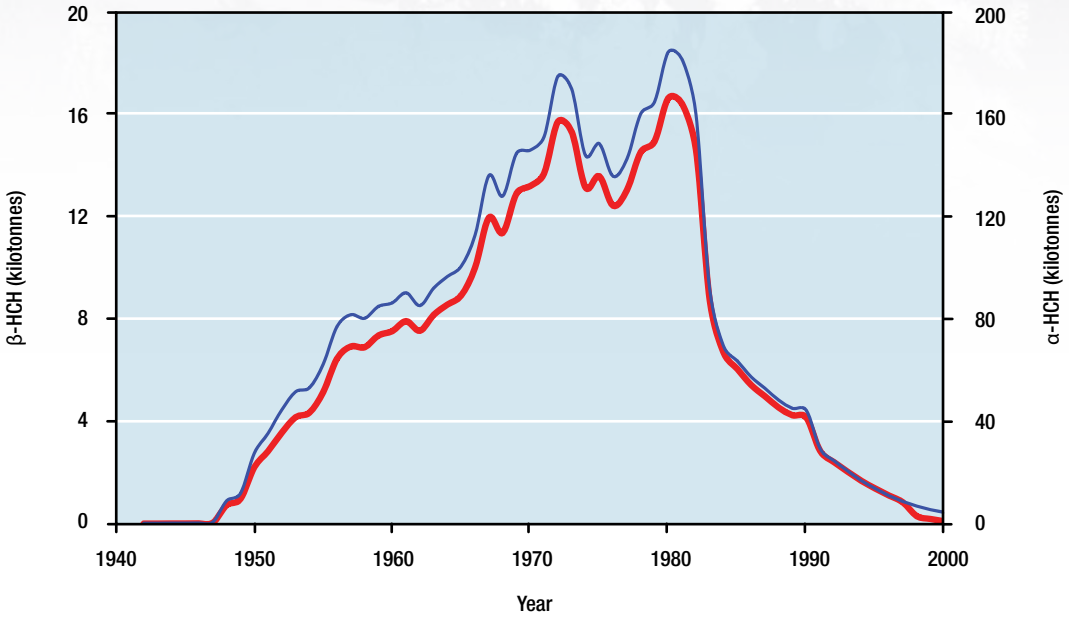


FIGURE 2.43

Global annual β-HCH (red line) emissions (in kt) from 1940 to 2000 (Li et al. 2003b). Global annual α-HCH (blue line) emissions are also shown for comparison (Li et al. 2000).

2.3.5.4.3. Global emissions and monitoring for α-HCH and β-HCH in the arctic air and water

Global emissions of β-HCH are assumed to derive entirely from the technical formulation (β: 5–12%) and therefore parallel those of α-HCH (Figure 2.43), which also derives from the technical formulation. The total emissions to the atmosphere during the 60 years between 1945 and 2000 were 4,300 kt for α-HCH (Li et al. 2000) and 230 kt for β-HCH (Li et al. 2003b). Monitoring data for α-HCH and β-HCH, which are relatively sparse for the Arctic, are summarized in Annex Table A2-6 and Table A2-7.

2.3.5.4.4. Scenarios for the AMBBM applied to β-HCH

Two scenarios for the air concentrations of β-HCH in the Arctic have been used in the AMBBM study. In the first scenario, we assume that air concentration of β-HCH in the Arctic follows the global emission history (Figure 2.43) as a direct response to LRAT. In the second scenario, the assumption is that air concentration of β-HCH in the Arctic is controlled entirely by air-sea partitioning based on the β-HCH residue in the surface Arctic Ocean.

In scenario 2, the net exchange direction of β-HCH between air and sea is controlled by the relative fugacities (partial pressures) of surface water and air. The water/air fugacity ratio (*FR*) is given by McConnell et al. (1993), see equations 10, 11 and 12 in section 2.3.3.2. We therefore assume that a state of equilibrium was established for β-HCH between air and seawater in the North American Arctic Ocean (NAAO) as early as 1945 and that air concentrations of β-HCH (C_A) can be calculated from Eq. (13) provided the water concentration in the NAAO is known.

Su et al. (2006) tested this hypothesis by calculating *FR*, assuming C_W = 0.25 ng L^{-1} and median C_A ranging from 0.86–0.30 pg m^{-3} at Valkarkai (VKK) and Point Barrow (PTB). Resulting estimates of FR were 1.4 and 0.50 at PTB and VKK respectively; that is, the net volatilization and deposition at these two sites. Elevated concentrations of β-HCH in air at PTB could be partly explained by outgassing from the nearby ocean. However, advective inputs from external sources other than outgassing from seawater also likely contributed to high β-HCH in VKK air (Su et al. 2006).

2.3.5.4.5. Input data

Historical β-HCH loadings to the Arctic Ocean via Siberian rivers (Figure 2.44) were assumed to be one-fifth of the α-HCH loadings for 1945–1995 (Li et al. 2004), and were extended to 2005 using data from Carroll et al. (2008). Higher fluxes of β-HCH (and α-HCH) are associated with the 1960s and 1970s when technical HCH was extensively used in the former Soviet Union.

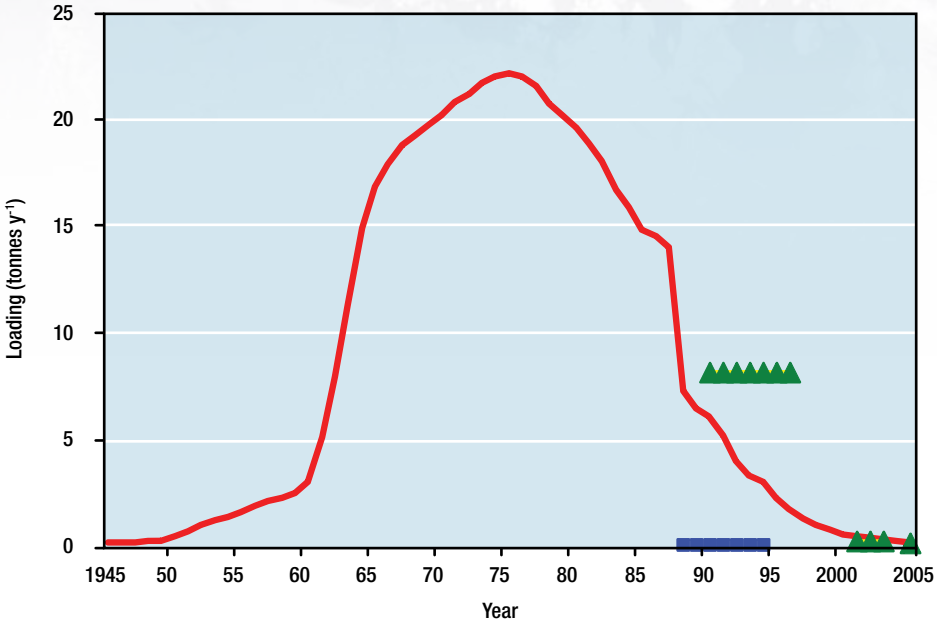


FIGURE 2.44

β-HCH loading to the Arctic Ocean from Russian rivers between 1945 and 2000. The total β-HCH loading to the Arctic Ocean from Russian rivers between 1945 and 2000 is 530 t (β-HCH usage in the former Soviet Union was estimated as 59 kt). Estimations from measurement data are also presented for comparison. The data for blue squares was calculated as 1/5 of the α-HCH data presented in Li et al. (2004), and those with green triangles were calculated by using the data from Alexeeva et al. (2001), Carroll et al. (2008), Kimstach and Dutchak (2004).

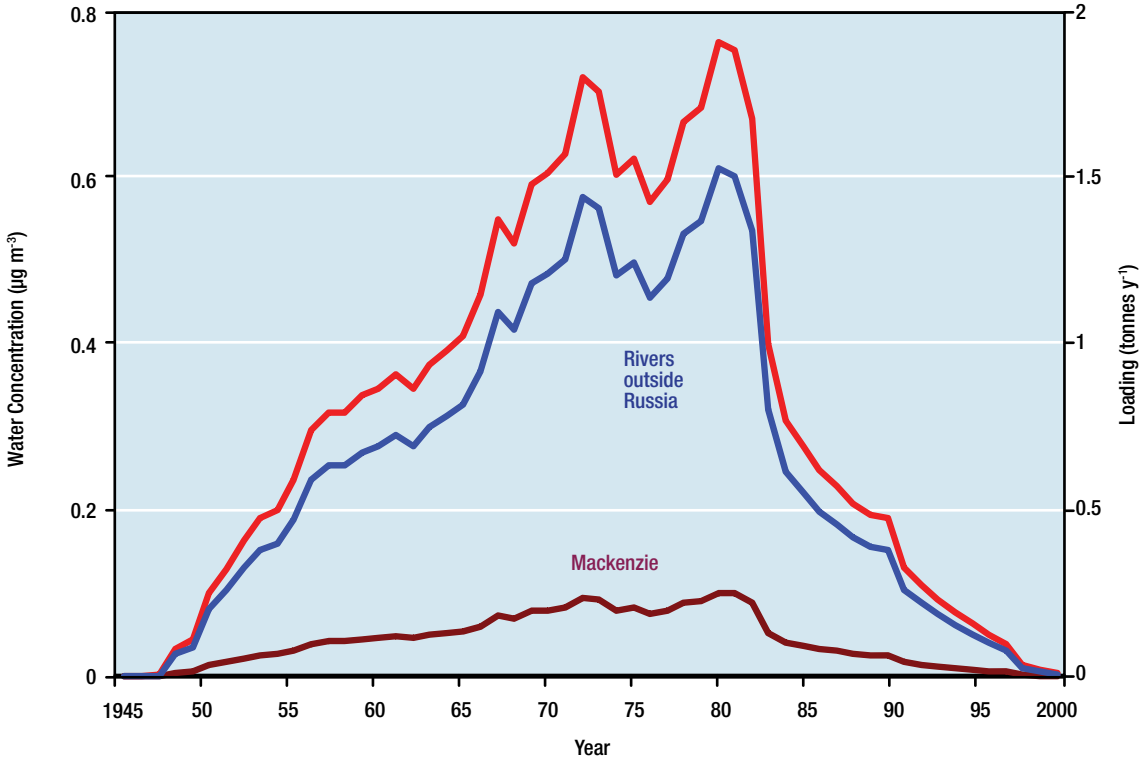


FIGURE 2.45

Estimated historical water concentration of β-HCH in the Mackenzie River from 1945 to 2000 (the red line). Annual fluxes of β-HCH to the Arctic Ocean from the Mackenzie River (the purple line) and from all the rivers outside Russia (the blue line) are also shown in the figure. The total β-HCH loading between 1945 and 2000 was estimated at 35.8 t from all arctic rivers outside Russia.

For the North American and Scandinavian rivers, the loading history (Figure 2.45) was reconstructed by assuming atmospheric equilibrium such that β-HCH loadings are equal to one-fifth of the α-HCH loadings (Li et al. 2004).

There are very few historical data on surface water concentrations in the Bering Sea and western Arctic Ocean for estimating β-HCH loadings to the Arctic Ocean via the Bering Strait. Thus the trends in Figure 2.46 were estimated by assuming that both β-HCH concentrations and loadings were equal to one-fifth of the α-HCH loadings (Li et al. 2004). The same treatment was made for the concentrations of β-HCH in the North Atlantic Ocean, based on which the β-HCH loadings to the Arctic Ocean from the North Atlantic Ocean was calculated.

2.3.5.4.6. Model results—air concentrations

In the first scenario described above, β-HCH concentration in arctic air mirrors the temporal trend of β-HCH usage, exhibiting peaks in 1974 and 1980 (Figure 2.47a). The second scenario, however, shows a peak 1986 and generally much smaller concentrations than those found in Scenario 1 (Figure 2.47b). Figure 2.47 demonstrates good consistency between modeled results and monitoring data for both scenarios.

It is interesting to note that the difference of β-HCH budgets in the Arctic Ocean for the two different scenarios is minor (Table 2.10). The dominant loading of β-HCH to the Arctic Ocean was ocean currents, 70.7% for Scenario 1 and 76.7% for Scenario 2; and gas exchange was the minor portion, 2.4% for Scenario 1 and 1.1% for Scenario 2. Thus, in the rest of the discussion, we present the results for Scenario 1 only.

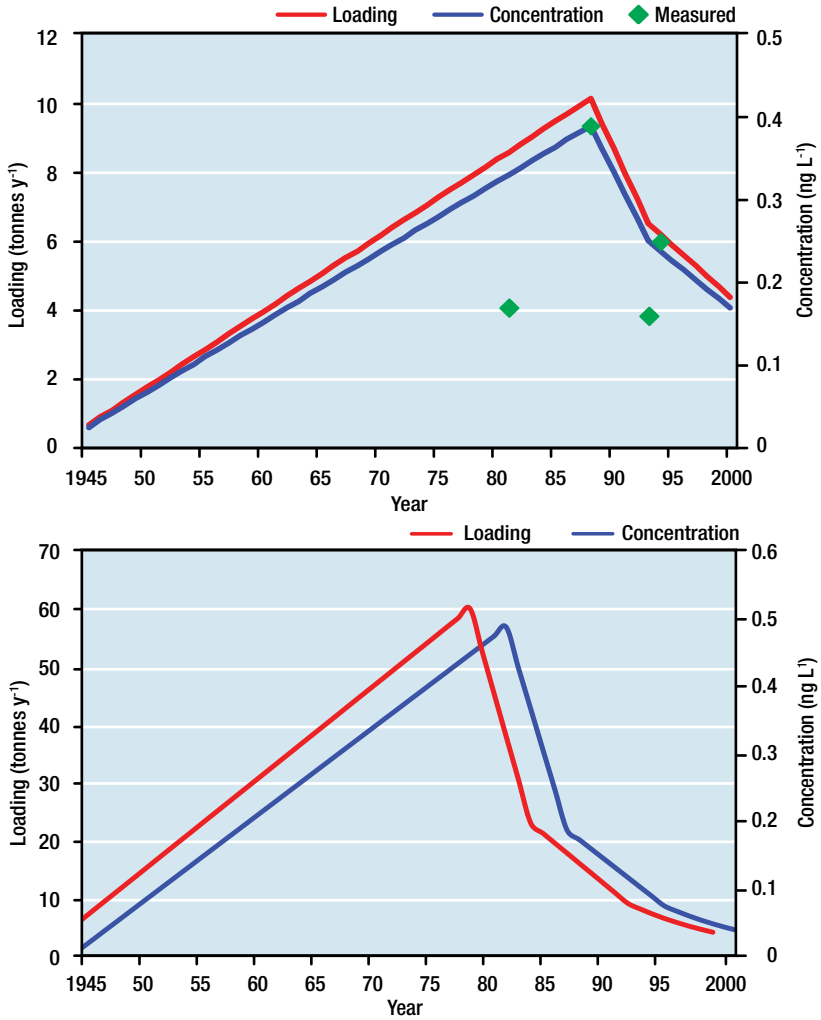


FIGURE 2.46

Concentrations of β-HCH in water of Bering (top panel, Sources of monitoring data Annex Table A2-7) and in water of the North Atlantic Ocean (bottom panel).

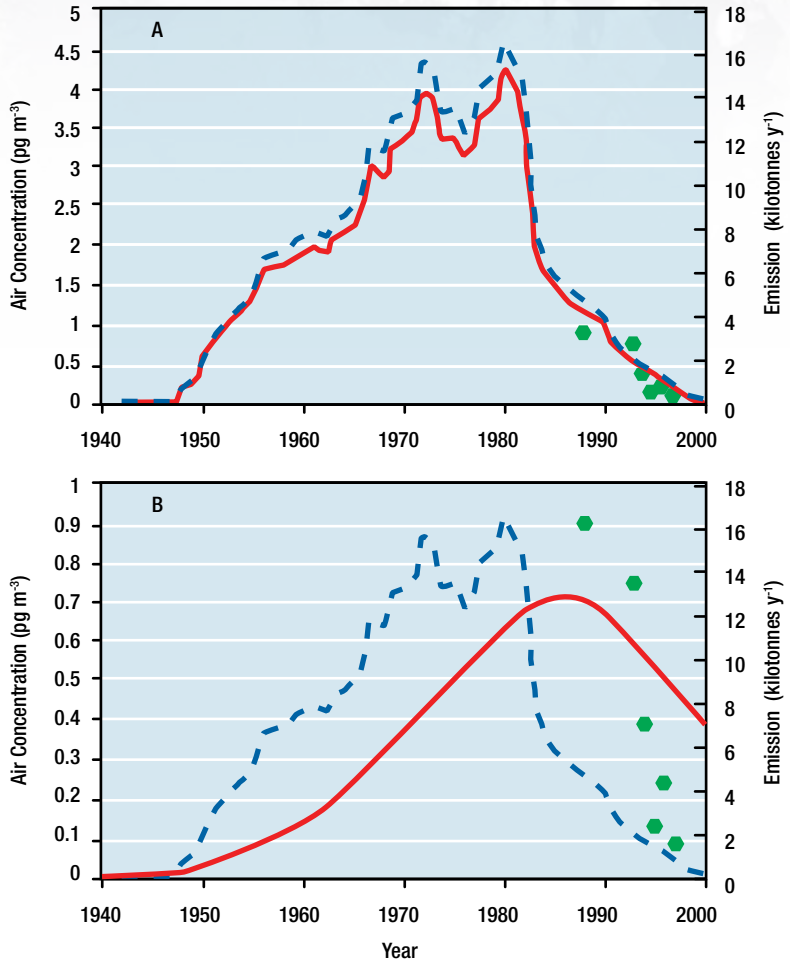


FIGURE 2.47

The concentrations of β-HCH in the Arctic (red lines) for a) Scenario 1: β-HCH concentration in air follows the global emission history (Figure 2.43) and b) Scenario 2: β-HCH concentration in air (solid red line) is controlled by air-sea exchange in the upper Arctic Ocean. The annual global emissions between 1940 and 2000 (dashed blue lines) and measurements (green hexagons) in arctic air are presented for comparison. The monitoring data are from the Canadian Alert Station (Annex Table A2-6).

TABLE 2.10. Comparison of the budgets of β-HCH for two scenarios

	Scenario 1		Scenario 2	
Pathway	Loading (%)	Removal (%)	Loading (%)	Removal (%)
Gas exchange	2.4	0.4	1.1	1.6
Ocean Currents	70.7	35.3	76.7	36.9
Microbial degradation	0.0	36.9	0.0	36.7
Hydrolysis	0.0	7.2	0.0	4.7
Deeper water	0.0	17.6	0.0	17.5
Ice export	0.0	2.6	0.0	2.6
Rivers	22.3	0.0	21.5	0.0
Rain	3.6	0.0	0.6	0.0
Snowmelt	0.9	0.0	0.2	0.0
Particle deposition	0.0	0.0	0.0	0.0

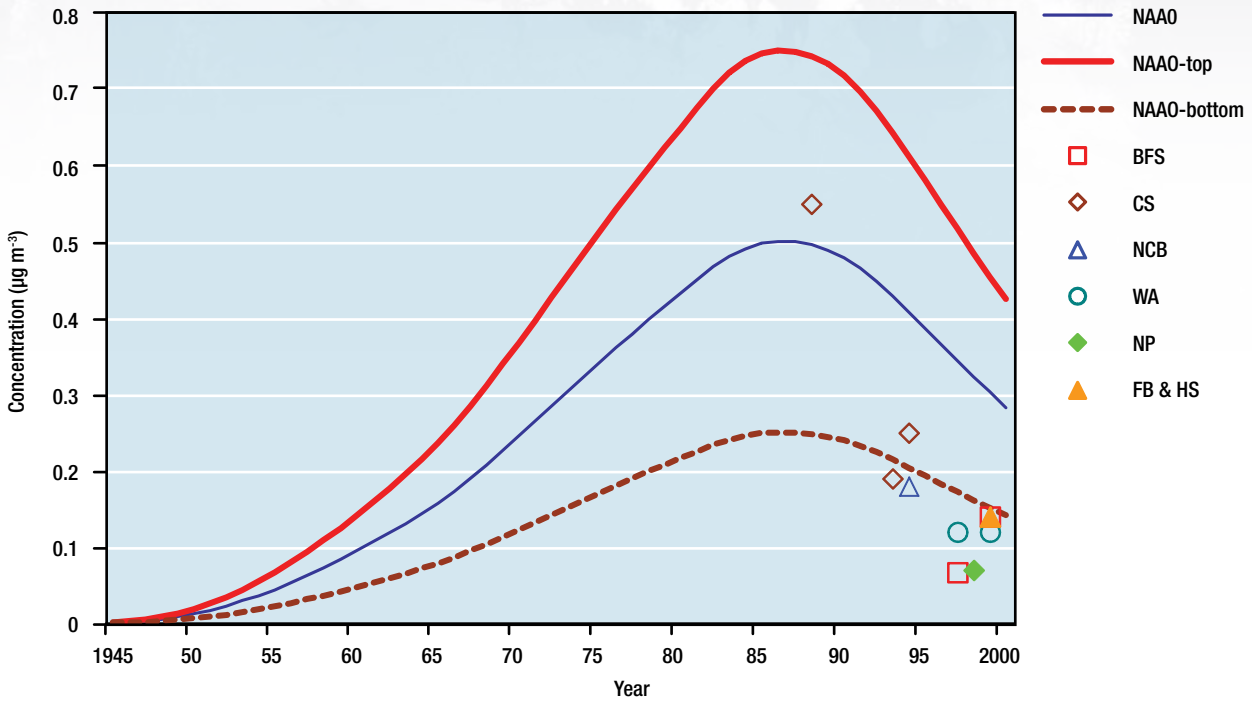


FIGURE 2.48

Comparison of concentrations of β-HCH in NAAO waters between model results and measurements for various locations (NAAO – North America Arctic Ocean; BFS – Beaufort Sea; CS – Chukchi Sea; NCB – North Canadian Basin; WA – West Archipelago; NP – Northwater Polynya; FB & HS – Foxe Basin, Hudson Strait and Gulf of Boothia (data taken from Annex 5. Summarized in Li et al. (2002); See Annex Table A2-7).

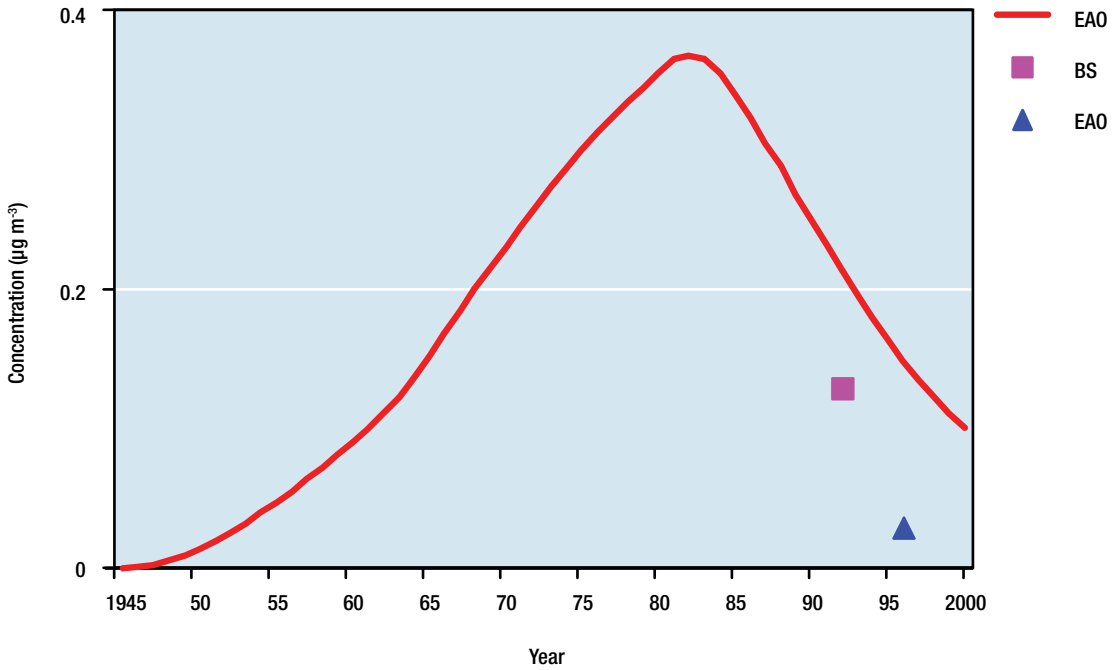


FIGURE 2.49

Comparison of modelled concentrations of β-HCH in Eastern Arctic Ocean (EAO) waters (red line) with measurements for the Barents Sea (BS) and EAO. See Annex Table A2-7.

2.3.5.4.7. Water concentrations

Based on the above inputs, we find that concentrations of β-HCH are higher in the North American Arctic Ocean (NAAO) than in the Eastern Arctic Ocean (EAO) (Figure 2.48 and Figure 2.49).

Sparse measurements of vertical profiles for α-HCH in the Arctic Ocean show that concentration decreases rapidly with depth, in the upper 200 m, in the Canada Basin (Hargrave et al. 1988, Jantunen and Bidleman 1996, Macdonald et al. 2000, Macdonald et al. 1997) and we may assume that β-HCH exhibits a similar profile but at lower concentrations. In contrast, the vertical distribution of α-HCH in the EAO appears relatively uniform in the upper 200 m of the water column. A comparison of the model output for surface-water concentrations of β-HCH with observational data (Figure 2.48 and Figure 2.49) indicates that the model produces substantially higher concentrations with the caveat that observational data are exceedingly sparse in time and space.

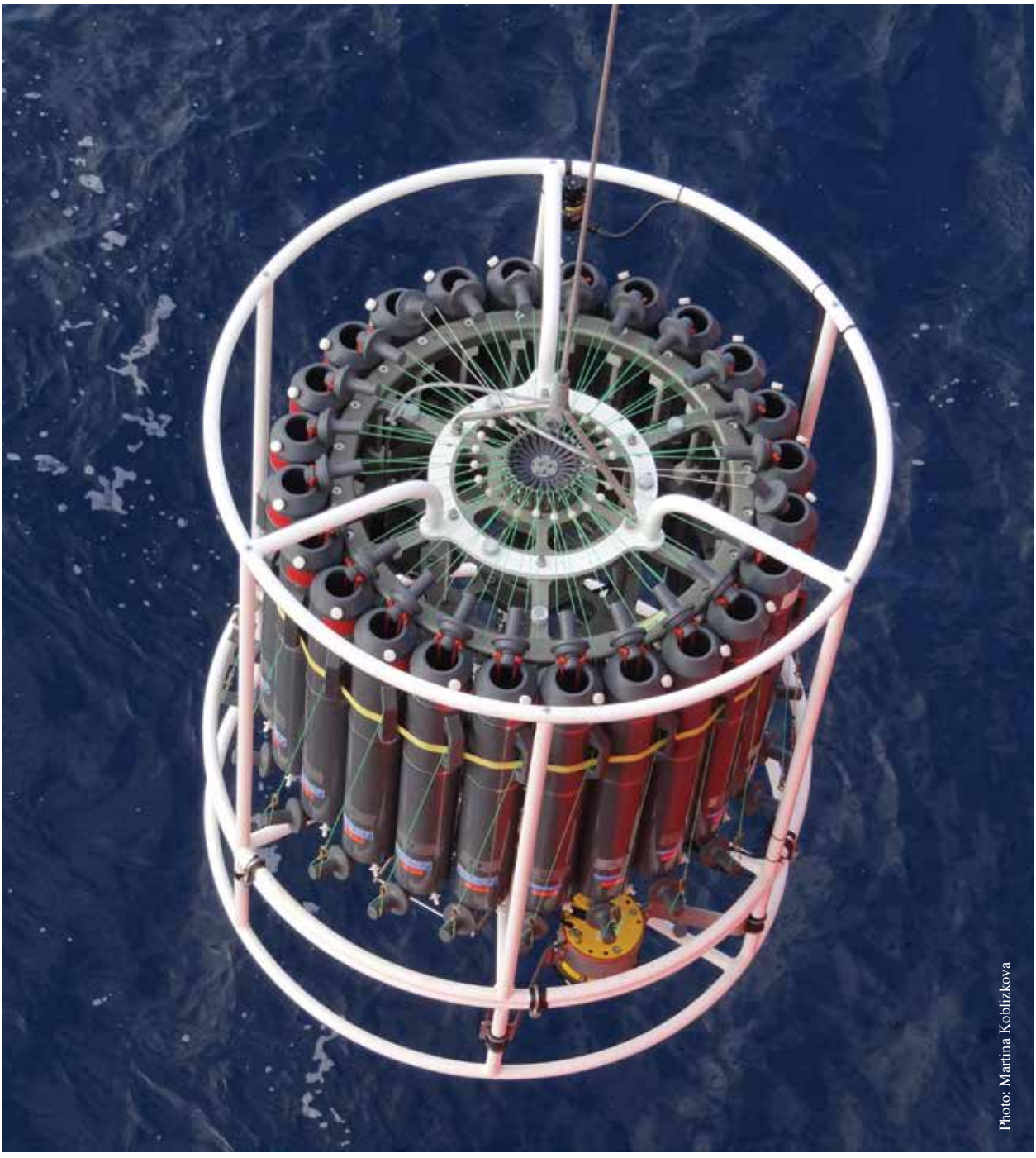


Photo: Martina Koblizkova

2.3.5.4.8. β-HCH burdens and loading in arctic waters from 1945 to 2000

Starting in the 1940s, the burden of β-HCH in the Arctic Ocean increased monotonically, reaching the highest value (816 t) in 1982, after which it decreased rapidly (Figure 2.50). By 2000, the burden of β-HCH in the top 200 m of the Arctic Ocean had declined to 280 t, or about one-sixth of the burden of α-HCH (approximately 1,560 t) (Li et al. 2004).

Between 1945 and 1990, ocean currents provided the highest β-HCH loadings to the Arctic Ocean followed by river inputs (Figure 2.51; top panel), whereas degradation due to microbes and hydrolysis was the dominant removal pathway followed by ocean currents flowing out of the Arctic (Figure 2.51; bottom panel). It must be stressed that the microbial degradation pathway is highly uncertain for β-HCH, since it is based on no experimental evidence. A half-life of 20 years was assumed in the AMBBM, similar to the half-lives

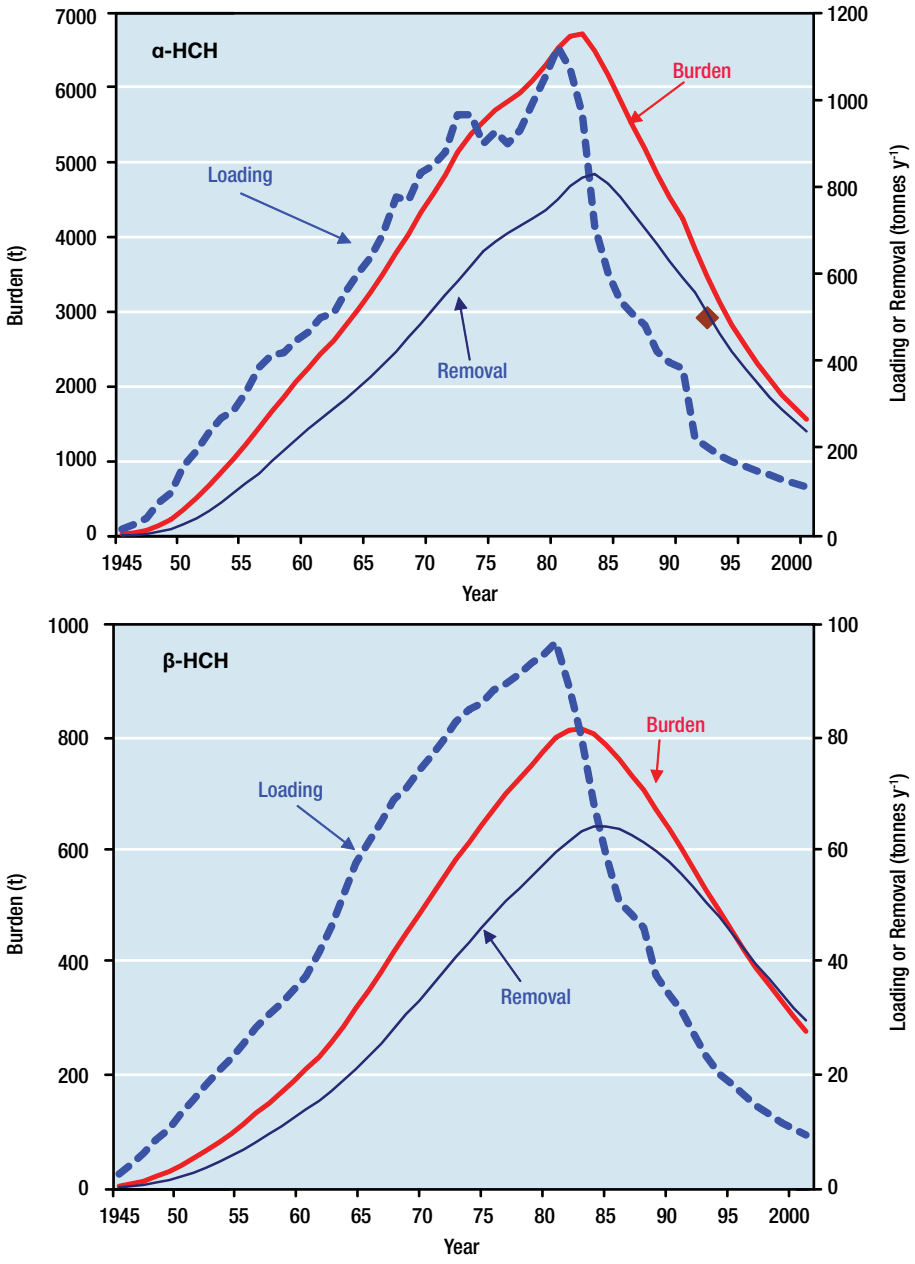


FIGURE 2.50

Loading to (dashed blue line), removal from (thin solid line), and total burden (red line) of α-HCH (the top) and β-HCH (the bottom) in the Arctic waters. The diamond indicates the estimated burden of 2910 t of α-HCH in the early 1990s by Macdonald et al. (2000).

for microbial degradation of (–)α-HCH and γ-HCH in the EAO (Harner et al., 2000, Harner et al., 1999), but considering that the hydrolysis rate of β-HCH is much slower than for α- and γ-HCH, the microbial degradation rate β-HCH may also be much slower.

For α- and β-HCH, the patterns and relative strengths of the removal pathways are similar (Figure 2.52). In contrast, the loadings are very different. For example, for the entire period between 1945 and 2000, ocean currents (71%) and river currents (22%) dominate the entry of β-HCH into the Arctic Ocean, while for α-HCH, it is gas absorption (50%) and ocean currents (34%).

The AMBBM results presented here for the NAAO for 1980, 1985 and 1995 compare well with the budget proposed by Li et al. (2002) (Annex Table A2-8). However, due to a poor estimate for the water budget of the NAAO in the budget in Li et al. (2002), loading of β-HCH from the EAO was not included. It should also be noted that the estimate for β-HCH loading through snowmelt based on β-HCH concentrations in air is larger than the estimate made by Li et al. (2002), where β-HCH concentrations in snowpack were used.

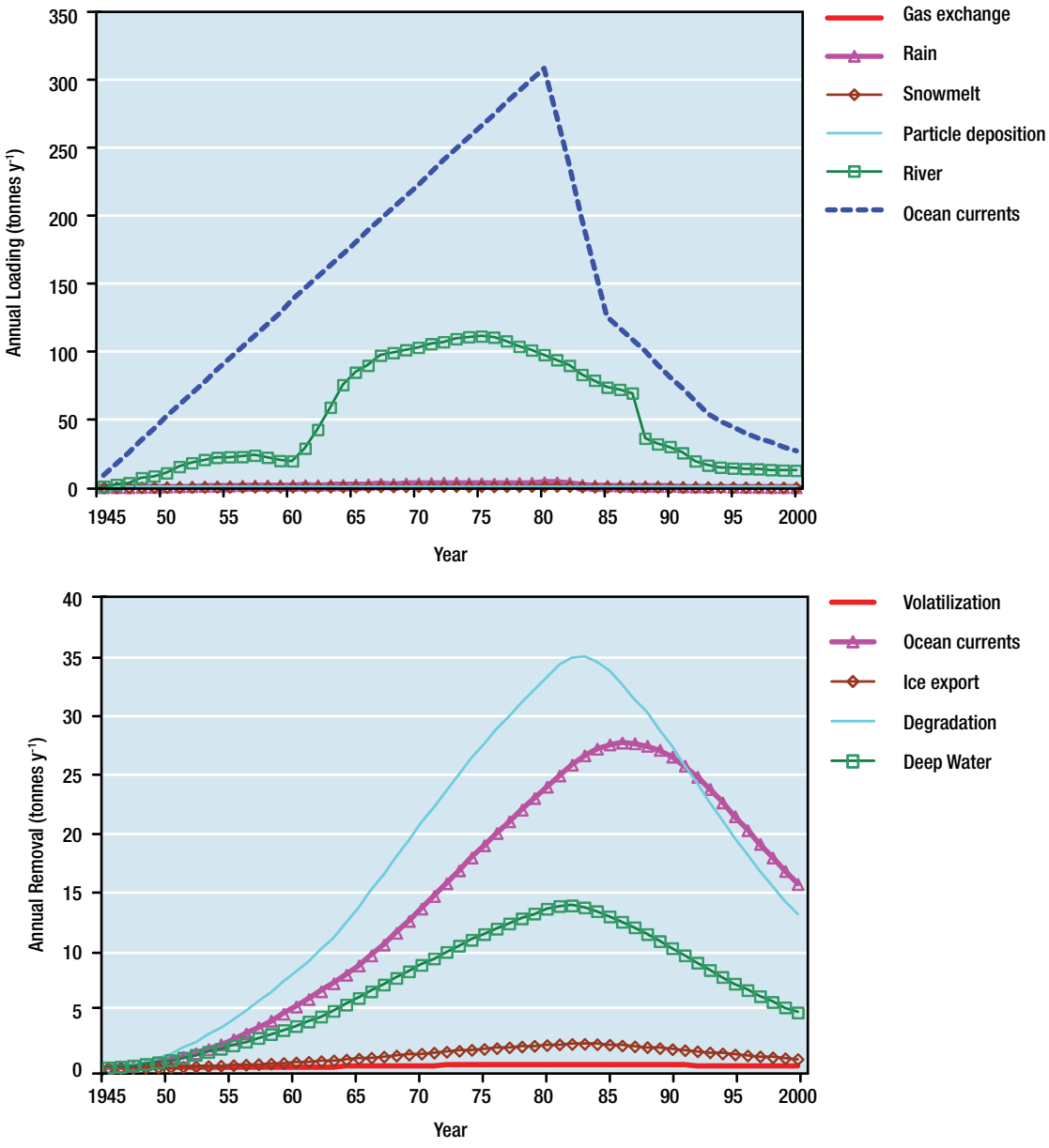


FIGURE 2.51

Annual β-HCH loading to (top) and removal from (bottom) the arctic waters.

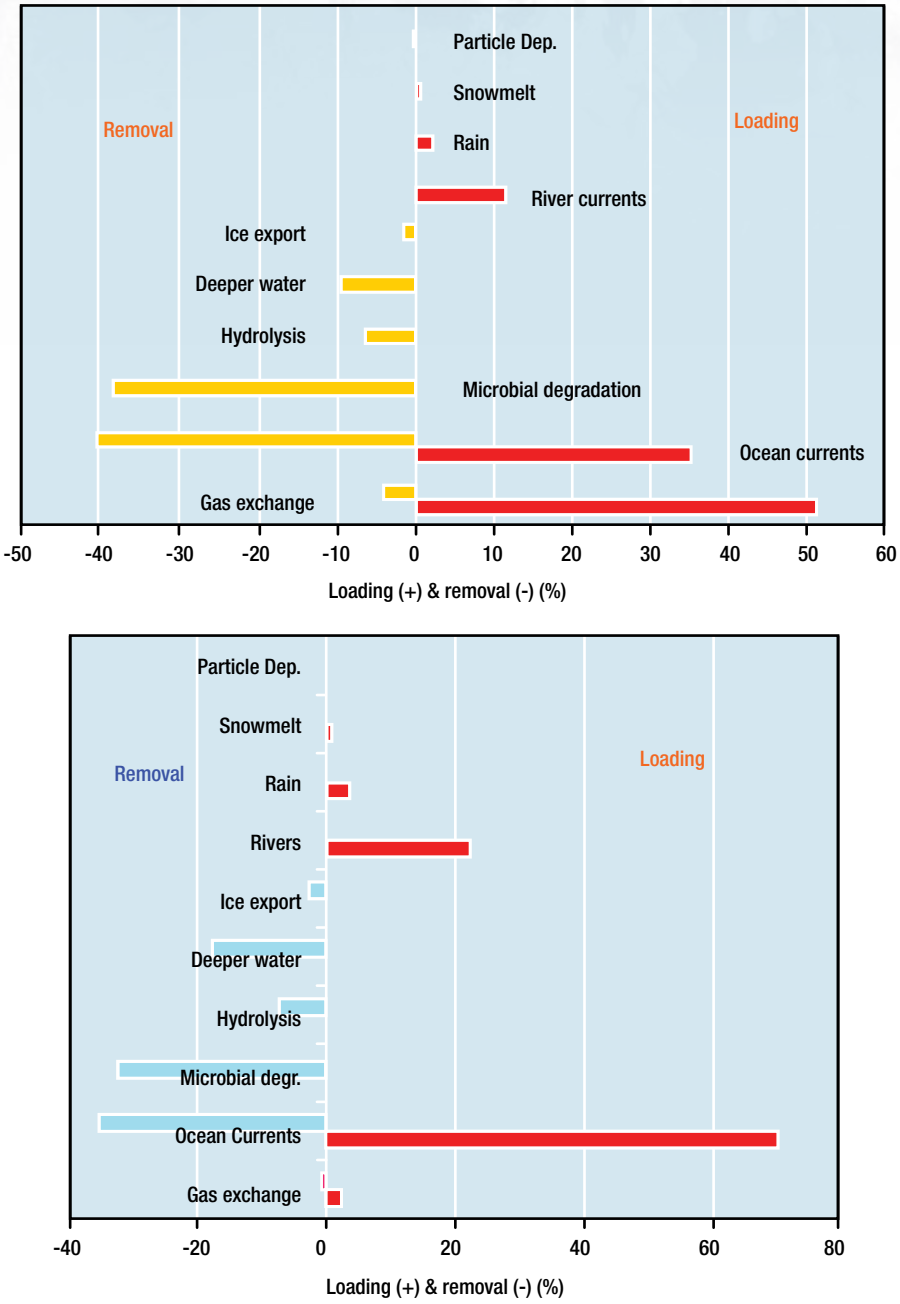


FIGURE 2.52

Percentage of α-HCH (top) and β-HCH (bottom) loading to (right) and removal from (left) the Arctic waters from 1945 to 2000.

2.3.5.4.9. Conclusions

The model confirms the hypothesis made by Li et al. (2002) that differing pathways involved in the entry of α- and β-HCH into the Arctic Ocean govern the observed distributions in that ocean. Furthermore, the model implies that differences in the input functions over time have been more influential in altering the trends of these two isomers than have been the output functions. However, the output estimates are based on the assumed similarity of microbial degradation rates of the HCH isomers, which may not be the case. Further research into degradation pathways would lead to improved model estimates. One implication is that for gases that strongly partition into water, the aquatic pathways are crucial to understand—including ocean currents and rivers. However, this is clearly not a linear process in that the atmospheric pathway has been very important for β-HCH despite its potential

to partition into rainwater and surface ocean water before arriving within the Arctic. We propose that the difference between α- and β-HCH in their capacity to reach the Arctic Ocean is governed almost entirely by the rate of medium transport (air, water) compared to the residence time within each medium.

Given the very simple approach of box modeling, the annual resolution developed between 1945 and 2000 matches well with the sparse set of air and water observations of β-HCH made during the 1990s. Cumulative loadings and removals over a 50-year period resulted in a β-HCH burden of approximately 500 t in the Arctic Ocean during the early 1990s. Time trends for β-HCH also match reasonably well with the trends observed in ringed seals from Ulukhaktok (Addison et al. 2009). See Chapter 4, section 4.2.1.3.

2.3.5.5. Spatial distribution and pathways of α-, β- and γ-HCHs in surface water of the Canadian Archipelago during 1999

2.3.5.5.1. Introduction

Measurements taken predominantly in the NAAO from the mid–1980s to the present by various investigators (Annex Table A2-7), have revealed that the upper interior ocean in the western Arctic contains a dynamic reservoir of HCH stationed between the Bering Sea and the Canadian Archipelago. HCH has been lost from this reservoir (see section 2.3.5.4) through degradation and outflow throughout the Archipelago (Li and Macdonald 2005, Li et al. 2004), with downstream consequences in Baffin Bay and the North Atlantic Ocean (Shen and Wania 2005). With the exception of a few measurements of HCH made in 1992– 1993 near Resolute (Annex Table A2-7) there are no data from which to evaluate how the projected large transport of HCH is processed while passing through the vast channels of the Archipelago. The Swedish Tundra Northwest 1999 (TNW-99) expedition provided an opportunity for a survey of HCH concentrations and isomeric composition in surface water and air across the Canadian Archipelago and the estimation of air-water gas exchange. This section describes the spatial distribution and pathways of α-, β- and γ-HCHs in surface water in the Archipelago, as observed from TNW-99. Air-water gas exchange of α- and γ-HCHs during TNW-99 and a 2007–2008 International Polar Year (IPY) expedition are covered in Jantunen et al. (2008a), Wong et al. (2011) and section 2.3.3 on air-water gas exchange.

The TNW-99 expedition was made on the CCGS *Louis S. St-Laurent* from July, 1999 to September, 1999. Following a route generally outlined by the sequence of stations shown in Figure 2.53, the ship traveled from Nuuk, Greenland across the Davis Strait to Iqaluit, Canada (stations 1,2) then traversed the Archipelago from Hudson Strait (stations 3,4) to Barrow Strait (station 9) along a southern route to Tuktoyaktuk (stations 10,14) and the southern Beaufort Sea (stations 11, 12, 13, 15). The ship then returned along a northern route to Barrow Strait near Resolute Bay (station 19), passed Ellef Ringnes Island (stations 21, 22), continued over to Devon Island through Jones Sound (station 24), past the mouth of Lancaster Sound (stations 25-27), and through Baffin Bay and the Davis Strait (stations 28-30). Locations are listed in the Supporting Information of Bidleman et al. (2007) and shown in the upper half of Figure 2.53. Methodology and quality control are also detailed in that paper.

2.3.5.5.2. Spatial distributions in surface water and depth profiles

Surface water concentrations (ng L^{-1}) of HCHs in the southern Beaufort Sea and Archipelago ranged from 1.1–5.4 (α-HCH), 0.056–0.16 (β-HCH) and 0.19–0.45 (γ-HCH). The tendency toward higher concentrations and higher ratios of α-HCH/γ-HCH in the southern Beaufort Sea and western Archipelago, and lower ones in the central-eastern Archipelago is a dominant feature of these data (Figure 2.54). Enantiomer fractions (see section 2.3.6.1), EF = (+)/[(+) + (–)], of α-HCH ranged from 0.432–0.465, indicating preferential degradation of the (+) enantiomer. EFs were lowest in the southern Beaufort Sea and increased across the Archipelago from west to east (Figure 2.54). Linear regressions vs. longitude were significant ($p < 0.001$ to 0.003) for α-HCH, β-HCH, γ-HCH, EF of α-HCH and α-HCH/γ-HCH, but not for α-HCH/β-HCH. Regressions vs. latitude were significant ($p < 0.001$ to 0.049) for α-HCH, γ-HCH, EF of α-HCH and α-HCH/β-HCH.

Principal component analysis (PCA) using the variables α-HCH and γ-HCH concentrations, α-HCH EF, latitude and longitude, resulted in the first two principal components accounting for 71% and 16% of the variance (Figure 2.55). Samples were clustered into four main groups, representing (1) the Davis Strait and lower Baffin Bay (stations 1–6), (2) upper Baffin Bay and Lancaster Sound (stations 25–28), (3) central, north and west Archipelago (stations 9, 17–14), and (4) the southern Beaufort Sea (stations 10–15). Transition stations 7,8, 16, 29 and 30 fall in between these groups. The variables plot (vectors in Figure 2.55) shows that α-HCH is most strongly associated with longitude and γ-HCH with latitude.

Surface water concentrations of α-HCH, β-HCH and γ-HCH in the central and north Archipelago stations 7–9,19–24 ranged from 2.8–4.8 ng L^{-1},

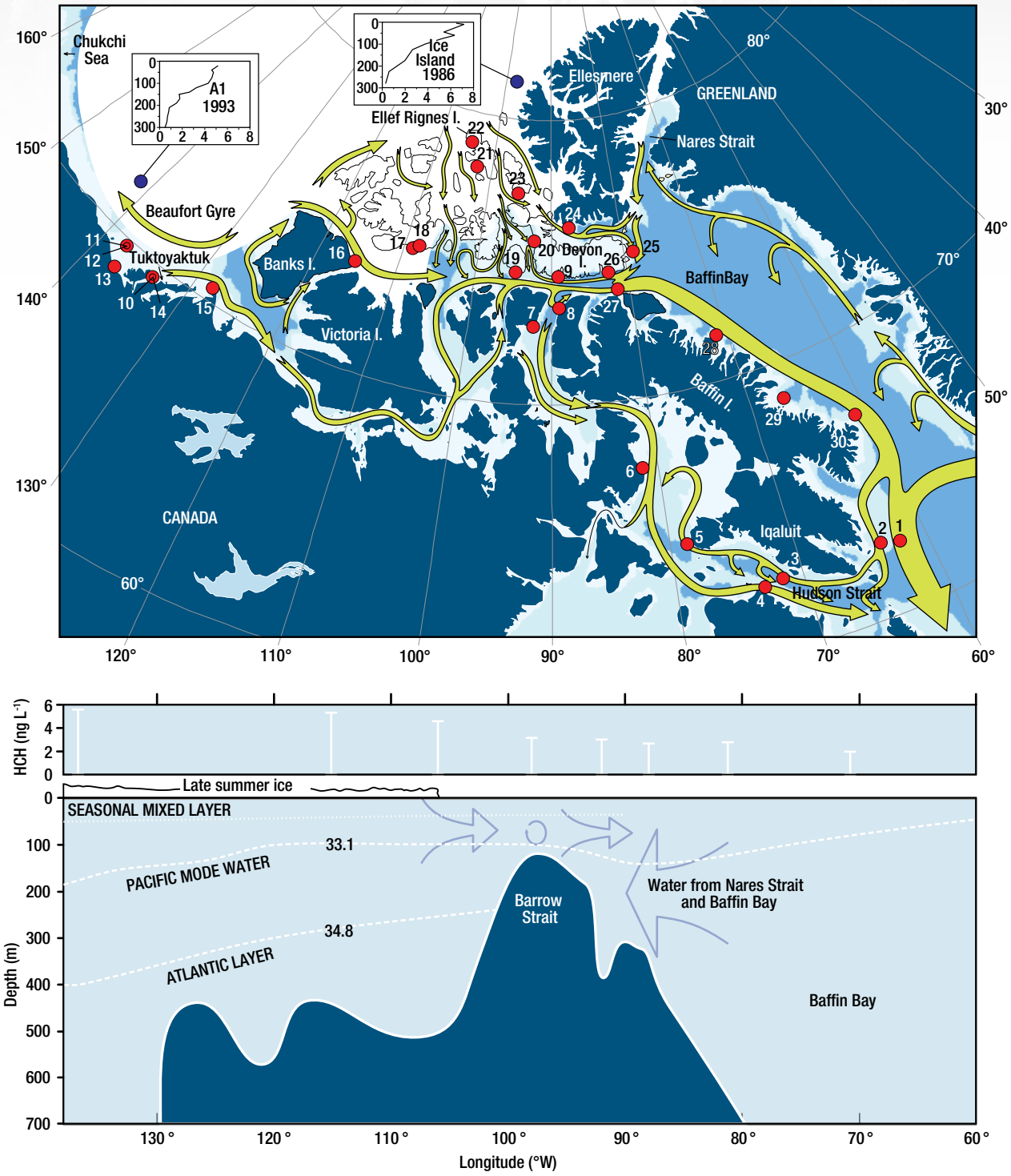


FIGURE 2.53

Map of the Canadian Archipelago and eastern Beaufort Sea. Top: TNW-99 sampling stations and surface water flow pathways. Insets show depth profiles of α-HCH (ng L^{-1}) at the Ice Island in 1986 (Hargrave et al. 1988, Macdonald et al. 2000) and the southern Beaufort Sea in 1993 (Macdonald et al. 2000). Bottom: topography and vertical distribution of water masses. Representative concentrations of ΣHCHs are shown as bars at the top.

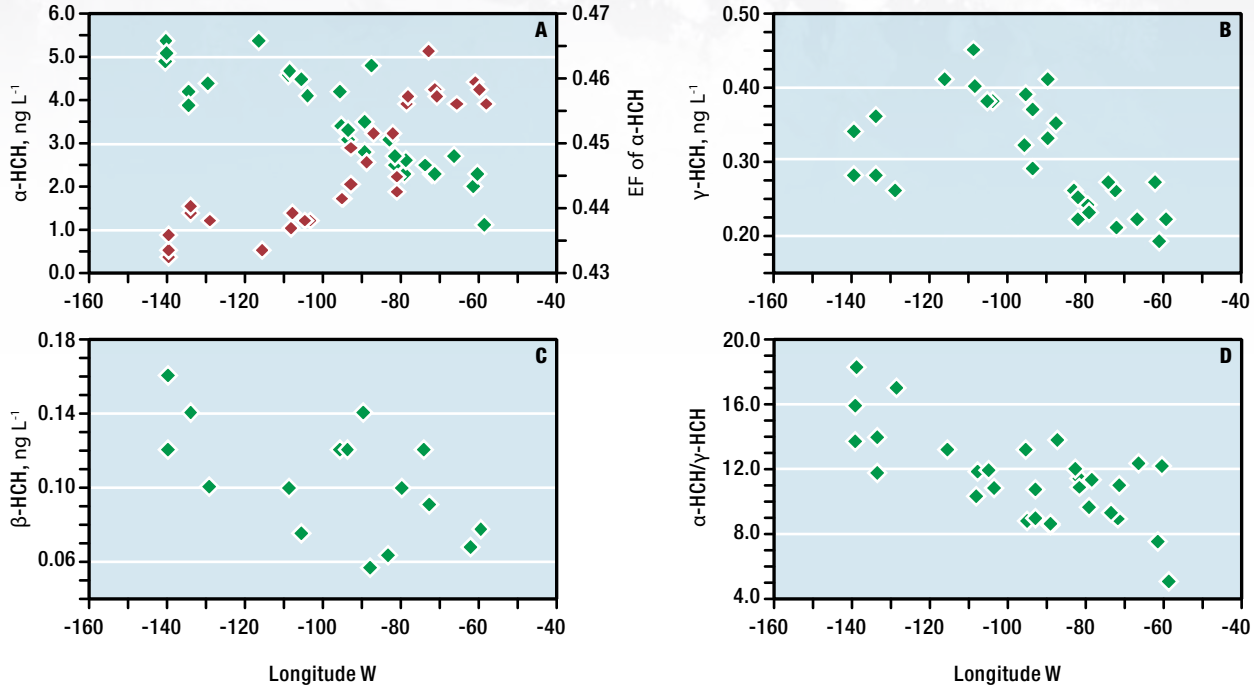


FIGURE 2.54

Trends of HCHs in surface water with longitude across the Archipelago. Panels A, B and C, green diamonds: concentrations (ng L^{-1}) of α-HCH, β-HCH and γ-HCH, respectively. Panel A, red diamonds and right scale: enantiomer fractions of α-HCH. Panel D, green diamonds: ratios of α-HCH/γ-HCH.

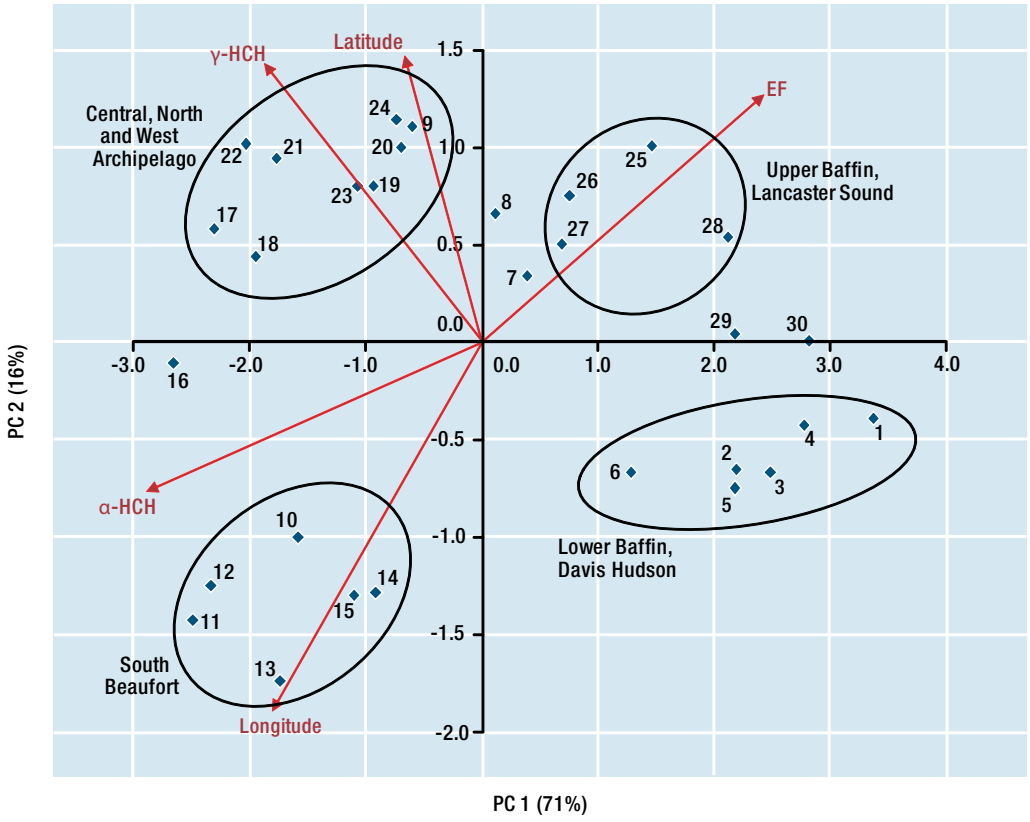


FIGURE 2.55

Principal component analysis with variables α-HCH, γ-HCH, EF of α-HCH, latitude and longitude. PCs 1 and 2 account for 71% and 16% of the variance. Red arrows show the direction of influence of the vector variables.

0.075–0.12 ng L^{-1}, and 0.29–0.41 ng L^{-1}, respectively. Two investigations of HCHs in Barrow Strait during 1992–1993 found average α-HCH concentrations of 3.6–4.7 ng L^{-1} and γ-HCH concentrations of 0.44–0.52 ng L^{-1} (Falconer et al. 1995, Hargrave et al. 1997). Falconer et al. (1995) found no vertical gradients of either HCH isomer between 2–100 m and an average EF (0.481) higher than that measured during TNW-99. Hargrave et al. (1997) noted that surface water concentrations varied seasonally, with higher values in winter and early spring and lower ones in late summer.

Although no significant differences were seen between average concentrations at 1 m and 50 m, those at 1 m tended to be slightly higher during the periods of ice cover and equal to or slightly lower than the 50 m concentrations recorded during the summer. Lower concentrations of α-HCH (1.1–3.1 ng L^{-1}), β-HCH (0.056–0.12 ng L^{-1}) and γ-HCH (0.19–0.27 ng L^{-1}) and EFs of α-HCH (0.441–0.463) in the eastern Archipelago can be compared with 1.1 ng L^{-1}, 0.07 ng L^{-1} and 0.2 ng L^{-1} and EF = 0.450 reported for the Northwater Polynya (Northern Baffin Bay, 76–79°N, centred on 74°W) in 1998 (Hoekstra et al. 2003). Measurements in Hudson Bay during 2007 were lower, averaging 0.63 ng L^{-1} α-HCH and 0.18 ng L^{-1} γ-HCH, and the EF of α-HCH was 0.447 (Wong et al. 2011).

Concentrations of HCHs in surface waters surrounding the Archipelago are summarized in Annex Table A2-7 and in Bidleman et al. (2007) and follow the order: Beaufort Sea > northern Canada Basin from 80°-90°N and Lincoln Sea between Ellesmere Island and Greenland > East Greenland Current and North Atlantic between 42.85° to 42.92°N and 42.33° to 56.50°W. Average EFs of α-HCH in the Northern Canada Basin in 1994 were 0.470 ± 0.009, while those in the North Atlantic in 1998 from 36 to 53°W were 0.466 ± 0.007.

Depth profiles were not taken during TNW-99, but were obtained at the Ice Island in 1986 (Hargrave et al. 1988), in the southern Beaufort Sea in 1992–93 (Carmack et al. 1997, Jantunen and Bidleman 1995) and across the arctic basins in 1994 (Carmack et al. 1997, Jantunen and Bidleman 1996, Macdonald et al. 2000). Profiles (shown for α-HCH, insets in Figure 2.53) show fairly constant or weakly decreasing concentrations in the upper 100 m and steeper gradients between 100–300 m. Below is a description of water and HCH transport pathways through the Archipelago and discussion of processes that may lead to the changes in concentrations and EFs en route.

2.3.5.5.3. Water pathways

Annually, 1.32 x 10^5 km^3 of water exits the Arctic Ocean, 24% through the Archipelago, 72% via the East Greenland Current and 4% by ice export (Li et al. 2004). The many water pathways through the Archipelago vary in magnitude and include complex internal circulations because the channels are wide (Melling 2000). Their mean surface currents have been outlined very simply in Figure 2.53. Total flow through Canadian Archipelago channels has been estimated between 0.7–1.7 Sv (Melling 2000). Surface water from the Beaufort Sea enters the Archipelago on the west and northwest sides. The surface mean flow passes through the Archipelago, likely taking several years to make the transit, undergoing mixing and recirculation, and exits to the east into Baffin Bay and Davis Strait, mainly through Hudson Strait (stations 3 and 4), Lancaster Sound (stations 26 and 27) and Jones Sound (station 24). Drainage also occurs from the north via the Nares Strait between Ellesmere Island and Greenland, entering the Northwater Polynya.

Water within the Archipelago is strongly stratified, showing a seasonally mixed surface layer which varies from 15–50 m depth (Hargrave et al. 1997) separated from deeper water by a halocline. To the west of the central Archipelago sills, arctic waters of predominantly Pacific origin occupy the upper ocean (approximately 0–225 m) with Atlantic Layer water dominating below (Figure 2.53) (Macdonald et al. 1989). See also discussion in section 2.3.5.2. The Pacific mode water, centred at a salinity of 33.1, is produced from Bering Sea inflow to the Chukchi Sea through cooling and ice formation whereas the Atlantic Layer, which is identified by a temperature maximum at salinity of approximately 34.8, has transported cyclonically around the Arctic with a delay of 15 or more years after passing through Fram Strait (Gobeil et al. 2001). The bottom topography features a shallow sill (at approximately 125 m) at Barrow Strait (Figure 2.53), which effectively prevents deeper Atlantic Layer water from penetrating further east. Surface water from North Atlantic and arctic (East Greenland Current) sources enters through the east side of Davis Strait and branches; some flowing northward into Baffin Bay and some recirculating and exiting on the west side of Davis Strait (Figure 2.53). Flow coming along the west side of Nares Strait (sill depth of approximately 200 m) branches at the major exits to the Archipelago (Jones and Lancaster Sounds) with a mixture of this water and Baffin Bay water penetrating westward along the north side of these channels (Figure 2.53).

2.3.5.5.4. HCH pathways

Drainage of the Arctic Ocean via the Archipelago and East Greenland Current accounts for 24% and 72% of total water export, respectively. Because of the higher α-HCH concentrations in surface water, which dominates the Archipelago throughflow, loss from this outflow accounts for 16% and the East Greenland Current accounts for 12% of the 566 tonnes removed annually from the upper 200 m of the Arctic Ocean. The remainder is lost by microbial breakdown (47%), transfer to deeper water (10%), hydrolysis (8%), volatilization (5%) and ice export (2%) (Li et al. 2004). The estimated removal budget is similar for β-HCH (Section 2.3.5.4).

A satisfactory explanation of the trends shown in Figure 2.54 should take into account the attenuation in HCH concentrations and the rise in EFs of α-HCH from west to east. Consideration of hydrolysis (Harner et al., 1999, Harner et al., 2000, Ngabe et al., 1993), particle sinking (Hargrave et al. 1997, Harner et al. 1999b) and volatilization (Hargrave et al. 1997, Jantunen et al. 2008a) indicate that these are too slow to account for the observed decrease in HCH concentrations. Also, of the above processes, only microbial degradation has the capability of altering EFs. Preferential degradation of (–)α-HCH has been reported in surface water of the Bering and Chukchi seas (Jantunen and Bidleman 1996, Jantunen and Bidleman 1998), but degradation over the remainder of the NAAO (Falconer et al. 1995, Jantunen and Bidleman 1996, Moisey et al. 2001) and EAO (Harner et al. 1999b, Harner et al. 2000b) favours the (+) enantiomer. Thus, further degradation of (+) α-HCH as water moves through the Archipelago should lower, not raise, the EFs. The west-to-east trends in Figure 2.54 are explained by the variation in the Beaufort Sea end member, and dilution of Beaufort water with other end members having lower HCH concentrations and higher EFs.

The surface water properties in the shelf area of the southern Beaufort Sea are strongly influenced by seasonality in ice cover and fresh water input from the Mackenzie River (Carmack and Macdonald 2002). It would thus not be surprising if surface water HCH concentrations and EFs vary seasonally and annually, although such variation has not been well documented. The concentration of α-HCH in the Mackenzie River was 0.1–1.3 ng L^{-1} in the early 1990s (Li et al. 2004) such that Beaufort Sea surface water, as represented by stations 11 and 12 (4.9–5.4 ng L^{-1}), would exhibit the dilution observed at the nearshore stations off Tuktoyaktuk and Cape Bathurst (stations 10, 14, 15; 3.9–4.4 ng L^{-1}) if mixed with 15–25% river water. Indeed, such a plume was observed by satellite imagery during August 1999 (Macdonald, R., Fisheries and Oceans Canada, personal communication). During the 1997–98 SHEBA experiment in the Beaufort Sea, the concentrations of α- and γ-HCHs in the upper water column decreased by 4–7 fold as the ship drifted across the southern Beaufort to the Chukchi Cap, where high-concentration interior water mixed with water advected from the Bering Sea (Macdonald et al. 1999). EFs in surface water of the southern Beaufort Sea averaged 0.436 ± 0.003 during TNW-99, but have varied in the past. In 1993, EFs at Station A1 (inset in Figure 2.53 shows the location and depth profile of α-HCH concentrations) were 0.489 in the upper 50 m and decreased to 0.353 over the next 100 m (personal communications with Macdonald, R., Fisheries and Oceans Canada, and Jantunen, L., Environment Canada). A pulse of Beaufort surface

Photo: Martina Koblizkova

water, containing lower-than-usual HCH concentrations and higher EFs may have entered the Archipelago in earlier years and worked its way east to appear in the eastern Archipelago in 1999. Indeed, the EF at Barrow Strait was 0.489 in 1992 (Falconer et al. 1995). Such a scenario could account for the Figure 2.54 trends, but this cannot be verified.

Advection of water from Baffin Bay westward into the Archipelago is depicted in Figure 2.53. Water in the currents along the western margin of Baffin Bay derives partly from the Bering Sea via the Archipelago outflow through Nares Strait and Jones Sound, and partly from the North Atlantic and Arctic Ocean outflow at Fram Strait, which penetrates past Davis Strait via the West Greenland Current and recirculate in Baffin Bay. Nutrient tracer studies indicate that water of Pacific origin dominates in the upper bay, while a mix of Atlantic and Pacific waters is found in the lower bay and Davis Strait (Jones et al. 2003, Tremblay et al. 2002). Spatial trends of α-HCH and γ-HCH in the eastern Archipelago are considered to be the mix of three end members: (1) Nares Strait, (2) Beaufort Sea, west and north Archipelago, and (3) North Atlantic water entering through Davis Strait. With the view that properties of these three end members are likely to be variable, a combination of properties was sought which would best predict observed α-HCH and γ-HCH concentrations and EFs in the eastern Archipelago (stations 1–9, 19, 20, 25–30). Concentrations and EFs for three end members were selected according to considerations detailed in Bidleman et al. (2007):

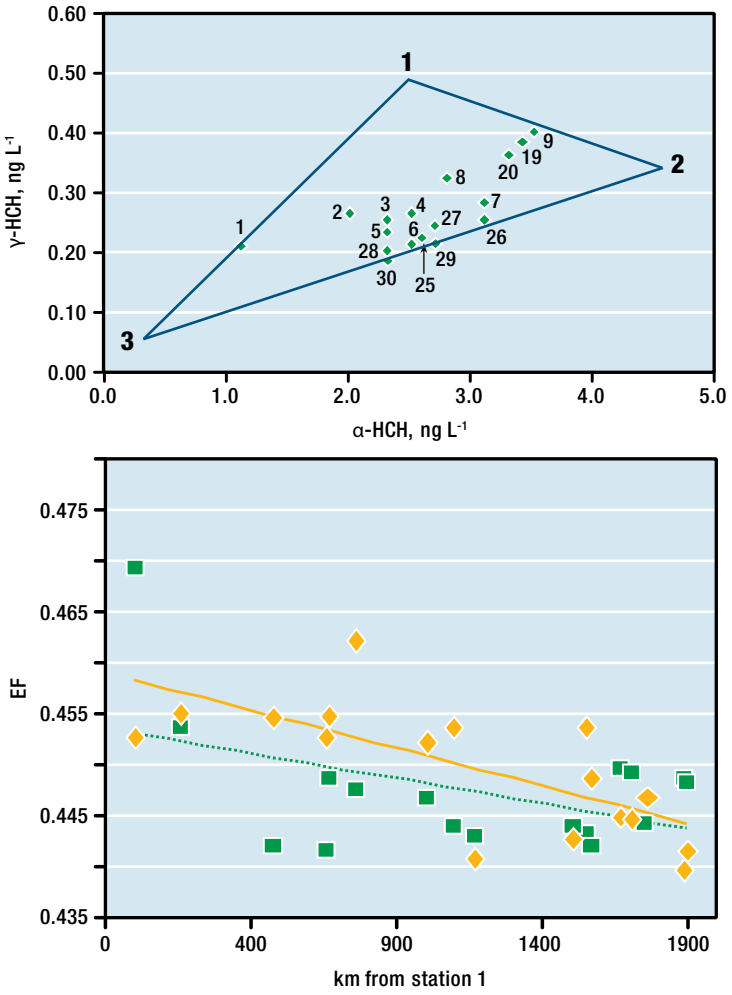


FIGURE 2.56

Measured α- and γ-HCH concentrations and measured and predicted EFs of α-HCH in the eastern Archipelago. Top: measured concentrations of α-HCH and γ-HCH in the eastern Archipelago. Small numbers indicate stations (Figure 2.53) circumscribed by conservative mixing lines of three end members (large bold numbers): 1) Nares Strait water, 2) Beaufort Sea – west and north Archipelago water, and 3) North Atlantic water entering through Davis Strait. Concentrations and α-HCH EFs in these end members are defined in the text and in Table S4 of Bidleman et al. (2007). Bottom: Measured (orange diamonds, $r^2 = 0.49$, $p = 0.0016$) and predicted (green squares, $r^2 = 0.20$, $p = 0.069$) EFs of α-HCH in the eastern Archipelago related to distance from station 1.

for end member (1) α-HCH = 2.4 ng L^{-1}, γ-HCH = 0.50 ng L^{-1}, EF = 0.47, end member (2) α-HCH = 4.6 ng L^{-1}, γ-HCH = 0.35 ng L^{-1}, EF = 0.44 and end member (3) α-HCH = 0.2 ng L^{-1}, γ-HCH = 0.03 ng L^{-1} , EF = 0.47. The upper panel of Figure 2.56 shows that the measured concentrations in the eastern Archipelago can be circumscribed by a triangle which represents conservative mixing of these three end members.

Volume fractions at a station due to mixing of waters from three end members can be estimated using two chemical tracers (Dorsch and Bidleman 1982, Zimmermann and Rommets 1974). Using this approach and the tracers α-HCH and γ-HCH, the volume fractions of water delivered by the three end members were obtained. These volume fractions were multiplied by end member concentrations and EFs to obtain the predicted (+)-α-HCH contributions of the end members and the EFs in the water sampled at each station. The calculations are detailed in the main paper and the supporting information of Bidleman et al. (2007). The three end member model accounts for the rise in EFs in the eastern Archipelago and the predicted EFs range (0.442–0.470) is within the range of the end member EFs and those measured at the eastern stations. However, the predicted EFs are relatively constant over most of the eastern Archipelago with higher values at the two Davis Strait stations, whereas measured EFs show a linearly decreasing trend ($p = 0.0016$) with distance from station 1 (bottom panel of Figure 2.56).

Over a decade ago, Macdonald et al. (1997) suggested that the upper ocean in the Canada Basin was likely to become the last refuge for global contamination by α-HCH. The set of measurements presented here suggest that, in fact, the loading of the Canada Basin with HCH sets the stage for a continued release of the chemical into the Archipelago where it undergoes mixing with Northern Canada Basin and Atlantic water during a relatively unimpeded passage back into the temperate western Atlantic Ocean. As noted above, HCH concentrations in the southern Beaufort are subject to variations that occur spatially and perhaps seasonally, and this may be true for the other end members. Observations from TNW-99 are only a snapshot in time, but exemplify the use of HCH tracers to follow spatial trends and mixing in the Archipelago. Such knowledge provides a basis for interpreting similar trends observed in HCH concentrations in the biota of the Archipelago (Addison et al. 2009, Li and Macdonald 2005, Verreault et al. 2005). See Chapter 4, section 4.1.5 on spatial trends in marine biota.

2.3.6. Chemical tracers

Contributors: Terry Bidleman and Perihan Kurt-Karakus

2.3.6.1. Chiral chemicals as tracers of sources and air surface exchange

A chiral chemical contains an asymmetric center and thus can occur in two non-superimposable mirror-image stereoisomers (isomers that differ only in the three-dimensional orientations of their atoms in space). These stereoisomers are called enantiomers (or atropisomers, for rotational stereoisomers such as PCBs). Chiral chemicals are usually produced as racemates (equimolar mixture of a pair of enantiomers). Once released into the environment, microorganisms will preferentially metabolize one of the two stereoisomers (stereoselective metabolism) leading to accumulation of nonracemic residues in soil and water. For enantiomers 1 and 2 of a specific chiral compound, data are often expressed as enantiomer fraction, $EF = E_1/(E_1+E_2)$, where E_1 and E_2 may refer to the order of chromatographic peak elutions, R and S absolute configurations, or (+) and (–) optical signs.

Chiral tracers provide a means of distinguishing emissions of microbially processed and unprocessed residues. The latter may include currently used chemicals or older residues which have been protected from microbial attack (Bidleman and Falconer 1999, Eitzer et al. 2003, Garrison 2006, Hühnerfuss and Shah 2009).

2.3.6.1.1. Chiral tracers of soil-air exchange

Field-scale studies have shown that when nonracemic OCP residues volatilize from agricultural soil, the EFs in overlying air are also nonracemic (Bidleman 1999, Bidleman and Falconer 1999, Bidleman and Leone 2004a, Eitzer et al. 2003, Leone et al. 2001, Meijer et al. 2003b).

Chlordane was formerly used in the US and Canada for both agriculture and structural termite control. Chlordanes are enantioselectively degraded in agricultural soils, but are racemic in residential air (Leone et al. 2000) and soil near house foundations (Eitzer et al. 2001). Residues of chlordanes in ambient air tend to be closer to racemic in some cities, due to evaporation of racemic termiticides, than in rural locations (Gouin et al. 2007, Shen and Wania 2005) although this was not always the case (Venier and Hites 2007). Residues of *o,p'*-DDT in soil (Wong et al. 2010) and ambient air (Wong et al. 2009a) were closer to racemic in southern Mexico, where DDT had been more recently used, than in the northern part of the country, and *o,p'*-DDD was nonracemic in air at sites in the southern US. (Venier and Hites 2007).

Degradation of PCB atropisomers in soil is often stereoselective (Jamshidi et al. 2007, Kobližková et al. 2008, Lehmler et al. 2010, Robson and Harrad 2004, Wong et al. 2009b) and chiral tracers have been exploited for source apportionment of PCBs in urban air. Chiral PCBs 95, 136 and 149 were nonracemic in soils, but racemic or nearly so in indoor air and ambient air of UK cities. This suggested that the dominant source of PCBs to ambient air in those cities was primary emissions from ventilation of indoor air, not secondary emissions from soils as previously thought (Jamshidi et al. 2007, Robson and Harrad 2004).

Enantioselective analysis is useful for distinguishing primary from secondary emissions of chiral chemicals (Bidleman and Falconer 1999, Hühnerfuss and Shah 2009) and may be helpful in tracing 'grasshopping' over large spatial scales. Chlordanes were nonracemic in ambient air sampled in 1998–2001 from two arctic locations and a rural site in southern Sweden, but racemic in atmospheric deposition collected in background locations during the early 1970s (Bidleman et al. 2002, Bidleman et al. 2004). Residues of *trans*-chlordane in laminated sediments from a lake in the Canadian Arctic were close to racemic in the 1940s and 1950s, and became increasingly less racemic from the 1960s to 1990s (Bidleman et al. 2004, Stern et al. 2005). Similar trends were found for chlordanes in lake and river sediments in the US. (Ulrich et al. 2009). These findings suggest that primary emissions of racemic chlordanes dominated in earlier decades, with secondary emissions of nonracemic chlordanes from soils playing a larger role in recent years (Bidleman and Leone 2004b). Chlordanes arriving via trans-Pacific transport at mountainous sites in the western US were racemic in most cases, with occasional events of nonracemic chlordane transport. Racemic chlordanes were also found in air samples collected at low elevation in Okinawa, Japan. The racemic chlordane signatures and *trans*-/*cis*-chlordane (TC/CC) ratios, similar to the composition of technical chlordane, suggest that Asian air masses are influenced by relatively fresh sources of chlordane and/or that limited biotransformation of chlordane has occurred (Genualdi et al. 2009b).

EFs of chiral chemicals in background soils vary greatly due to differences in microbial populations and other soil properties (Kobližková et al. 2008, Kurt-Karakus et al. 2005, Kurt-Karakus et al. 2007, Shen et al. 2009). Simulated climate warming experiments and studies in forested vs. deforested soils showed switching in the enantiomer degradation preference of chiral pesticides (Lewis et al. 1998). Monitoring stereoisomer proportions of chiral chemicals in air may reveal the integrated influence of long-term microbial diagenesis in soil (Bidleman et al. 2012).

2.3.6.1.2. Chiral tracers of air-water gas exchange

Similar to soil-air exchange processes, chiral compounds allow additional information to be derived on compound origin and air-water gas exchange. Apportionment of an airborne chiral chemical between two sources categories can be done knowing the enantiomer fraction of the chemical in source A (EF_A), source B (EF_B) and in the air sample, resulting from mixing of these sources (EF_M) (Harner et al. 2000b); i.e.,

$$\text{percentage from source A} = \left[\frac{EF_M - EF_B}{EF_A - EF_B} \times 100\%\right] \quad \text{Eq. 17}$$

When the chemical in background air (source B) is close to racemic, EF_B is approximately 0.5. This situation might occur if source B is from current use of a racemic chemical or from air transport of an aged residue that has not been subjected to microbial degradation.

The enantiomers of α-HCH have been the most used as gas exchange tracers to provide evidence of water-to-air exchange. Enantioselective degradation by microbial processes in oceans and lakes produces nonracemic α-HCH (Harner et al. 1999a, Helm et al. 2000, Law et al. 2001). Volatilization releases nonracemic α-HCH into the air boundary layer, where it mixes with the racemic α-HCH in background air.

Genualdi et al. (2009b) sampled air in the western US at mountain sites above and below the marine boundary layer. Nonracemic α-HCH was found in regional air masses at the low elevation site, possibly due to volatilization from the Pacific Ocean and regional soils. The α-HCH was closer to racemic during transport events from Asia; EFs in air at Okinawa and in Chinese and South Korean soils were racemic. EFs were consistently racemic at the high elevation site. Nonracemic α-HCH was generally found in air sampled from shipboard on a transect from the North Pacific to the Beaufort Sea (Ding et al. 2007). Lohmann et al. (2009) found nonracemic α-HCH in air and surface water of the northern North Atlantic and eastern Arctic Ocean. EFs of α-HCH in air and surface water declined in parallel along a transect in the South Atlantic Ocean between 35–70°S (Jantunen et al. 2004).

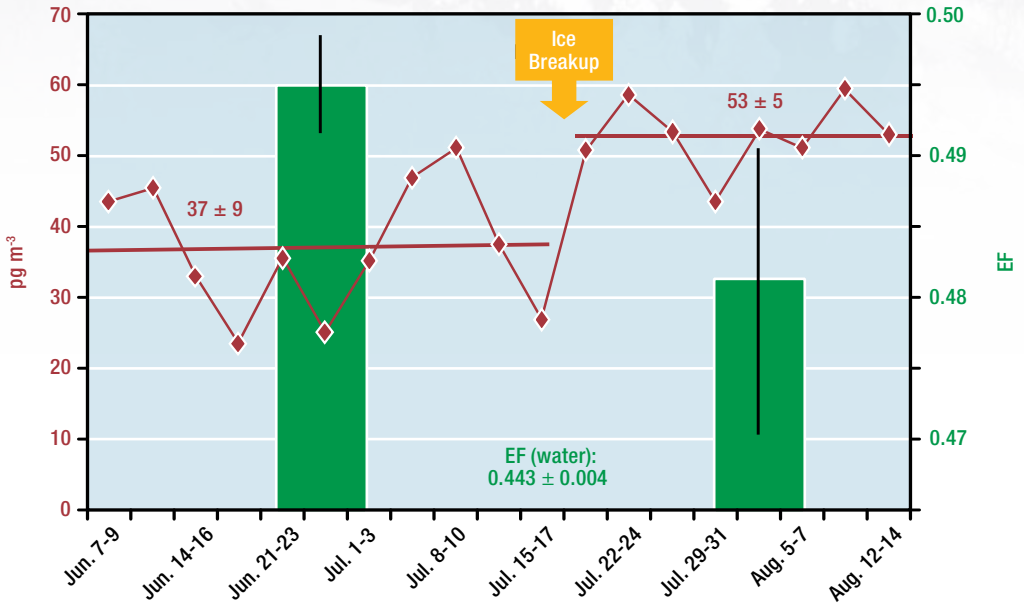


FIGURE 2.57

Increase in α-HCH concentrations in air in the Canadian Archipelago at Resolute Bay during and following ice breakup (red diamonds). The rise in air concentrations was accompanied by a decrease in EFs in air from the near-racemic value of 0.496 ± 0.003 to 0.482 ± 0.010, in response to volatilization of nonracemic α-HCH from seawater. Green bars are average EFs for the before and after ice breakup periods (Jantunen et al. 2008a).

Shen et al. (2004) deployed passive air samplers from Central America to the Canadian Arctic and reported concentrations and EFs of several OCPs. EFs of α-HCH were close to racemic at inland sites. Greatest deviations from racemic occurred on the shore of Lake Superior (see above), in the Canadian Archipelago and along the eastern and western seaboards of Canada. Nonracemic EFs in air at coastal sites in eastern Canada were associated with volatilization of nonracemic α-HCH from arctic seawater transported southward by the Labrador Current.

Significant correlations between nonracemic EFs in air and water were found on transects of open water, or where ice had receded, in the Arctic Ocean and regional seas. The α-HCH in air was close to racemic when traversing ice-covered regions and not correlated to EFs in water (Jantunen and Bidleman 1996, Jantunen et al. 2008b, Wong et al. 2011). The α-HCH in air of the central and western Canadian Archipelago was racemic during periods of ice cover and became abruptly nonracemic at the onset of ice breakup. Reduction of EFs in air was accompanied by a rise in α-HCH concentrations (Figure 2.57) (Jantunen et al. 2008b, Wong et al. 2011). Source apportionment analysis, as given above, estimated the increase in the central Archipelago at 32%, compared to 43% from concentration measurements (Jantunen et al. 2008b).

2.3.6.2. Isomer and parent/metabolite tracers of sources and pathways

Ratios of isomers in multicomponent OCPs (e.g., technical HCH, DDT and chlordane) and breakdown products such as DDE can be useful indicators of sources and exchange pathways. Whereas physicochemical properties are identical for enantiomers, they usually differ for isomers and parent/metabolite compounds. For example, the order of liquid-phase vapour pressures for DDT compounds is: *p,p'*-DDE > *o,p'*-DDT > *p,p'*-DDT, and for chlordane compounds is: *trans*-chlordane (TC) > *cis*-chlordane (CC) > *trans*-nonachlor (TN) (Hinckley et al. 1990, Shen and Wania 2005). Henry's law constants for the HCHs decrease in this order: α-HCH > γ-HCH > β-HCH (Xiao et al. 2004). Such differences result in fractionation during air-surface exchange that must be considered when using compound ratios for source apportionment.

2.3.6.2.1. Hexachlorocyclohexanes

The most frequently quoted composition of technical HCH is: 60–70% α-HCH, 5–12% β-HCH, 10–15% γ-HCH and other isomers (Iwata et al. 1993b). Breivik et al. (1999) report a wider range for these three isomers: 55–80% α-HCH, 5–14% β-HCH, 8–15% γ-HCH. From the Iwata composition, ratios of α-HCH/β-HCH in the range of 4–7 would be

expected to result from air transport of the unfractionated mixture, and this range is often used to discriminate technical HCH vs. lindane (pure γ-HCH). Higher ratios in air might result from preferential volatilization of α-HCH (Xiao et al. 2004), its longer atmospheric lifetime from slower OH radical reaction (Brubaker and Hites 1998), to selective removal of γ-HCH by rainfall scavenging and air-to-water exchange (Iwata et al. 1993b, Su et al. 2006). Lower ratios imply emissions of lindane superimposed on a technical HCH background.

Historically, highest usage of technical HCH occurred in Asian countries (Li and Macdonald 2005), but this changed with the switch to lindane in China (1983) and the former Soviet Union (1990) (Li and Macdonald 2005) and in India (1997) (Primbs et al. 2008c, Zhang et al. 2008a). Recently measured α-HCH/γ-HCH ratios in Asian air were 1.0–2.9 in China and Korea (Primbs et al. 2008b). The reported ratio was 0.3–3.8 on the Tibetan Plateau (Li et al. 2008, Wang et al. 2010c), 4.5 (mean) in the Wolong Nature Reserve (WNR) of Sichuan Province, China (Liu et al. 2010b), 0.48 (mean) at Waliguan Baseline Observatory (WBO)—a high altitude Global Atmospheric Watch (GAW) site—(Cheng et al. 2007), and 0.11–4.00 at multiple stations across India (Zhang et al. 2008a). Ratios of α-HCH/γ-HCH across Europe were generally ≤ 1 (Jaward et al. 2004c).

HCHs in air were reported between 2000–2003 at six arctic stations: in Canada, Alert (ALT), Kinngait (KNG) and Little Fox Lake (LFL), in the US at Point Barrow (PTB) Alaska, in Russia at Valkarkai (VKK) and in the Norwegian Arctic Ny-Ålesund on Zeppelin Mountain (ZPN) (Su et al. 2006). Median ratios of α-HCH/γ-HCH were about the same or higher than the range for technical HCH at KNG, LFL, VKK and PTB (7–13) and lower at ALT and ZPN (3–4), which may be more influenced by lindane transport. On an expedition in the northern North Atlantic and Arctic Ocean, ratios of α-HCH/γ-HCH varied from 0.2–8.3, with a mean of 2.8 (Lohmann et al. 2009). Ratios α-HCH/γ-HCH in air along a transect from China to the Beaufort Sea were compared between 2003 and 2008 (Wu et al. 2010). In 2008, ratios ranged from 1.3–4.8 with an average of 2.5 (Wu et al. 2010), and were about half those values in 2003 (Ding et al. 2007). Continued use of lindane in source regions after phase out of technical HCH was offered as an explanation. In both studies, the ratio showed a statistically significant increase from low to high latitudes, attributed to selective removal of γ-HCH by precipitation washout enroute and volatilization of α-HCH from arctic waters (Wu et al. 2010).

A twelve-year record of weekly atmospheric α- and γ-HCH concentrations at Ny-Ålesund (1994–2005) and Alert (1993–2004) stations was analysed by Becker et al. (2008) using digital harmonic analysis (DHR). Concentrations of both isomers declined significantly at both stations, and there appeared to be little evidence of a lag between the banning of lindane in Europe and a decline in concentrations at either station. Annual mean ratios of α-HCH/γ-HCH varied from 3–7 at Ny-Ålesund and 3–11 at Alert, and except for 2001, were significantly lower each year at Ny-Ålesund. This may reflect the use of lindane in Europe during those years and the influence of Eurasian sources at Ny-Ålesund. Concentrations of γ-HCH displayed a springtime maximum, noted in other studies (Hung et al. 2005). Seasonality of α-HCH was shown in elevated concentrations in summer with lower levels in winter, and most apparent after 2000. An influence of Arctic Oscillation (AO) fluctuations was seen on α-HCH at Ny-Ålesund but not at Alert, and not for γ-HCH at either site.

2.3.6.2.2. DDT compounds

The "typical" composition of technical DDT according to the World Health Organization (WHO 1989) is 77% *p,p'*-DDT, 15% *o,p'*-DDT, 4% *p,p'*-DDE and 0.3% *p,p'*-DDD. However, DDT has been manufactured in many countries and the composition of these mixtures is generally not known. Spencer and Cliath (1972) reported 74.6% *p,p'*-DDT, 21.1% *o,p'*-DDT, 0.8% *p,p'*-DDE and 0.07% *o,p'*-DDE in US produced technical DDT. When emission from soil is the main source of DDTs in air, proportions of *p,p'*-DDT, *o,p'*-DDT and metabolite *p,p'*-DDE in air can be predicted from the residue composition in soils and relative volatilities of the chemicals. Higher volatility leads to preferential emission of *o,p'*-DDT and *p,p'*-DDE over *p,p'*-DDT from soils (Kurt-Karakus et al. 2008, Kurt-Karakus et al. 2006). This information has been applied to interpret soil-air fractionation of DDT compounds in Mexico (Wong et al. 2010) and in Chinese cities (Liu et al. 2009).

DDT is metabolized to DDE, DDD and other breakdown products. Ratios of *p,p'*-DDT/*p,p'*-DDE are often used as indicators of "fresh" (> 1) vs. "aged" (< 1) sources of DDT (Pozo et al. 2009), but these limits are not well defined. Kurt-Karakus et al. (2006, 2008) predicted the ratio of *p,p'*-DDT/*p,p'*-DDE in air over soil by multiplying *p,p'*-DDT/*p,p'*-DDE in soil by the ratio of liquid-phase vapour pressures, which is 0.147 at 20 °C (Hinckley et al. 1990). A survey of DDT residues in global agricultural and background soils found ratios of *p,p'*-DDT/*p,p'*-DDE ranging from approximately

0.6–4.0 (Kurt-Karakus et al. 2008), which when multiplied by 0.147 suggests 0.09–0.60 as an expected range of *p,p'*-DDT/*p,p'*-DDE from soil emissions. Characteristic proportions of DDT, DDE and DDD compounds in North American soils and predicted ratios in volatilized residues have been catalogued (Bidleman et al. 2013).

An examination of DDT signatures at six arctic air-monitoring stations (mentioned above) was carried out by Su et al. (2008). Concentrations of total DDT were considerably higher at VKK than at the other sites. Median ratios of *p,p'*-DDT/*p,p'*-DDE ranged from 0.2–0.5 at ALT, KNG, PTB and ZPN, suggesting transport of "aged" DDT. Ratios were higher (0.8–0.9) at VKK and LFL. Median ratios of *p,p'*-DDT/ *o,p'*-DDT at LFL and VKK (1.0–1.5) were close to that expected for vapour-phase technical DDT (1.2), and lower ratios were measured at ALT, ZPN and KNG (0.3–0.8).

Analysis of DDT compound concentrations and ratios from 1994–2006 at Ny-Ålesund station by DHR showed slow long-term decline of *p,p'*-DDT only. The seasonality of concentrations was characterized by a winter maximum and summer minimum, with *p,p'*-DDT dominating in summer and *p,p'*-DDE in winter (Becker et al. 2009). Occasional high ratios of *o,p'*-DDT/*p,p'*-DDT suggested the influence of DDT-contaminated dicofol. The fraction *p,p'*-DDT/(*p,p'*-DDT + *p,p'*-DDE) in air at Alert decreased from 1993-2001, then rose between 2002-2005, with no significant overall trend from 1993-2005. In contrast, this fraction in air decreased significantly from 1994-2006 at Ny-Ålesund, indicating greater transport of "aged" DDTs in recent years (Bidleman et al., 2013).

2.3.6.2.3. Chlordane compounds

Technical chlordane produced in the US contained *trans*-chlordane (TC) and *cis*-chlordane (CC) in a TC/CC ratio of 1.0–1.2 (Jantunen et al. 2000, Mattina et al. 1999). The slightly high vapour pressure of TC (Hinckley et al. 1990) raises the expected TC/CC ratio in equilibrium with technical chlordane to 1.4–1.7 in the temperature range 0–25 °C. Technical heptachlor is reported to contain 20–22% TC (WHO 2006), thus applications of heptachlor may act to increase TC/CC in the environment. Ratios of TC/CC in US cities and Toronto, Canada, where chlordane was applied as a termiticide, ranged from 1.1–1.9 (Gouin et al. 2007, Offenberg et al. 2004). TC/CC ratios characteristic of "aged" chlordane are generally lower and more variable in rural and background air, e.g., 0.72–0.95 in the Great Lakes region (Gouin et al. 2007, Sun et al. 2006) and often show a seasonal cycle of lower ratios in summer than winter (Gouin et al. 2007). TC/CC ratios across North America ranged from 0.1–1.6 and were strongly correlated with TC + CC concentrations. Higher ratios and concentrations were found near urban centers (Shen et al. 2005).

Median TC/CC ratios were 0.3–0.7 at arctic air monitoring stations, and *trans*-nonachlor (TN) was elevated over its proportion in the vapour phase of technical chlordane (Su et al. 2008). Although these signatures generally indicate "aged" chlordane, stations PTB and VKK showed the highest ratios. Moreover, events of TC/CC at approximately 1.5 were occasionally observed at PTB and were associated with elevated heptachlor concentrations. Thus, PTB may be under the influence of recent chlordane emissions. Trends of high TC/CC in winter-spring (mean 0.55) and low in summer-fall (mean 0.30) were observed at ALT, KNG, LFL and ZPN, although this trend was not observed at PTB. While TC was depleted during summer, oxidation products oxychlordane (OXY) and heptachlor epoxide (HEPX) were elevated (Su et al. 2008). The annual mean TC/CC ratio declined from 0.72 to 0.45 between 1984–1998 (Bidleman et al. 2002). It was speculated that TC is less stable photochemically than CC, resulting in its depletion during summer (Bidleman et al. 2002), although there is no experimental evidence of this. Summertime TC/CC ratios in air over the northern North Atlantic and Arctic Ocean ranged from 0.04–0.88 and averaged 0.24 (Lohmann et al. 2009).

Time trends of chlordanes in air at Ny-Ålesund station between 1994–2005 and including some earlier campaigns were examined using DHR (Becker et al. 2009). Both isomers declined slightly between 1994 and 2005, although there was a temporary increase in CC between 2000 and 2002. TC was marked by distinct winter maxima and summer minima and a weaker six-month pattern. In contrast, CC showed a stronger six-month (bi-modal) pattern, again with winter maxima, but with two more distinct "peaks" in spring (March–May) and September–November. Average annual TC/CC ratios ranged from 0.12–0.58 in summer and 0.59–0.88 in winter. These ranges exclude 2001, when remarkably high TC/CC ratios were observed, averaging 1.49 in summer and 1.03 in winter, although there was nothing unusual about their concentrations in that year. The year 2001 was marked by several events with high TC/CC ratios, possibly due to heptachlor use.

2.3.6.2.4. Toxaphene compounds

CHB congeners and enantiomers have been extensively studied in biota and sediments as indicators of selective metabolism (Kucklick and Helm 2006), but there have been few applications as source tracers. CHBs from

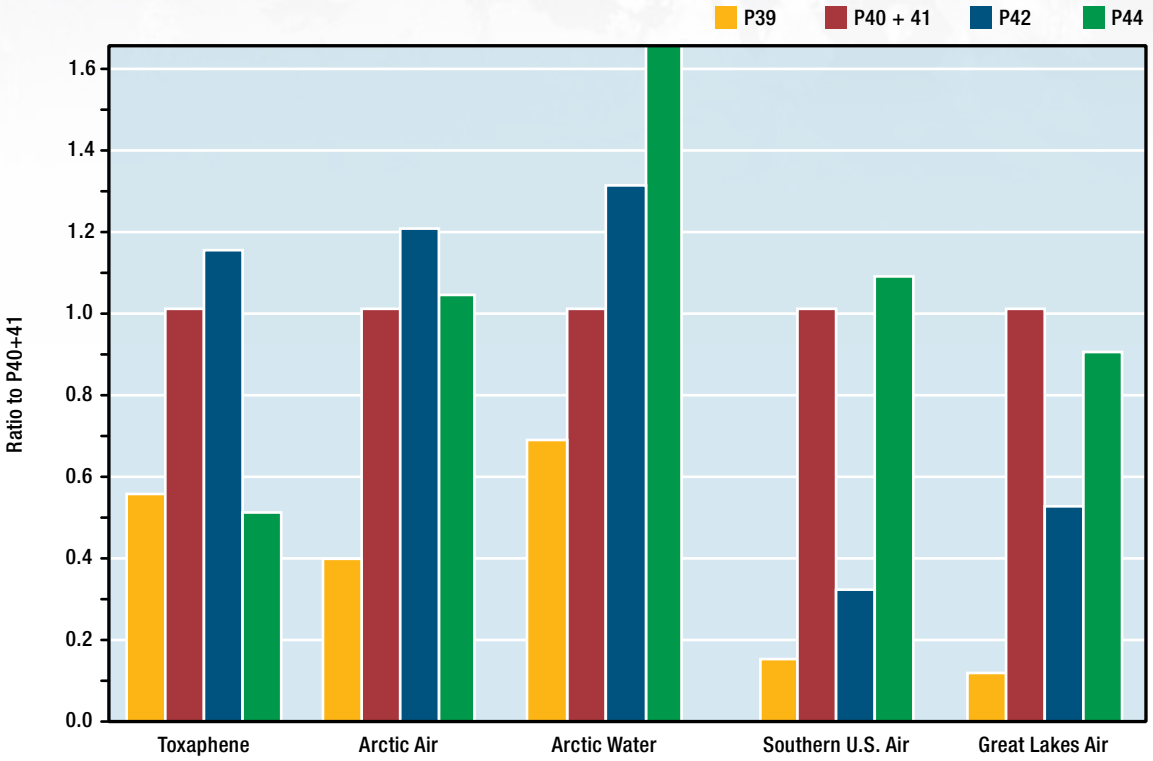


FIGURE 2.58

Profiles of octachlorobornanes B8-531 (P39), B8-1414 + B8-1945 (P40+41), B8-806 + B8-809 (P42) and B-2229 (P44) + a coeluting octachlorobornane in the toxaphene technical mixture and environmental samples. Note the depletion of labile compounds P39 and P42 relative to P40+41 in southern U.S. air and Great Lakes air, but no depletion in arctic air or water.

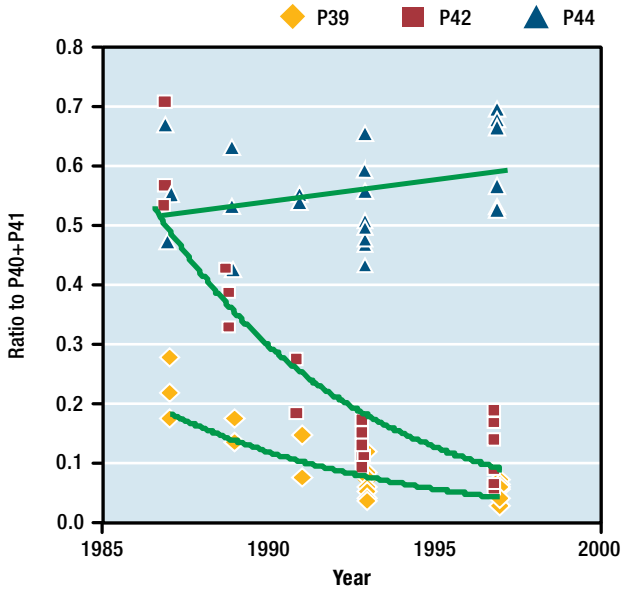


FIGURE 2.59

Ten-year time trend of P39, P42 and P44 ratios relative to P40+41 in Atlantic Ocean water. As primary emissions decrease, depletion of the labile compounds P39 and P42 is seen over time, whereas P44 undergoes gradual enrichment.

former toxaphene application are prominent residues in agricultural soils of the southern US (Bidleman and Leone 2004a, Bidleman and Leone 2004b, Harner et al. 1999a, Kannan et al. 2003) and Mexico (Wong et al. 2010). Toxaphene components span a wide range of volatilities, and soil/air fractionation is related to their vapour pressures (Bidleman and Leone 2004b, Wong et al. 2010). Profiles of octachlorobornanes in these soils, normalized to a chromatographic peak containing congeners B8-1414 + B8-1945 (Parlar compounds P40 and P41), show relative depletion of congeners B8-531 (P39) and B8-806 + B8-809 (P42) and enrichment in a peak containing B8-2229 (P44) plus an unidentified coeluting octachlorobornane (Bidleman and Leone 2004a, Bidleman and Leone 2004b, Wong et al. 2010). Air and water samples from the Great Lakes region show similar depletions and enrichment (Jantunen and Bidleman 2003, Muir et al. 2006). B8-531 and B8-806 + B8-809 are more labile congeners, lacking the alternating *endo-exo-endo-exo* substitution of chlorines around the six-membered ring which confers stability towards metabolism (Vetter and Scherer 1999).

Octachlorobornane congener distributions in arctic air and water samples, collected between 1993–1999, differ from those in the Great Lakes and in southern US air by showing less depletion of B8-531 and B8-806 + B8-809 relative to B8- 1414 + B9-1945 (Figure 2.58)(Jantunen 2010). The greater abundance of the labile congeners suggests "fresher" CHBs in the Arctic, but the source is unclear. A clue is provided by examination of congener profiles in Atlantic Ocean water between 1987–1997 (Jantunen 2010, Lakaschus 2010) (Figure 2.59). Relative proportions of B8-531 and B8-806 + B8-809 show a steady decline throughout the decade, whereas the proportions of B8-2228 + a coeluting octachlorobornane, increase. The profiles are consistent with continuing diagenesis of toxaphene in seawater following the US deregistration that occurred between 1982–1986 and other regional bans of toxaphene-like products. Viewed from this perspective, the fresher CHB signatures in arctic water may not reflect a recent source, but preservation of labile compounds in the cold environment, and similar profiles in arctic air might arise from water-to-air exchange.

2.3.6.2.5. Polychlorinated naphthalenes

The occurrence of PCNs in air and biota of polar regions has been reviewed (Bidleman et al. 2010) and this section on marker compounds of PCN sources is taken from that review.

Several approaches have been used to assess whether combustion processes contribute to PCN residues in environmental media. Meijer et al. (2001) found increasing proportions of combustion-related congeners relative to their homologue totals in archived UK soils. The lack of correlation of combustion congeners with other PCNs in air supports their use as indicators (Jaward et al. 2004b). Lee et al. (2007) calculated the fraction of combustion congeners in the Halowaxes (< 0.11) and compared this to observed fractions in air samples to estimate the influence of combustion sources. Similarly, Helm and Bidleman (2003) calculated the proportion of combustion contributions in air based on the enrichment of PCN indicator congeners over what was expected from evaporation alone.

Ratios or fractions of selected congeners have been used to indicate possible sources. Takasuga et al. (2004) found that the CNs 73/74 ratio was < 1 in summer but > 1 in winter for two air samples collected in urban Japan. The winter profile corresponded to the order of abundance in fly ash and flue gas and the enrichment of other combustion markers. However, CN 73/74 ratios vary in source samples, with values < 1 in Halowaxes (Järnberg et al. 1997, Noma et al. 2004), > 1 in combustion effluents (Abad et al. 1999, Jakobsson and Asplund 2000, Jansson et al. 2008, Takasuga et al. 2004), but mixed ratios in PCB mixtures. In eighteen commercial PCB mixtures examined by Yamashita et al. (2000), the CNs 73/74 ratio was > 1 in twelve, < 1 in four and approximately 1 in two. The ratio of CNs 73/74 was > 1 in Delor PCB products (Taniyasu et al. 2003).

While ratios can be useful, more diagnostic information about source contributions is obtained by examining relative proportions of many congeners using principal component analysis (PCA). Helm and Bidleman (2003) applied PCA to Toronto air samples and found a separation of loadings due to combustion CNs and non-ortho PCBs (which also occur in combustion effluents) and loadings due to CNs from evaporative sources. They concluded that evaporative PCN emissions dominated at both the downtown and suburban sites, but that combustion had a greater influence on the suburban site. Orlikowska et al. (2009) carried out a detailed examination of PCN homologue and congener profiles in Scots pine needles (*Pinus sylvestris L*) in Poland, collected in 2002. The ΣPCNs ranged from 70–1100 pg g^{-1} wet weight among the sites. Similarities, but also variations, in tri- to octa-CNs homologue and congener profiles were found. Tri- and tetra-CNs were major contributors at most locations, but hepta- and octa-CNs were also prominent and in many cases outweighed penta- and hexa-CNs. PCA was able to

sort the congener profiles into factors related to molecular weight and specific substitution patterns, which could be related to source categories such as industrial emissions, evaporative losses from dumped products containing PCNs, technical PCB formulations, and combustion.

PCNs are widespread in arctic air, with higher concentrations in the European Arctic (Bidleman et al. 2010). Several workers have noted the occurrence of combustion indicator CNs in arctic air. Helm et al. (2004) found small peaks for CNs 29, 44 and a prominent peak for CN 54 in the cold period air samples from Dunai. Although these CNs are absent in Halowax mixtures (Noma et al. 2004), they occur at low levels in some PCB mixtures (Yamashita et al. 2000) and so may not be unequivocal indicators of combustion CNs. Nonetheless, the abundance of CN 54 in proportion to other penta-CNs was suggestive of combustion input. The average IF66–67 was 0.54 in Dunai and Alert air samples from the cold period, which was closer to the IF66–67 for fly ashes (0.45–0.62) and Aroclors (0.5–0.62) than to IF66–67 of Halowaxes (0.6–0.94) (Helm et al. 2004). Jaward et al. (2004b) used a GC peak containing CNs 28/29/43 to speciate evaporative and combustion PCN sources in air. After subtracting evaporative contributions, combustion-derived PCNs were still indicated in air samples from Ny Ålesund and Iceland. Lee et al. (2007) used a suite of indicator CNs to speciate combustion and evaporative PCNs at Ny Ålesund. Based on the fraction of combustion PCNs/ΣPCNs present in the Halowax series, the PCNs at Alert appeared to be derived from mostly evaporation sources, while combustion influence was more evident at Ny Ålesund. Over the three-month period of the GAPS sampling campaign, combustion PCNs amounted to 4.8% of ΣPCNs at Alert and 19% of ΣPCNs at Ny Ålesund.

2.3.6.2.6. PFAS isomers

Isomers of PFOA in environmental samples have been used to examine sources of PFASs (Benskin et al. 2010a, Benskin et al. 2012b). The basis for this is that there are two major production sources, electrochemical fluorination (ECF) and telomerization. ECF, the oldest process, results in a mixture of branched and linear isomers. It is estimated that the majority (80–90% in 2000) (Prevedouros et al. 2006) of historic global PFOA manufacturing (1950s until 2002) was by ECF. PFOA produced via ECF had a consistent isomer composition of 78% linear (stdev 1.2%) and 22% branched (stdev 1.2%) in 18 production lots over a 20 year period based on analysis by ^{19}F-nuclear magnetic resonance (Reagen et al. 2007). The 3M Co. voluntarily phased out ECF perfluorooctyl chemistries in 2002, and while the extent of current global ECF PFOA manufacturing is unknown, it is likely minor today.

Telomerization is distinct from ECF in that the isomer composition of products is pure, with typically linear geometry. This process accounted for only 10–20% of ammonium PFOA produced globally from 1975–2004 (Prevedouros et al. 2006) but is currently the dominant manufacturing process in North America and Europe for perfluorinated carboxylic acids (PFCAs) and fluorotelomer products (i.e., $CF_3(CF_2)xC_2H_4R$) some of which can degrade to PFCAs in the environment (Butt et al. 2010, Wallington et al. 2006, Wang et al. 2009).

Benskin et al. (2012a) applied an isomer-profiling technique for seawater (Benskin et al. 2010b) to assess the relative extent of ECF PFOA in seawater samples from the Canadian Arctic Archipelago and North Baffin Bay, for the first time. The relative profile of individual isomers was also carefully examined for potential abiotic fractionation. They determined individual isomers by liquid chromatography-tandem mass spectrometry PFOA (i.e., sum of n, iso, 5m, 4m, 3m-PFOA peaks in m/z 369 product ion) and n-PFOA separately, and compared the relative proportions of individual branched isomers in samples to the corresponding proportions in an ECF PFOA standard. Quantifying the contribution of ECF and telomer PFOA to total PFOA concentrations was accomplished using a calibration curve of percent branched (by weight, based on the aforementioned quantification method) versus percent ECF prepared with standards containing known quantities of ECF and telomer-manufactured PFOA. They found that PFOA collected off the coast of southwestern Greenland was predominantly of ECF origin (76–87% ECF) while samples collected along the Northwest passage from the Mackenzie River delta to Barrow Strait had predominantly telomer contributions (17% and 30% ECF). These results are discussed further in Chapter 3, section 3.2.3.1.

De Silva and Mabury (2004) and De Silva et al. (2009) determined isomers of ECF PFOA using GC-MS. Their approach involved derivatization of PFOA isomers with 2,4-difluoroaniline to make a volatile derivative. The use of GC permitted separation of seven PFOA isomers. They applied this to sediment and lake water from Char Lake


Photo: Derek Muir

and Amituk Lake on Cornwallis Island. Branched PFOA isomers were detected in sediment and surface water (De Silva et al. 2009) (see Chapter 3, section 3.2.3.2) and in ringed seals and polar bears (De Silva and Mabury 2004) (Chapter 4, Sections 4.1.5.3.1.2 and 4.1.5.3.5.2).

2.3.6.3. Assessment of enantiomer and compound ratios

- Interpretation of enantiomer and compound ratios is a complex matter. Uncertainties arise from shifting patterns of product usage and variation in technical mixture compositions.
- Uncertainties in compound ratios also arise from variation in enantiomer profiles and even reversal of enantiomer abundances occur due to the enantioselective degradation capabilities of different microbial communities in soil and water.
- Differences in physicochemical properties lead to fractionation of isomers and metabolites when undergoing air-surface exchange and further alteration in ratios may result from differences in atmospheric reactions.
- Interpretation of compound ratios is best carried out in concert with other tracers such as enantiomers (for chiral compounds), combustion products (Eckhardt et al. 2007, Genualdi et al. 2009a, Primbs et al. 2008a) and isotopes (Cheng et al. 2007) and diagnostic characteristics of air pathways (trajectories, air boundary layer height, etc.).
- Chemical concentrations and profiles in source regions are being investigated under the Global Atmospheric Passive Sampling (GAPS) campaign (Pozo et al. 2009). See Chapter 3, section 3.1.5.

2.3.7. Local sources

Contributors: Tanya Brown, Monica Danon-Schaffer, Perihan Kurt-Karakus, Daniela Loock, Carol Luttmer, Derek Muir, Ken Reimer

2.3.7.1. Introduction

Although the focus of the NCP has largely been on contaminants originating from long-range transport, there are several reasons to address local sources in this assessment report. First of all, NCP is interested in any information concerning contaminant levels in Canada's North, especially as it relates to traditional/country foods and spatial trends. Secondly, contaminated sites, as sources of local contamination, are of serious concern at a local level since many are located close to communities. Third, local sources might contribute to global sources of POPs as the soil burdens and residues in contaminated sites are becoming more dominant sources of POPs compared to the declining direct emissions of many legacy POPs (Bidleman et al. 2003). There is also a need to assess these sites with a view to the impacts that may arise as a result of climate warming. These changes relate primarily to the destabilization of contaminated materials currently sequestered in permafrost. Therefore, contribution of local sources within the Canadian Arctic to the remaining global source cannot be ignored.

In previous POPs assessments abandoned Distant Early Warning Line (DEW-line) military radar stations were discussed as sources of PCBs (Jensen et al. 1997 Murray et al. 1998, Bidleman et al. 2003). Based on work carried out by the Department of National Defense (DND), it was concluded that contamination from DEW-line stations generally

contribute a "halo" of elevated PCB levels within a 10 km radius of each site. While the DEW-line stations were considered the most important source of PCB contamination at a local level, long-range atmospheric transportation was considered to be the most important source on an arctic-wide basis (accounting for 99%; Macdonald et al. 2000). CACAR-II summarized studies related to assessment and, if necessary, clean up, of contaminated sites in the Canadian Arctic that are administered by the Department of National Defence and the Aboriginal Affairs and Northern Development Canada (Fisk et al. 2003). That assessment provided several case studies of sites that contained relatively large amounts of contamination and that have seen substantial investigation and, in some cases, have been remediated. The extent of contamination at these sites is not representative of all contaminated sites in the North—in several cases they represent extreme examples.

The Canadian government has undertaken several programs to assess, and if necessary remediate, contaminated sites in the Canadian Arctic, most notably the DEW-line cleanup project, through the Department of National Defence (DND), and the Northern Contaminated Sites Management Program (INAC 2010). These programs have led to a comprehensive inventory of contaminated sites in the Canadian North that can be broken down into three main categories: abandoned military sites (e.g., DEW-line stations); abandoned mines; and, other industrial sites.

Many local sources of contamination exist within the Canadian Arctic. These include operational and abandoned mining and industrial sites, waste disposal sites, and abandoned military sites (Stow et al. 2005). Since NCP-I, various federal, territorial and provincial departments have remediated, or are in the process of cleaning up contaminated sites in the Arctic (INAC 2010). Many of the sites that have been remediated are former radar stations that were built by the Canadian and United States governments in the 1950s. Initial assessment work provided information on the extent and patterns of local contamination and its relative influence compared to long-range transport. The assessments formed the basis for agreements, standards, and protocols for the remediation of the sites. The primary impetus for cleanup was to prevent redistribution of contaminants into the surrounding environment. Long-term monitoring programs have been initiated to ensure no future distribution of contaminants from these sites. These programs focus on evaluating the stability of facilities (e.g., engineered landfills) created as part of the remedial solution. The effectiveness of cleanup work in terms of ecosystem recovery has also been studied at some of the sites. For example, at Saglek, a radar site on the coast of Labrador, temporal trends have shown recovery of the marine ecosystem following the cleanup of the terrestrial polychlorinated biphenyl (PCB) contamination (Brown et al. 2009).

In this section, we present an overview of the local sources of POPs in the Canadian Arctic that are extensively discussed in CACAR-I and CACAR-II and discuss new results that have become available over the period 2003–2010. Several case studies studying local sources are presented in Chapter 3, Section 3.4.2.

2.3.7.2. Radar sites

The former radar stations located along the 66th parallel from northwestern Alaska, across Canada to Iceland, are known collectively as the Distant Early Warning (DEW) Line. The DEW Line was part of a larger radar network that included the Pine Tree Line and Mid-Canada Lines that ran west to east at approximately 50^{o}N and 55^{o}N, respectively, as well as the Pole Vault Line, which ran north to south along the east coast of Canada. Forty-two of the DEW Line sites were located within Canada. These sites varied in size from large main sites that housed up to 200 people, auxiliary sites (up to 30 personnel) to smaller intermediate sites designed to fill the gaps in the radar between the auxiliary sites. The intermediate sites were only operational for a short time period before advances in radar technology made them obsolete in the 1960s. In the 1980s, the former radar sites were replaced with the current North Warning System. The decommissioned sites are currently administered by several different bodies. The larger main and auxiliary sites from the DEW Line are the responsibility of DND (Annex Table A2-9). The majority of the intermediate sites and other radar and communication sites are administered by INAC (Annex Table A2-10), while some sites are under other jurisdictions. For example, Hopedale, a former Mid-Canada Line site is within the jurisdiction of the Province of Newfoundland and Labrador and Saglek, a former Pole Vault Line Station on the Labrador Coast, is within the jurisdiction of the North Warning System Office at the Department of National Defence.

The CACAR-I and CACAR-II reports describe some of the initial environmental assessments completed for the DEW Line military radar stations and describe the relative importance of local sources versus long-range contamination in the Arctic.

Improper storage of chemicals and fuels, waste disposal, and demolition practices at the radar sites resulted in local contamination, both on land and in aquatic systems, across the Canadian Arctic. The main contaminants of concern were PCBs, hydrocarbons and inorganic elements (primarily copper, lead and zinc). Initial assessments determined that in general, the sites do not pose an acute risk to human or environmental health, but are chronic sources of contaminants that could potentially be injurious to the ecosystem and traditional harvested food sources. In fact, the abandoned radar sites have been the greatest local source of PCBs in the Canadian Arctic (Stow et al. 2005) and studies on PCB contamination in soil, plants, and lake sediments at a radar station at Saglek, Labrador demonstrated that short-range transport of PCBs resulted in a halo of contamination up to 50 km in diameter (Pier et al. 2003). Many of the abandoned radar sites are located near communities, and therefore raise concerns about community health, the health of country foods, and current land use and development.

DND initiated the DEW Line Clean Up (DLCU) Project for the assessment, remediation, and monitoring of the sites within its jurisdiction. The goal of the DLCU is to make the sites environmentally safe and prevent contaminants from migrating into the food chain. DND has completed the assessment of all of its sites, and the majority (76%) have been remediated and are in the long-term monitoring phase (Annex Table A2-9). INAC has also completed the remediation of a number of sites including the Iqaluit Upper Base, Resolution Island (BAF-5), Horton River (BAR-E), Sarcpa Lake (CAM-F), FOX-C, PIN-B and Pearce Point (PIN-A) (Annex Table A2-10). The approach adopted for remediation of these sites has generally been consistent with the DLCU methodology and this was formalized in 2009 with standard protocols and criteria for the assessment and remediation for INAC's remaining sites (INAC 2009a, b).

The distribution of contamination found at the decommissioned radar sites across the Arctic was often similar, as they generally reflect historical demolition and disposal practices. The majority of the contamination has been found in sewage outfalls and lagoons associated with human waste and down-the-drain disposal of contaminants; stained soils on fuel tank pads, and work and refueling areas associated with the spillage of used oil, leaded fuels, and other related wastes; and down-gradient of landfills and dumps over slopes and cliffs associated with leaching and/or erosion of non-engineered landfills and dumps. However, the extent of soil contamination varies depending on site specific characteristics, namely, the type and operational life of the site, decommissioning practices, and physical geography and climatic factors that control contaminant redistribution mechanisms such as migration along drainage pathways, aerial redistribution, erosion of contaminated soils, and shoreline runoff into the marine environment.

Several of the radar sites with PCB contamination have been subject to site-specific ecological risk assessments (ERA) and human health risk assessments (HHRA). At Saglek, Labrador, studies in the late 1990's to early 2000's showed that the PCB contamination present at this time was associated with ecological risks and could lead to potential human health risks if wild foods from the area were consumed. The source of PCB contamination has now been removed and long term monitoring to assess ecosystem recovery is underway. At Hopedale, the results of the HHRA indicate that prolonged exposure to the PCB-contaminated areas at the former military site may pose a potential health risk (ESG 2009). Arctic hare and berry data collected by local residents next to the PCB-contaminated areas at the Hopedale former military site show elevated levels of PCBs. Therefore, local foods like berries and wild game should not be collected around areas with elevated PCB levels. Additional assessments and a remediation plan were undertaken in 2010 and the Newfoundland and Labrador government has initiated remedial activities at Hopedale (ESG 2009).

The radar sites with extensive PCB contamination provided a unique opportunity to study the effects of PCBs on the health of arctic biota over a wide range of exposures due to the combination of long-range and local sources of PCB contamination. Monitoring in the marine and terrestrial environment at Saglek, Labrador has shown that PCB concentrations in the surrounding environment (sediments, plants, deer mice, sculpin, and black guillemots) have decreased since the source of PCBs has been removed (Brown et al. 2009, ESG 2009), and companion studies have shown that the decline in the PCB concentrations are associated with a decline in biological effects. However, some biomarkers measured in deer mice, shorthorn sculpin and black guillemot nestlings indicate that some biological effects may still be present even at the lower PCB concentrations.

Previous studies at Saglek showed that migratory species, such as arctic char, ringed seals and great-backed gulls do not appear to show significant influence from the local PCB source (Kuzyk et al. 2005). However, PCB concentrations in ringed seals of the same age and sex than those from Saglek, range

from arctic background levels of approximately 1,000 ng g^{-1} ww to 15,000 ng g^{-1} ww (ESG 2008, Kuzyk et al. 2005). Organochlorine contaminants, including PCBs, were more recently measured in ringed seals from the north Labrador coast, and contaminant data to date have shown that elevated PCB levels in ringed seals persist along the coast. Saglek ringed seal satellite telemetry data show that there are distinct differences in the movement and foraging patterns as well as the PCB contaminant levels among the tagged ringed seals. Blubber PCB concentrations were variable, showed no correlation with age or sex, and were surprisingly high (six fold) in juvenile females that spent minimal time in Saglek fiord relative to an adult male ringed seal that remained in Saglek Bay. Preliminary results of a coastal food web study suggest there may be differences in the feeding patterns of ringed seals in the four northern Labrador fiords studied (Saglek, Nachvak, Okak, and Anaktalak fiords), which may have potential implications for the transfer of contaminants to this species. These results raise the question of other potential local marine sources along the coast. Studies in progress are further investigating the patterns of ringed seal PCB levels and congener profiles, movement and foraging behaviour, food web dynamics, and health. Arctic sites with local contamination like Saglek warrant further study to advance our understanding of contaminant processes, pathways, exposure and biological effects. These studies are described in more detail in Chapter 3, section 3.4.2.2.

2.3.7.3. Dumpsites in Yellowknife, Cambridge Bay and Iqaluit

A preliminary study was performed in the Canadian North to investigate PBDE congener patterns in aqueous media (leachate, effluent and background water), and in soil, and furthermore to understand how PBDEs are entering and being transferred among landfill leachates, sediments and soils in the Canadian Arctic. Moreover, fate and transport of PBDEs and spatial distribution of contamination were assessed by investigating leachability of PBDEs from e-wastes. Soil, leachate, effluent and background aqueous samples were collected from northern Canadian dumpsites and nearby areas (Danon-Schaffer 2010). Soil samples were collected from various sites within Yellowknife, Cambridge Bay, and Iqaluit (see map in Figure 3.42). Higher brominated PBDE congeners such as BDE206 and BDE207 were the dominant congeners in leachate samples at most of the sampling sites. Soil samples from major dumpsites in Iqaluit, Cambridge Bay and Yellowknife showed significantly higher ΣPBDE concentrations compared to corresponding background sites in these locations, suggesting that PBDEs leach from the landfill. The study also reported, for the first time, potential commercial penta-BDE and octa-BDE profiles in soils in the Canadian North. The distributions of BDE congeners in soil samples from Iqaluit and Cambridge Bay were similar to those in commercial formulations. It is important to note the differences between the sites were related to the different types of facilities closeby, i.e., municipal dump site vs. metal dump site, and showed substantially different congener profiles. PBDE congener profiles near the municipal dump site were similar to those of the commercial Penta-BDE whereas congener profiles near a metal dump site were similar to those of the Octa-BDE commercial formulation, suggesting the different local sources of PBDEs at different sampling sites. Further details on results of the study are presented in Chapter 3, section 3.4.2.1.

2.3.7.4. Chlorinated paraffins in the Iqaluit area

Dick et al (2010) determined concentrations and sources of short-chain (SCCPs) and medium-chain chlorinated paraffins (MCCPs) in and around Iqaluit (NU). Sediments in Airport Creek (near Iqaluit's airport) were analysed along with water draining from the sewage lagoon and sediments near the lagoon's outlet. Sediments in Airport Creek averaged 32.0 ± 44.1 ng g^{-1} (dry weight) for SCCPs and 14.6 ± 17.1 ng g^{-1} for MCCPs. The highest values of SCCPs and MCCPs were detected in the upper reaches of Airport Creek near a gravel pit that may have been a waste disposal area in the past. The sewage outflow had relatively high levels of SCCPs (117 ng L^{-1}), while concentrations of MCCPs were comparable to the average value in Airport Creek. SCCPs were highest in terrestrial soil samples from sites that were or are currently utilized for waste disposal. Significant concentrations of CP in sediment and water from some sites indicate ongoing local sources of contamination. However, as discussed in Chapter 4, section 4.1.2.1.1., anadromous char from the Sylvia Grinnell River near Iqaluit and from Peterhead Inlet, a more remote site, had low levels of SCCPs and MCCPs suggesting that contamination was low in the food web of Frobisher Bay.

2.3.8. Climate change impacts

Contributor: Jianmin Ma

2.3.8.1. Introduction

An emerging challenge for scientists studying POPs is to link climate events, particularly "arctic amplification" (the greater warming occurring in the Arctic compared to average global changes),

with global and pole-ward transport of POPs. Understanding this link requires knowledge in the association of emissions, transport in the atmosphere and water, deposition, phase partitioning, degradation and transformation, and even biotic transport of POPs with climate change. Figure 2.60 presents a schematic view of major processes of arctic climate change interacting with global warming and the environmental fate of POPs associated with climate change. In the context of POPs transport to the Arctic, the major processes governing pole-ward transport of POPs can be summarized below.

2.3.8.2. Emissions

The geographical pattern of POPs releases and their distribution in the environment is associated with their global production and usage pattern. Past and current uses of intentionally produced POPs lead to their primary emissions into the environment through direct dispersion on soils and into the air (pesticides), volatilization into air (semi-volatile technical chemicals, e.g., PCBs, PBDEs), and leaching into water from initial applications (water-soluble technical chemicals, e.g., PFOS/PFOS-F). Increasing or decreasing air temperature with climate change as well as variability will affect the intensity and pattern of POPs application. For example, higher temperatures may lead to an increasing number of pests and hence increasing application of pesticides. Increasing global temperatures are also expected to intensify the propagation and spread of malaria and other vector-borne diseases in tropical countries. The existing public health exemption on the use of DDT for combating malaria may lead to enhanced demand for DDT, which in turn will result in increasing emissions of DDT (UNEP/AMAP 2011). Increasing frequency of extreme climate events under global warming will significantly alter the use pattern of POPs. It is expected that both serious droughts and floods during crops seed tilling and growing seasons would either increase or decrease the use of pesticides, and more forest fires in a warming environment will release more toxic chemicals to atmosphere and terrestrial surfaces.

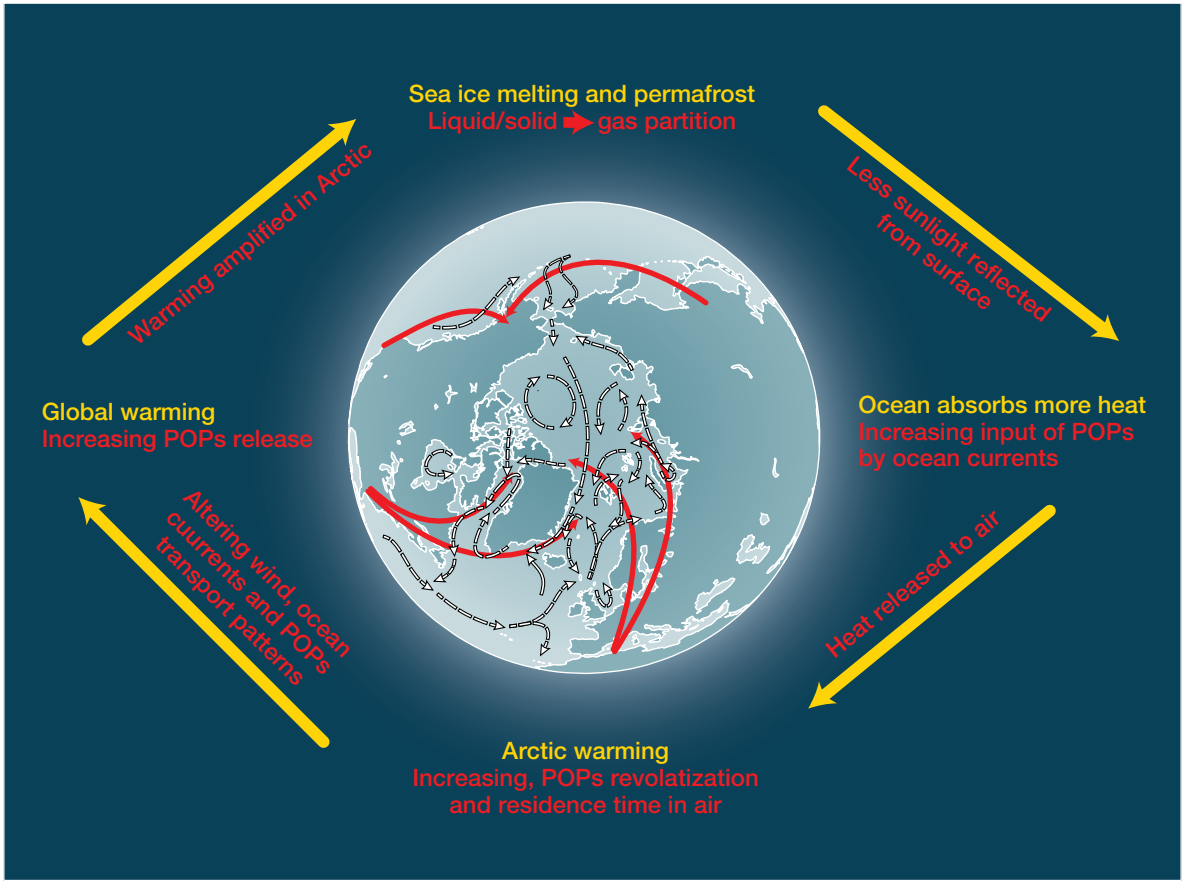


FIGURE 2.60

A schematic view of the major processes of arctic climate change and POPs environmental fate. Red solid lines indicate major atmospheric transport pathways of POPs from North America and Eurasia continents to the Canadian Arctic. White dashed lines highlight ocean currents into, out of, and within the Arctic Ocean.

Higher temperature also leads to stronger volatilization of POPs from their reservoirs where they were stored and accumulated from past applications, enhancing secondary emissions. These reservoirs are formed either near the sources of direct application (primary emissions) or formed due to transport and deposition from primary emission sources. In the latter case, increasing temperatures will increase reemissions from the secondary emission sources. As diagnosed by the Arctic Contamination Potential (Meyer and Wania 2007), increasing emissions in warmer latitudes will enhance the risk of POPs contamination to the Arctic, primarily via atmospheric transport and deposition. Rapid warming and melting are the most significant changes in the Arctic in recent decades. It has been reported that temperatures in the Northwest Territories have risen as much as two to four degrees in the last century—three to five times faster than in the rest of Canada (BBC 2001). Such a change in the arctic environment has been linked with the increasing release of POPs from the Arctic Ocean, snow, and ice into the arctic atmosphere.

2.3.8.3. Atmospheric transport and deposition

Changes in climate conditions alter transport patterns and temporal trends of POPs from interannual to decadal scales. Many climate change scenarios predict, and recent observations confirm, a decreasing arctic sea ice cover and a decreasing temperature gradient between Arctic and Tropics with a stronger temperature increase in colder areas compared to areas of lower latitudes (Braganza et al. 2004). Stronger arctic warming may reduce the atmospheric pressure gradient from the Arctic to mid latitudes so one would expect increasing pole-ward atmospheric transport of POPs from their sources in North American and Eurasia continents (Figure 2.60). Unfortunately, the increasing frequency of pole-ward long-range atmospheric transport has not been verified by either observations or modeling studies, particularly on a decadal scale. Nevertheless, the link between atmospheric transport to the Arctic and interannual and interdecadal climate variabilities, such as the North Atlantic Oscillation (NAO) and the Arctic Oscillation (AO), has been

Photo: Martin Fortier/ArcticNet

reported in several recent studies (Becker et al. 2008, Hung et al. 2005, Ma et al. 2004, Macdonald et al. 2005). Details can be found in Chapter 3, section 3.5.

Precipitation is projected to increase in some regions and decrease in other regions during the 21st century. During the journey of POPs from mid to low latitudes to the Arctic, increasing precipitation would reduce their atmospheric concentration, and hence atmospheric burden, but enhance loadings to the arctic surface media, and vice versa. For the Canadian Arctic, an increasing trend of mean precipitation from 1970 to 2010 has been recorded. This will decrease the atmospheric concentration of POPs and increase their loadings to arctic surface media (Chapter 3, Section 3.5).

2.3.8.4. Oceanic and riverine transport

Climate change has increased river discharge to the Arctic Ocean (Peterson et al. 2002). Measurement data collected by Carroll et al. (2008) indicate that the Ob and Yenisei Rivers in Russia contribute 37% of riverine freshwater inputs to the Arctic Basin. In particular, rivers are important pathways for more water-soluble chemicals, such as perfluorinated acids. For example, inputs of total PFASs to Hudson Bay via the Nelson River were estimated to be 1.7 kg day^{-1} (Scott et al. 2009). Climate induced changes in oceanic transport of POPs is subject primarily to interactions between global ocean currents and climate change. Ocean currents have a profound influence on climate and are also carriers of water-soluble chemicals (see sections 2.3.5.3 and 2.3.5.4).

2.3.8.5. Degradation

In general, increasing temperature speeds up degradation of POPs in soils and water. Higher temperatures will also favour the vapour phase of chemicals. Both processes lead to stronger re-volatilization of POPs from their reservoirs to the atmosphere and, consequently, increase their lifetime in air.

2.3.8.6. Partitioning

Increasing the vapour pressure of POPs by increasing temperature alters both the partitioning between bulk phases (air vs. surface media such as soil, water and vegetation) and between the gaseous and particle-bound phases in air, leading to a shift towards higher gaseous fractions in air. All of these factors make POPs more available for long-range transport.

Increasing air temperatures may help to enhance the formation of secondary atmospheric particulate matter (Forster et al. 2007), including particulate organic matter in aquatic environments (Carrie et al. 2010, Macdonald et al. 2005). These changes would enable a larger fraction of the POPs to be associated with particulate matter in air and water. Consequently, the atmospheric transport of POPs to remote regions may be reduced due to temporary or permanent deposition to surfaces before reaching remote regions (UNEP/AMAP 2011). On the other hand, when sorbed to the particulate matter, the reactivity or half-life of a substance in the particulate phase can affect the substance's long-range transport potential. For example, if the reactivity in the particulate phase is reduced substantially, its half-life in this phase will increase and its long-range transport potential will also increase. The impact of the particulate phase reactivity is therefore significant for highly sorbed substances.

2.3.8.7. Biotic transport

Climate change has been demonstrated to affect the populations of animals and their migration (Macdonald et al. 2005). Migratory animals have the capacity to magnify and transport contaminants within their migration routes (Blais et al. 2007, Macdonald et al. 2005). The obvious examples include anadromous fish (e.g., Pacific salmon), whales and birds. Although the contaminant transport potential inherent in these biovectors is of a smaller scale than atmospheric or oceanic transport, it is still significant because the contaminants are focused within the animals' life cycles and impinge on sensitive areas like nursery ponds or lakes. See further discussion in Chapter 3, section 3.6.

Except for the processes highlighted above, changes in organic carbon in soil and particulate organic matter in surface waters (Macdonald et al. 2005) incurred by climate change would likely alter redistribution and mobilization patterns of POPs. It is not clear yet if those processes occurring in the atmosphere would affect atmospheric transport patterns of POPs, such as the "global fractionation" and "cold trapping" effect, or single and multi-hop transport. Further studies are needed on these aspects.

2.4. Conclusions, Knowledge Gaps and Recommendations

2.4.1. Physicochemical properties of persistent organic pollutants

2.4.1.1. Conclusions

- Physical-chemical properties for legacy POPs are reasonably well established, however, uncertainties remain particularly for per- and polyfluorinated chemicals and other polar compounds.
- While uncertainty in physical-chemical property estimates for PFCAs and PFAS may have limited influence on the assessment of long-range oceanic transport potential these uncertainties are important when assessing global fate and transport in a broader context (e.g. atmospheric vs. oceanic inputs to remote marine environments.
- Both experimentation and modelling will be important for future progress as well as critical evaluation and analysis of data to obtain thermodynamic consistency.
- Predicting gas exchange cycles of legacy POPs and new and emerging chemicals of concern places a high demand on the accuracy of physical-chemical properties, particularly the air/water partition coefficient, K_{AW}.
- Predicting the chemical's property on the basis of screening and categorization methods that rely on a decision whether a chemical falls on either side of a threshold are likely to lead to a significant number of false positive/negative outcomes.
- Large-scale screening of chemicals on Canada's DSL and other lists of commercial chemicals for bioaccumulation and LRAT potential has shown that there are several hundred chemicals with properties similar to those of known persistent organic chemicals detected in the Arctic.
- There is much less certainty for prediction of Arctic Accumulation Potential of chemicals that lie outside the "training sets" for the models used to predict key LRAT properties such as air-water and octanol-air partition coefficients. Assessing the Arctic Accumulation Potential of transformation products is also difficult.

2.4.1.2. Recommendations

- Degradation rates of chemicals in air, water and soil under cold climate conditions are lacking and need to be determined for most arctic contaminants.
- Physical-chemical properties data are essential for modelling purposes and excessive reliance on QSARs is to be avoided. Therefore, for chemicals that are identified in the Arctic there is a need to measure and compile accurate and consistent physical chemical property data including partitioning data, reactivity data in air, aerosols, water (both fresh and marine), soils etc as a function of temperature from -40 deg C to +40 deg C.
- There needs to be more focus on ionising substances such as carboxylic acids, phenols and amines.
- More data are required on quantities of chemicals used and emitted in source regions.

2.4.2. Usage and emissions of POPs

2.4.2.1. Conclusions

- Global emissions data are important as a key input for global POPs models and for the study of sources and pathways of contaminants to the Arctic.
- Over the period 2003-2010 globally gridded (e.g. 1° lat x 1° long) estimates for chemical emissions were updated for a wide range of chemicals including PCBs, dioxins/furans (as g/TEQ), γ-HCH, endosulfan, PCNs and PFOSF.
- Chinese usage and emissions of endosulfan were documented for the first time.
- There is a need to identify and improve characterization both of primary and secondary emission sources of several legacy POPs as well as new chemicals such as the perfluorinated compounds. This is highly relevant for prediction of future levels and trends, as well as for the interpretation of monitoring data.
- Measurements of PFCAs and PFOS in background soils are scarce, as are empirical studies attempting to estimate remobilization fluxes.
- Models indicate that the terrestrial environment in source regions (particularly soil organic carbon pools) is an important determinant of long-range transport potential, particularly for POPs.

2.4.2.2. Recommendations

- Further research should be carried out to determine current emission inventories, especially for new and emerging chemicals. International cooperation is the most effective way for continuously updating and expanding global emissions datasets.
- The regional and global influence of contemporary production/use/emissions of PFOS warrants further investigation.
- Further investigation is needed to determine direct emission sources of the PFASs that yield PFCAs during atmospheric degradation.

2.4.3. Atmospheric and oceanic transport of POPs

2.4.3.1. Conclusions

- In addition to many legacy POPs, lower-brominated PCB and PBDE congeners have a long-range transport potential to be delivered to remote pristine regions.
- Major sources of new POPs occur throughout the Northern Hemisphere. Specific regions are being located and emissions estimated through a combination of modelling, emission inventory research, and targeted air monitoring; e.g., through the GAPS network.
- Quantitative understanding of the fate and transport of the wide variety of chemicals can contribute to international negotiations to reduce the impacts of long-range transport.
- Results of modeling studies can be used to assess the efficiency of transport, responsibilities for region to region contamination, assigning vulnerabilities and possibly designing a global scale strategy to assign tolerable rates of chemical usage and emission.

2.4.3.2. Recommendations

- Effects of climate change on transport mechanisms of POPs, particularly in air and water deserves a high priority for future research.
- There is a need to expand and harmonize temporal trend monitoring in air and water in circumpolar countries to assess how levels change and what impact climate change has on these levels.
- There is a need for monitoring data and assessment tools to evaluate the impact of climate change on changing POPs emissions and concentrations.

2.4.4. Mass balance modelling of contaminants in oceans, atmosphere

2.4.4.1. Conclusions

- Computer-run mathematical models of the environmental transport and fate of POPs are important tools for predicting the response of POPs to changes in environmental factors.
- There has been a tremendous expansion of modelling of ocean transport of contaminants, particularly of PFOA and PFOS to the Arctic in the last 5 years. Results are in reasonable agreement with currently available data suggesting that available emission estimates for these two compounds are plausible.
- Modeling results suggest that redistribution of these contaminants from lower latitudes to the Arctic Ocean is ongoing and the total mass (and average concentration) of PFOA and PFOS in the marine environment is expected to increase for the next 10 – 20 years.
- The Distant Residence Time concept can play a valuable role in guiding global modelling efforts and presenting findings in a relatively simple and understandable manner.
- A number of atmospheric transport modeling and trajectory calculations have revealed trans-Pacific transport of toxic chemicals from eastern Asia to the western part of the Canadian Arctic.

2.4.4.2. Recommendations

- Where different models exist there should be active model comparison programs to identify strengths and weaknesses with a view to improving predictive capabilities.
- Efforts should be made to devise internationally acceptable methods using models of identifying source-receptor relationships between geographic regions.
- More data are required on quantities of chemicals used and emitted in source regions.
- There is a need to build and/or improve models to forecast POPs fate and transport in air and water. However, for the credibility of models, evaluation of model results with field data is essential, which requires that adequate monitoring are are available.

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CHAPTER 3

Occurrence and Trends in the Physical Environment

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Photo: Janice Lang

CHAPTER 3

Occurrence and Trends in the Physical Environment

Coordinating authors: Hayley Hung and Perihan Kurt-Karakus

3.1. Legacy and New POPs in the Arctic Atmosphere

Contributors: Lutz Ahrens, Crispin Halsall, Tom Harner, Hayley Hung, Sum Chi Lee, Derek Muir, Mahiba Shoeib, Yushan Su, Ed Sverko, Penny Vlahos, and Hang Xiao

3.1.1. Introduction

The occurrence of anthropogenic organic pollutants in the arctic atmosphere has generally been regarded as evidence for long-range transport for pollutants that have little or no use in the arctic region. For new POPs that are consumer-product-related chemicals, e.g., flame retardants and PFASs, their occurrence in arctic air can result from both long-range transport and local emissions. Previous CACAR assessments gave summarized Canadian arctic atmospheric data for PCBs, PAHs, and OCPs in the 1990s for Alert, Nunavut (NU); Tagish, Yukon (YK); and Kinngait, Nunavut (NU) (Bidleman et al. 2003). Results included temporal trends (1993–1997) from Alert (NU), comparison of air concentrations and time trends to other Arctic stations and to remote Great Lakes sites, an analysis of fresh and secondary chlordane sources to the Canadian Arctic, a special study for atmospheric PCDD/Fs at Alert (NU) and evidence of trans-Pacific transport to the Yukon station of Tagish. More recent reviews for the AMAP POPs assessment have updated the atmospheric time trends to 2006 (Hung et al. 2010).

Photo: Eric Loring

This chapter provides an update on the status of knowledge of time trends in atmospheric concentrations, transport and deposition of legacy and new POPs in the Canadian Arctic. New atmospheric measurement data and trends from long-term monitoring programs, as well as from case studies and oceanographic cruise measurements is presented in sections 3.1.2–3.1.4. Studies conducted under the Global Atmospheric Passive Sampling (GAPS) Network are reviewed in section 3.1.5. Section 3.1.6 summarizes studies of POPs in ice cap and snow showing long-range atmospheric transport and deposition. Atmospheric transport and deposition and possible climate change influences are discussed in section 3.5. Local sources and bio-vector transport are discussed in several case studies (sections 3.4 and 3.6).

Refer to Tables 1.1 and 1.3 in Chapter 1, for a list of chemical names and abbreviations and to the Glossary for additional chemical nomenclature.

3.1.2. Air sampling in the Arctic

Atmospheric monitoring has been conducted in the Canadian Arctic under the NCP since 1992. Weekly integrated air samples are collected using pumped super high volume air samplers (super Hi-Vol) by passing approximately 13,000 m^3 of air through a glass fiber filter (GFF) and two polyurethane foam (PUF) plugs to collect particle and gas phase POPs respectively. The main station of measurement is at Alert, (NU) (82° 30'N, 62° 20'W, 200 m above sea level (asl)). Long-term time trends of legacy POPs are available up to the end of 2009 at this location (see section 3.1.3). A satellite station, Little Fox Lake, Yukon (YK) (61° 21'N, 135° 38'W, 1128 masl), was in operation in 2002–2003 for 1 year. This station was restarted in 2007 and operated for 2 years under the International Polar Year (IPY) program of Intercontinental Atmospheric Transport of Anthropogenic Pollutants to the Arctic (INCATPA) to monitor for intercontinental transport to the Yukon region. As mentioned in section Chapter 2, section 2.3.2, PAH transport to this station has been associated with forest fire emissions from British Columbia and the western US (Sofowote et al. 2011). Atmospheric PAHs observed at this location was also linked to emissions from the oil and gas production platforms in the Arctic. Atmospheric measurements of other POPs collected from this location are currently undergoing data analysis when this report goes to press and thus are not reported here. Detailed description of both field sites, sampling processes, analytical methods and quality assurance/quality control (QA/QC) procedures are given elsewhere (Hung et al. 2005, Hung et al. 2010, Su et al. 2008).

Starting in November 2005, a separate PS-1 Hi-Vol was installed at Alert (NU) equipped with a GFF and a PUF-XAD resin cartridge to capture particle- and gas-phase new POPs including current use pesticides (CUPs) and polyfluorinated alkyl substances. Results from this study will be presented in section 3.1.4.

A new type of sampler that has been designed specifically for measurement of POPs under cold conditions without the use of electricity, called the flowthrough sampler (FTS), was deployed at Alert (NU) in parallel with Hi-Vol air sampling in 2007. The FTS consists of a horizontally oriented, aerodynamically shaped, stainless steel flow tube, mounted on ball bearings which allow it to turn into the wind with the help of vanes. It is able to capture a large volume of air over a relatively short period of time (approximately 1 month). Air concentrations (gas and particle phase) can be calculated using the air volume recorded with a vortex wind sensor linked to a battery-operated data-logger on the sampler. Results from the FTS are also reported in section 3.1.3 and 3.1.4.

Besides routine air monitoring operations, independent cruise and land-based Hi-Vol sampling studies have reported atmospheric concentrations of various POPs in the Canadian Arctic. These results are also summarized in the next two sections.

In addition to pumped Hi-Vol air sampling, passive air samplers (PAS) have also been employed in the Canadian Arctic. These techniques are relatively low cost, low maintenance, easy to operate and do not require a power supply. The employment of PAS allows greater spatial coverage, providing much needed qualitative gas phase air concentrations where active air sampling is not possible. Under the GAPS Network, PUF disk-based and XAD-based PAS are deployed at approximately 60 global sites including 7 arctic and subarctic stations with up to 3 years of continuous sampling results starting in 2005. Sites include: Alert (NU); Barrow (AK); Dyea (AK); St. Lawrence Island (AK); Little Fox Lake (YK); Storhofdi, Iceland; and Ny-Ålesund, Svalbard, Norway. The regular sampling period for the PUF disk-based and the XAD-based PAS are 3 months and 1 year, respectively. A new sorbent-impregnated (SIP) PUF disk-based sampling device was tested in a pilot study for capturing more new polar chemicals of concern. Results from the GAPS Network are summarized in section 3.1.5.

3.1.3. Legacy chemicals in arctic air – active sampling results

For evaluation of long-term temporal trends, the Digital Filtration (DF) technique was used. DF is a statistical fitting technique that extracts seasonal cycles and inter-annual trends from time series which are statistically significant, with 95% confidence (Nakazawa et al. 1997). This technique has been successfully applied to derive long-term trends of atmospheric trace chemicals, including PCBs and OCPs at Alert (NU) (Hung et al. 2005). A detailed description of this technique can be found in Hung et al. (2005). Annex Tables A3-1 and A3-2 summarize the mean, standard deviations and ranges of the different legacy POPs measured at Alert (NU) (2002–2009) and Little Fox Lake (YK) (July 2002–July 2003). Total air concentrations (gas and particle phase) concentrations are used in the development of trends here since the gas and particle phases of each sample were combined for analysis between 2002 and 2005 as a cost saving measure.

In 2002, as part of a decision to integrate analytical activities within Environment Canada, chemical analyses of samples from Alert (NU) were moved from the Fresh Water Institute (FWI), Winnipeg, which is a laboratory of the Department of Fisheries and Oceans, to the National Laboratory for Environmental Testing (NLET), an Environment Canada laboratory in Burlington, ON. NLET maintains the historical analytical procedures employed by FWI with slight modifications (Su et al. 2011). Three rounds of rigorous inter-laboratory comparison between FWI and NLET were conducted. The first round of comparison in 2004 used regular air extracts taken at Alert (NU) in 2002; the second round in 2005 employed calibration standards and blind samples (a mixture of target compounds), in addition to regular air extracts taken at Alert (NU) in 2004; and the third round in 2008 compared calibration standards and a blind sample. The comparisons have shown that the analytical results reported by the two laboratories are in fact very comparable for most polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs); with divergence that are apparently random and non-systematic. For standards and blind samples with known concentrations, both laboratories reported results with good accuracy and consistency for most target compounds (within ± 20% of the target concentrations). Therefore, it is considered not advisable to correct for discrepancies observed between the two laboratories as doing so may introduce uncertainties in the dataset. Results of these inter-laboratory comparisons are summarized in Su et al. (2011). The median absolute inter-laboratory differences for blind samples and air extracts range from 32–53% for OCPs, 18–69% for PCBs and 36–43% for PAHs. Inter-laboratory measurement differences for standards (< 30%) and samples (< 70%) were generally less than or comparable to inter-laboratory differences reported for another comparison study among 21 laboratories (Su et al. 2010). These differences are within the range of air concentration variations for these chemicals measured within a specific year. Therefore, in the current report, the long-term trends have not been corrected for discrepancies between the two laboratories. The OCP and PCB air concentration data measured at Alert (NU) in 1992 did not meet quality control criteria as indicated in Stern et al. (1997). Therefore data from 1992 are not included in the current study.

3.1.3.1. Polychlorinated biphenyls (PCBs)

The ΣPCBs concentrations for the AMAP suite of 10 PCBs measured at Alert (NU) and Little Fox Lake (YK) are shown in Annex Tables A3-1 and A3-2. The air concentrations of PCBs measured at Alert (NU) remain the lowest among AMAP long-term air monitoring stations and were statistically significantly different (at a confidence level of 95%) from Storhofdi (Iceland) and Ny Ålesund (Svalbard/Norway) between 1998 and 2005. For example, the annual means (2004 and 2005) for the ten AMAP congeners were 12 and 7.8 pg m^{-3} at Storhofdi (Iceland) and 5.7 and 7.5 pg m^{-3} at Ny Ålesund (Svalbard/Norway) while those at the Alert (NU) station were 2.3 and 4.9 pg m^{-3}, respectively (Hung et al. 2010). The air concentrations of PCBs at Little Fox Lake (YK) in 2002 and 2003 are similar to those measured at Alert (NU).

Tri-chlorinated biphenyls (CBs) dominated the profiles of samples taken at Alert (NU). This corresponds to the fact that tri-CBs were the most important PCB homologue produced historically (Breivik et al. 2002). There was a slight decline in relative contribution of lower chlorinated CBs from the 1990s to the early 2000s with a slight increase in contribution of higher chlorinated homologues, e.g., tetra- to octa-CBs (Figure 2 in Hung et al. 2010). Since production of PCBs stopped in most industrialized countries during the 1970s and 1980s, this shift in homologue profile may be considered as an indication that the air concentrations of lighter congeners are starting to level off (or reaching an equilibrium state in exchange with the Earth's surfaces) as a result of environmental removal processes, e.g., photo- and

bio-degradation. Sharma et al. (2006) reported increasing trends of equivalent black carbon (EBC) at Alert (NU) between 1998 and 2002. The increase in EBC, which is a form of particulate matter, may also enhance input of heavier PCB congeners which have higher tendencies to associate with particles.

Figure 3.1 shows the temporal trends of PCB 52, 101, 153 and 180 at Alert (NU). The trends for other congeners are quite similar to these whereas a slight increase is seen in recent years. It can be seen that the air concentrations of PCBs at Alert (NU) were declining before 2002. After 2003, the PCB trends tend to be non-declining and therefore half-lives are not reported. Apparent first order half-lives are provided in Table 3.1. Only 9 AMAP suite PCBs are listed in this table as PCB 156 is usually below detection limits in arctic air. For PCBs, during the first year of the laboratory change, i.e., 2002, the atmospheric PCB data were apparently affected by certain cleanup artifact, resulting in low detections of most congeners. Since NLET adopted the historical analytical method of FWI in order to maintain consistency in analysis, results in the first year might have been affected by unfamiliarity with the analytical procedures. The cleanup and fractionation procedures were then modified as described by Su et al. (2011) to correct for this artifact. Therefore, PCB air concentration data reported for 2002 are not included in this analysis. From Figure 3.1 it can be seen that after 2002, this problem did not persist after the method was modified and the long-term trends were reasonably maintained.

From 2003 to 2009, an apparent increase in trends is observed for PCB 153 and PCB 180 in 2007 and 2008. One potential factor may be re-evaporation from the open ocean as sea-ice extent decreases in the summer in the Arctic in general. A slight increase in the atmospheric trend of PCB concentrations was also observed at Ny Ålesund in 2005 and 2006, which may be associated with ice-free winters along the west coast of Spitsbergen (Hung et al. 2010). According to records from the National Snow and Ice Data Center of the University of Colorado, Boulder, USA, arctic sea-ice during the 2007 melt season dropped to the lowest levels since satellite measurements began in 1979 (NSIDC 2011). However, it is also noted that the most significant increases were observed in the heavier PCBs, which have higher tendencies to be associated with particles, at both Alert (NU) and Ny Ålesund (Svalbard/Norway). The reason for such increases is unclear as both sulfate aerosol and black carbon concentrations measured at Alert (NU) (Gong et al. 2010), as well as at Barrow (AK) and Ny Ålesund (Svalbard/Norway) (Hirdman et al. 2010) have been relatively steady during this time. In other words, there is no evidence of increased influx of particulate matter to the Arctic in general that could explain such increases in PCB concentrations. One possible explanation may be the increase in boreal forest fires that release previously deposited organic chemicals, such as PCBs, resulting in increased input to the Arctic (Eckhardt et al. 2007). Half-lives were only derived between 1993 and 2001, i.e., before the laboratory change to NLET.

TABLE 3.1. Apparent first order half-lives of various POPs at Alert (NU).

PCBs	1993–2001[1]	
	$t_{1/2}$ (y)[2]	r^2
28	7.1	0.76
31	5.6	0.92
52	4.6	0.81
101	6.9	0.77
105	7.0	0.45
118	8.3	0.28
138	20	0.17
153	8.3	0.32
180	3.6	0.84
PCBs	**1993–2009**	
	$t_{1/2}$ (y)[2]	r^2
HCB	23	0.66
α-HCH	4.6	0.96
γ-HCH	4.2	0.97
trans-chlordane	11	0.51
cis-chlordane	14	0.70
trans-nonachlor	12	0.68
cis-nonachlor	17	0.31
α-endosulfan	37	0.17

[1] Half-lives are only reported for Alert (NU) between 1993 and 2001 where consistent declining trends were observed. See text for details.

[2] $t_{1/2}$=half-life, calculated as ln 2/slope. Compounds that do not show a consistent declining trend (i.e., greatly fluctuating or steady or slightly increasing trends) are indicated as N. D. = not determinable.

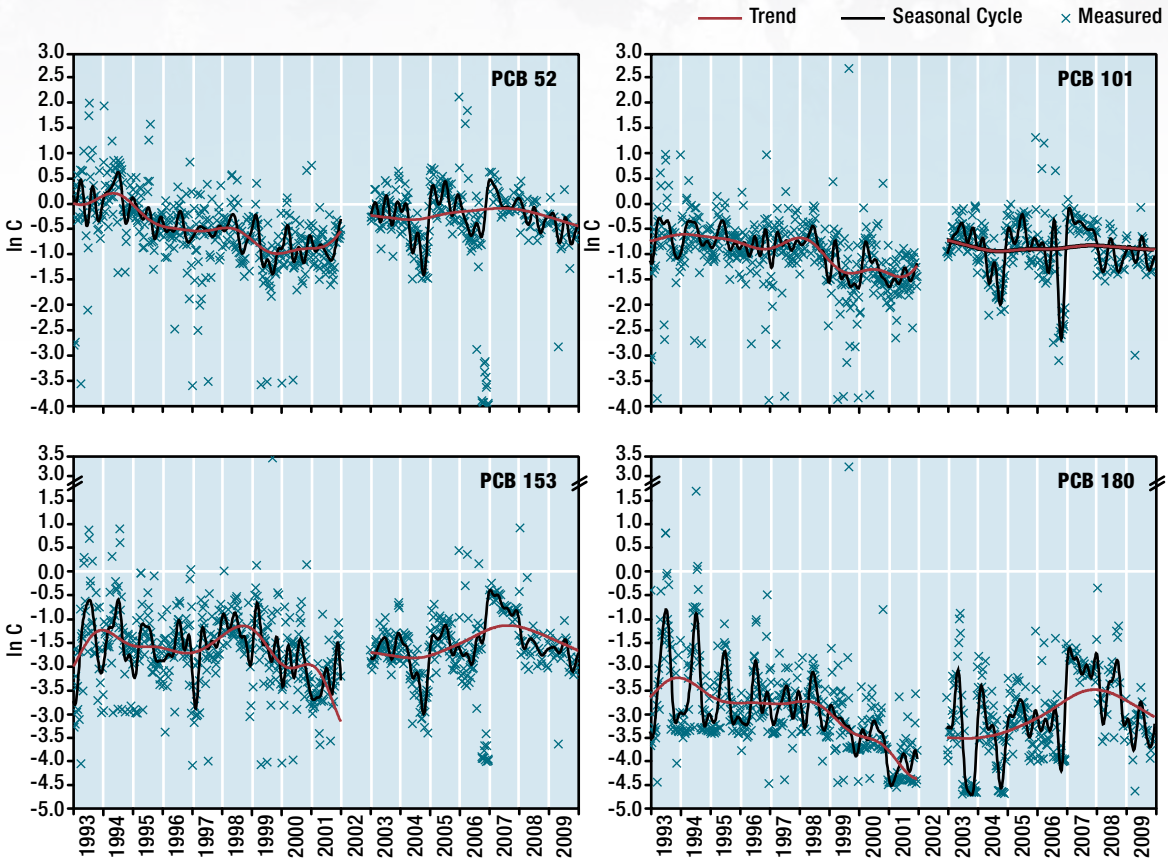

FIGURE 3.1

Atmospheric trends and seasonal cycles of PCBs at Alert (NU), 1993 to 2010 (pg m^{-3}). Concentration (C) is displayed using a natural log scale.

3.1.3.2. Organochlorine pesticides (OCPs)

The temporal trends of select OCPs are shown in Figure 3.2. It can be seen that heptachlor epoxide, α- and γ-HCH showed consistent and continuous declining trends throughout the time series. Lindane, which consists of almost pure γ-HCH, has been included in the Stockholm Convention for POPs for global control as of May 2009. Canada, a major user of lindane in North America, de-registered lindane for use on canola seeds in July 2001 and a ban was introduced in 2004 (Becker et al. 2008).

It is apparent that the air concentration decline of γ-HCH in arctic air has accelerated between 2002 and 2009 ($t_{1/2,\ 02–09}$ = 3.9 years) compared to between 1993 and 2001 ($t_{1/2,\ 93–01}$ = 7.3 years) (Figure 3.2).

This increase in decline rate is also clearly observed at the Zeppelin station (Ny Ålesund, Svalbard/Norway) after 2002 ($t_{1/2,\ 93–01}$ = 6.5 years and $t_{1/2,\ 02–09}$ = 3.2 years). This reflects the fact that organic contaminants, such as γ-HCH, can travel rapidly via the air to the remote Arctic and a decline in use in source regions will result in a rapid decrease in arctic air concentrations. This observation is consistent with the finding of Li and Bidleman (2003) who showed that arctic air concentrations of α-HCH responded rapidly to changes in global α-HCH emissions.

Figure 3.3 compares the total air concentrations for selected chemicals measured by active sampling and FTS at Alert (NU). For HCHs, both sampling methods gave comparable levels. Although only about a year's worth of flow-through measurements are available

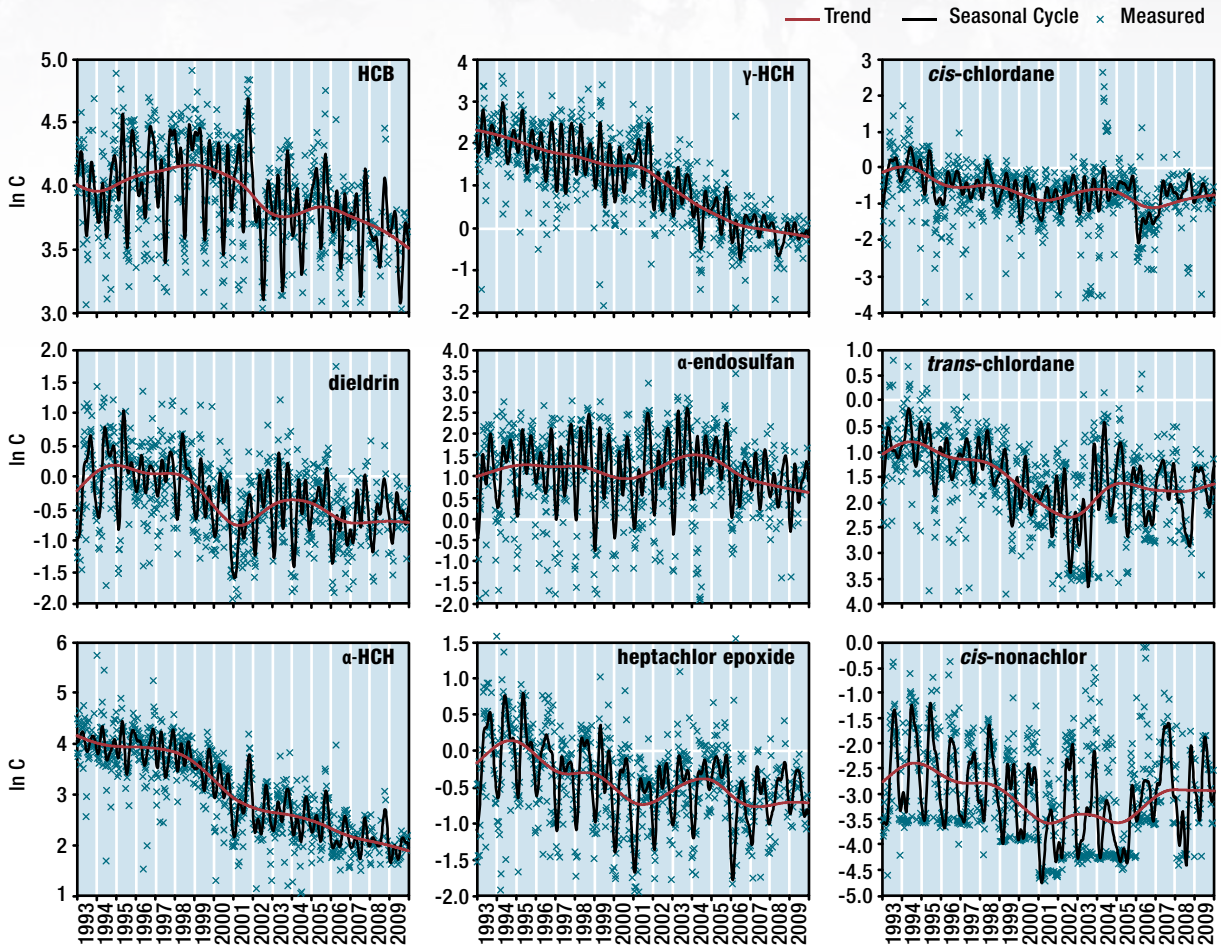

FIGURE 3.2

Atmospheric trends and seasonal cycles (gas and particle phase, pg m^{-3}) of selected OCPs at Alert (NU). Concentration (C) is displayed using a natural log scale.

now, the general trends and seasonality shown in the figure are quite comparable to those from the super Hi-Vol for both α-HCH and lindane.

While the air concentrations of α-HCH measured at all AMAP stations have declined to about 20–30 pg m^{-3} after 2000, those at Little Fox Lake (YK) were found to be much higher with an average concentration of 48 pg m^{-3} from July 2002–2003 (Annex Table A3-2). Su et al. (2006) have attributed the relatively higher air concentrations measured at Little Fox Lake (YK) to secondary emissions of previously deposited technical HCH from soil; and as a result of higher precipitation rate, which may enhance scavenging to surfaces when technical HCH was still in use, and higher air temperature, which facilitates volatilization, at this location compared to other arctic sites.

A slightly decreasing trend for α-endosulfan was observed at Alert (NU) for the first time in the period 2006–2009. A trend is further confirmed by the FTS measurements (Figure 3.4). The results given by the two sampling techniques both show similar values and decline trends. β-endosulfan has been measured in air at Alert (NU) since 2002, but the concentrations were very low and were mostly non-detectable (> 90%). Endosulfan sulfate was not being analyzed in these super Hi-Vol air samples but are analyzed in the samples collected with the PS-1 sampler (see section 3.1.4.4). In 2010, the USEPA (USEPA 2010) announced that all uses of endosulfan in the US will be cancelled and it was just added to the Stockholm Convention in 2011, with exemptions listed for India and Uruguay. Phase out needs to be completed in 6 years, with the option to extend it only once for 5 years. It can be expected that the air concentrations of α-endosulfan would continue to decline in the Canadian Arctic after the ban.

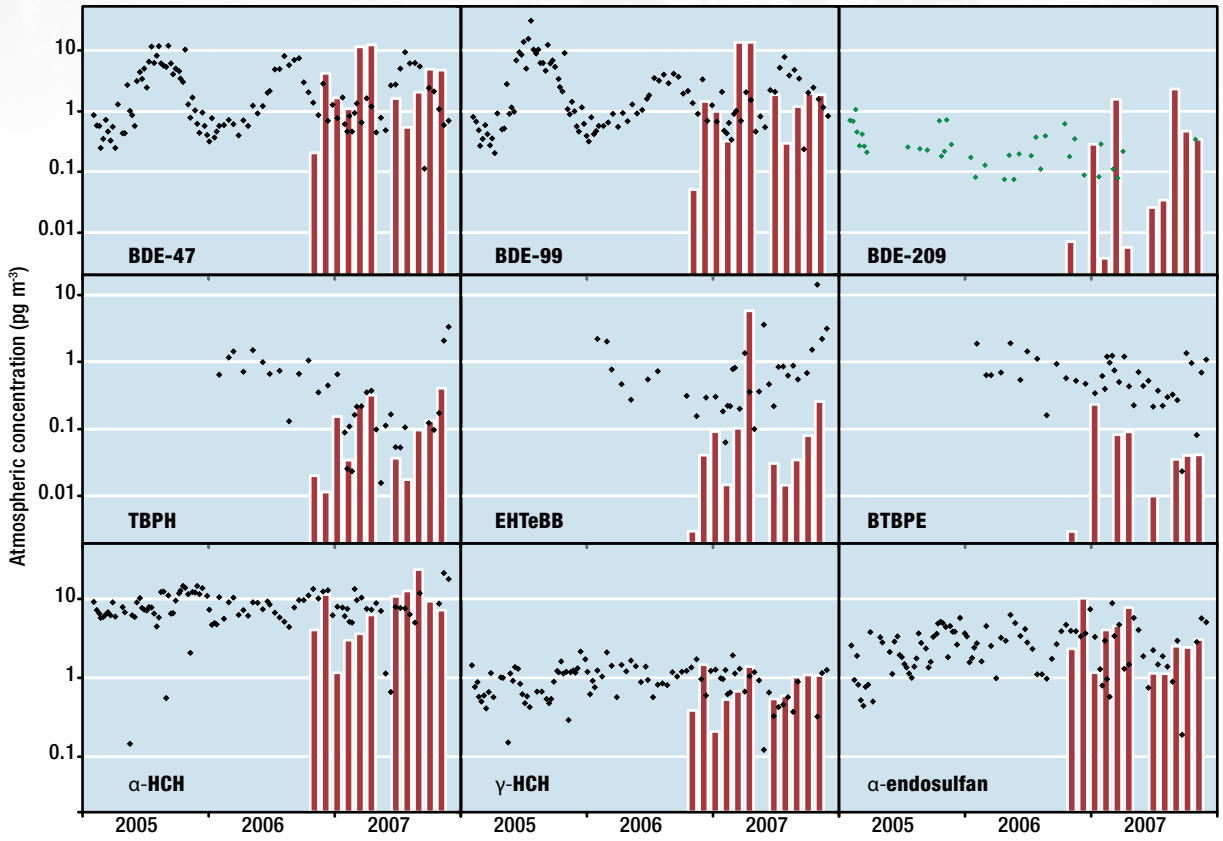

FIGURE 3.3

Comparison of the atmospheric concentration measurements from FTS (red bar) and super Hi-Vol sampler for selected PBDEs, brominated flame retardant (BFRs) and organochlorine pesticides (OCPs). Black diamonds represent the total atmospheric concentrations from super Hi-Vol measurements. For BDE-209, (shown as green diamonds) only particle phase concentrations were plotted here for comparison due to the higher PUF blanks (see text).

Cis- and *trans*-chlordane and *cis*- and *trans*-nonachlor showed extremely slow declining trends (half-lives of 11 to 17 years). This observation is consistent with the fact that technical chlordane has been banned for almost 20–30 years in most western industrialized countries; the decline in air concentrations might have started to level off.

DDT-related compounds were usually found at low levels at Alert (NU). Consistent long-term trends were usually not distinguishable in arctic air (Figure 3.4). However, apparent increasing levels were observed after 2006. This increase could be related to the re-volatilization of DDTs from oceans (Stemmler and Lammel 2009), especially in relation to the severe sea-ice retreat in the Arctic. Moreover, DDT is included in the Stockholm Convention under Annex B, which allows for some uses. Besides the fact that several countries re-introduced DDT, many countries never stopped using it. However, this use is restricted to vector control and not open applications. Thus there may be uses which violate the Stockholm Convention. Another possible source is the use of contaminated dicofol, which is signalled by a high proportion of *o,p'*- isomers.

Several high air concentration episodes of *cis*-chlordane, *p,p'*- and *o,p'*-DDE were observed at Alert (NU) and Ny Ålesund (Svalbard/Norway) in 2004. Primbs et al. (2008) have found that elevated air concentrations of pesticides measured at a remote high elevation mountain site in the western US were related to forest fires due to re-volatilization of these pesticides from soils and vegetation. While no high air concentrations of PCBs were noted at Alert (NU) during the summer forest fire in the Yukon

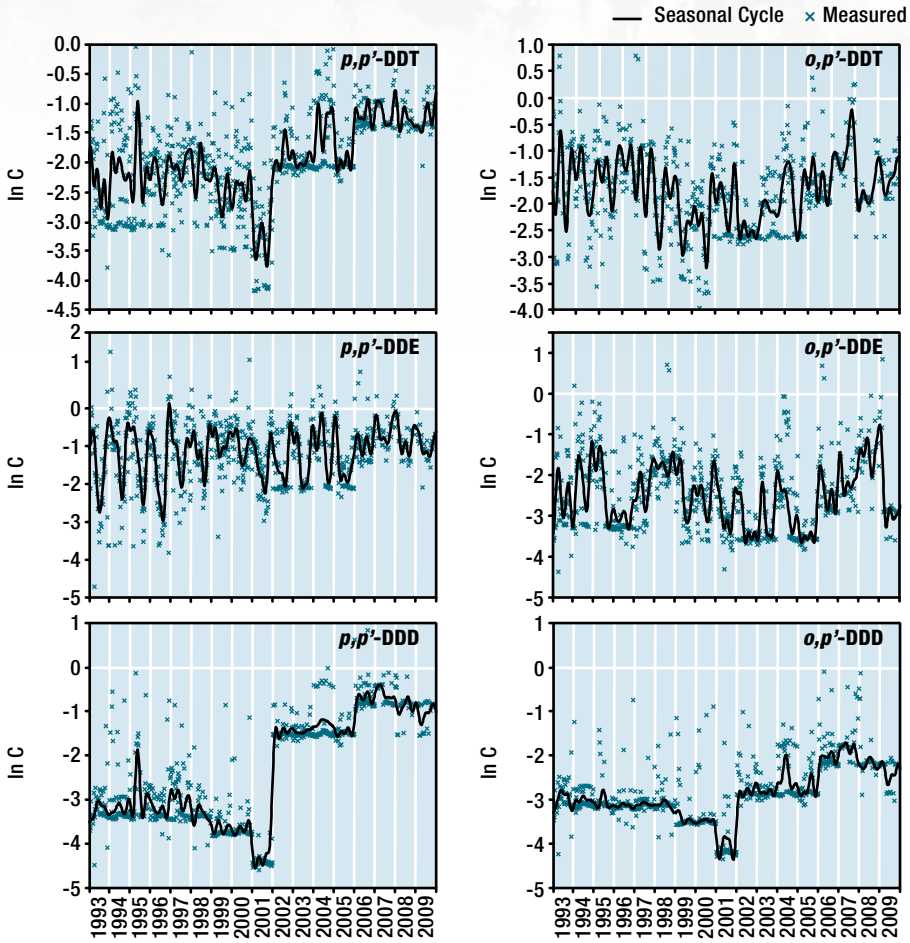

FIGURE 3.4

Atmospheric concentrations (gas and particle phase concentration, pg m^{-3}) of DDTs at Alert (NU). Concentration (C) is displayed using a natural log scale.

and Alaska, elevated concentrations measured for *cis*-chlordane and DDEs in summer 2004 could possibly be the result of biomass burning. Figure 3.5 shows the air concentrations of black carbon (BC), *cis*-chlordane and DDEs measured at Alert (NU) in 2004. Elevated air concentrations of all three OCPs were observed during the haze period from end of April to early May. This is consistent with the fact that *cis*-chlordane and *p,p'*-DDE showed elevated particle-bound concentrations during arctic haze seasons (December to April); with up to 80–90% of the total concentrations found on the filter (associated with particles). During the Yukon and Alaska forest fire event from June to August 2004 (indicated on Figure 3.6 by the blue box), EBC air concentrations were relatively low compared to the haze season. Therefore, higher concentrations of *cis*-chlordane and DDEs observed during this time may be the result of enhanced evaporation of previously deposited pollutants from forest soil during biomass burning. Higher concentrations of other chlordane- and DDT-related compounds were not observed during this period. This could be because *cis*-chlordane is relatively more stable and may remain in soil for prolonged periods of time—degradation half-life of chlordanes in soil is over 20 years (Mattina et al. 1999) and subject to evaporation when temperature increased during a forest fire event. DDTs were used in the Yukon and Alaska region before its ban. Previously deposited DDT would have been degraded to DDEs and DDDs.

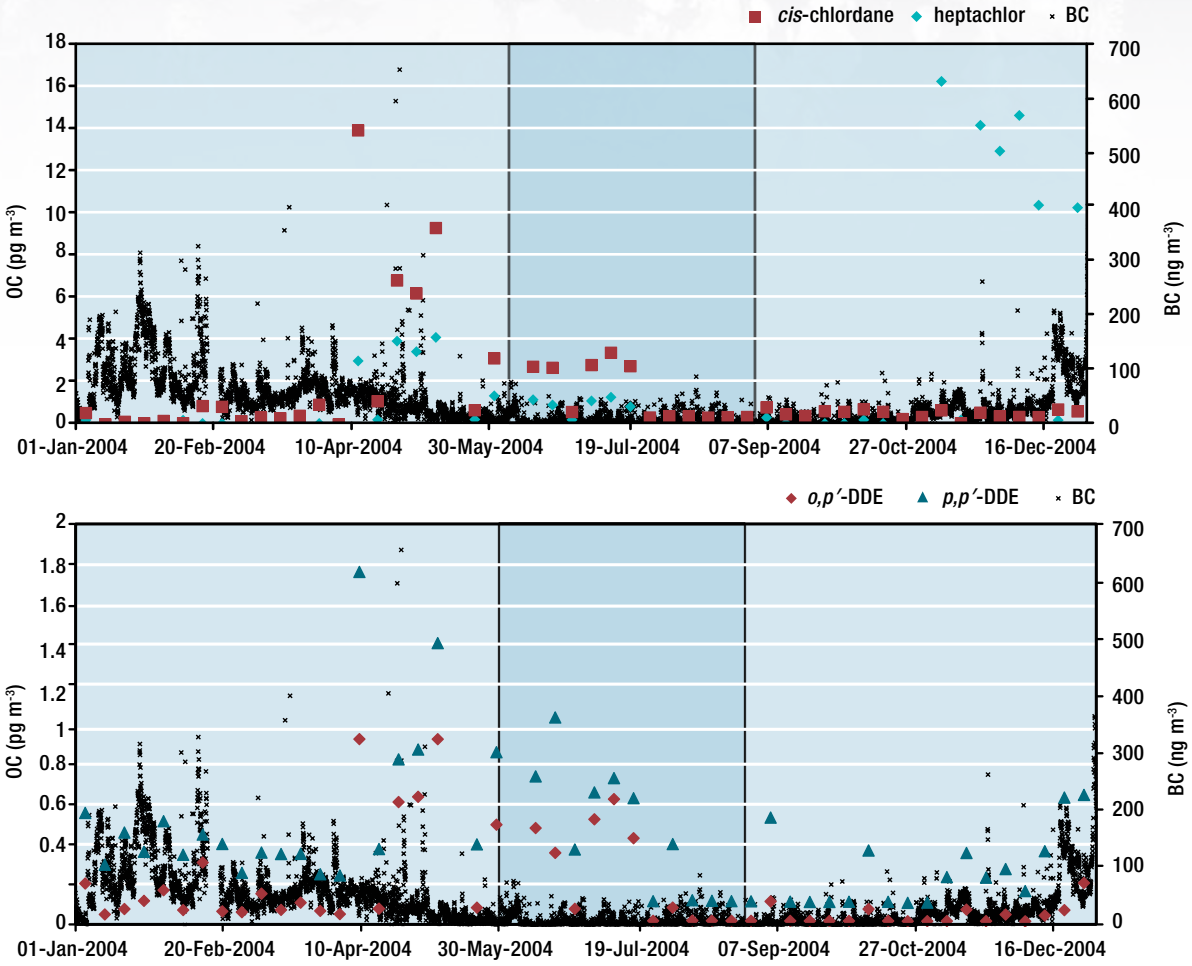

FIGURE 3.5

Air concentrations of BC (ng m^{-3}) and organochlorine (OC) pesticides (a) *cis*-chlordane and heptachlor; and (b) *o,p'*- and *p,p'*-DDE in pg m^{-3} measured at Alert (NU) in 2004. Blue rectangle indicates time period of Yukon and Alaska forest fire.

3.1.4. New persistent chemicals in arctic air – active sampling results

3.1.4.1. Flame retardants (including PBDEs and other new FRs)

Atmospheric PBDE levels have been monitored at Alert (NU) beginning in 2002; and since 2007, a series of "new" BFRs were also added to the list of screened chemicals. Measured concentrations of PBDEs at Alert (NU) are summarized in Annex Table A3-3. BDE 28, 33, 47, 99, 100, 153, 154 and 209 accounted for, on average, 86% (32–97%) of the total of 14 BDE congeners. Dominant congeners were BDE 47 (average 26%, range 3.7–51%), BDE-99 (average 24%, range 5.0–56%) and 209 (average 24%, range 0.66–79%, excluding 2006 data which did not meet QA/QC criteria, see below), reflecting the influence of penta-BDE and deca-BDE technical mixtures (Hung et al. 2010).

The only other arctic station that monitored for PBDEs in air is the station at Nuuk, Greenland, for the period 2004–2005 (Bossi et al. 2008). Despite the fact that Nuuk is a semi-urban location with a population of 13,500 while Alert (NU) is a military base with a crew of approximately 45, average air concentrations of BDE congeners measured at Nuuk were 2.5 to 5.9 times lower than those measured at Alert (NU). PBDE air concentrations measured at Nuuk seem to reflect background levels in the remote Arctic while Alert (NU) may be influenced by the historical use of PBDEs at the military base and the Global Atmospheric Watch (GAW) laboratory facility where the air sampler is located.

Figure 3.6 shows the temporal trends of PBDEs detected at Alert (NU) (2002–2009). For the dominant PBDE congeners, obvious seasonality and temperature dependence were observed. Increasing trends were found from 2002–2005 (Hung et al. 2010). With the addition of 4 years of data, most of the PBDE congeners 28 and 47 showed no significant increasing or decreasing trends while concentrations of PBDEs 99, 100, 153 and 154 appear to be declining after 2006. Measurements need to continue to confirm that such decline persists into the future. The overall estimated half-life ($t_{1/2}$) or doubling time (t_2), which is the time required to decline to half or increase to double of the original concentration, are generally longer than 15 years.

The penta- and octa-BDE technical mixtures have been included in the Stockholm Convention for global control as of May 2009. Certain states in the US, e.g., Maine and California, started to regulate their use as early as 2006. DecaBDE (BDE-209) is currently not under global control by the Stockholm Convention. It is interesting to note that BDE-209 increased continuously until 2005 with a doubling time of 3.5 years (Hung et al. 2010). Unfortunately, high vapour-phase (PUF) blank concentrations of BDE-209 were detected in 2006; rendering the continuation of the time trend impossible at this time. Air concentrations of BDE-209 measured from 2007 to 2009, which were not subjected to blank issues, are shown in Figure 3.6.

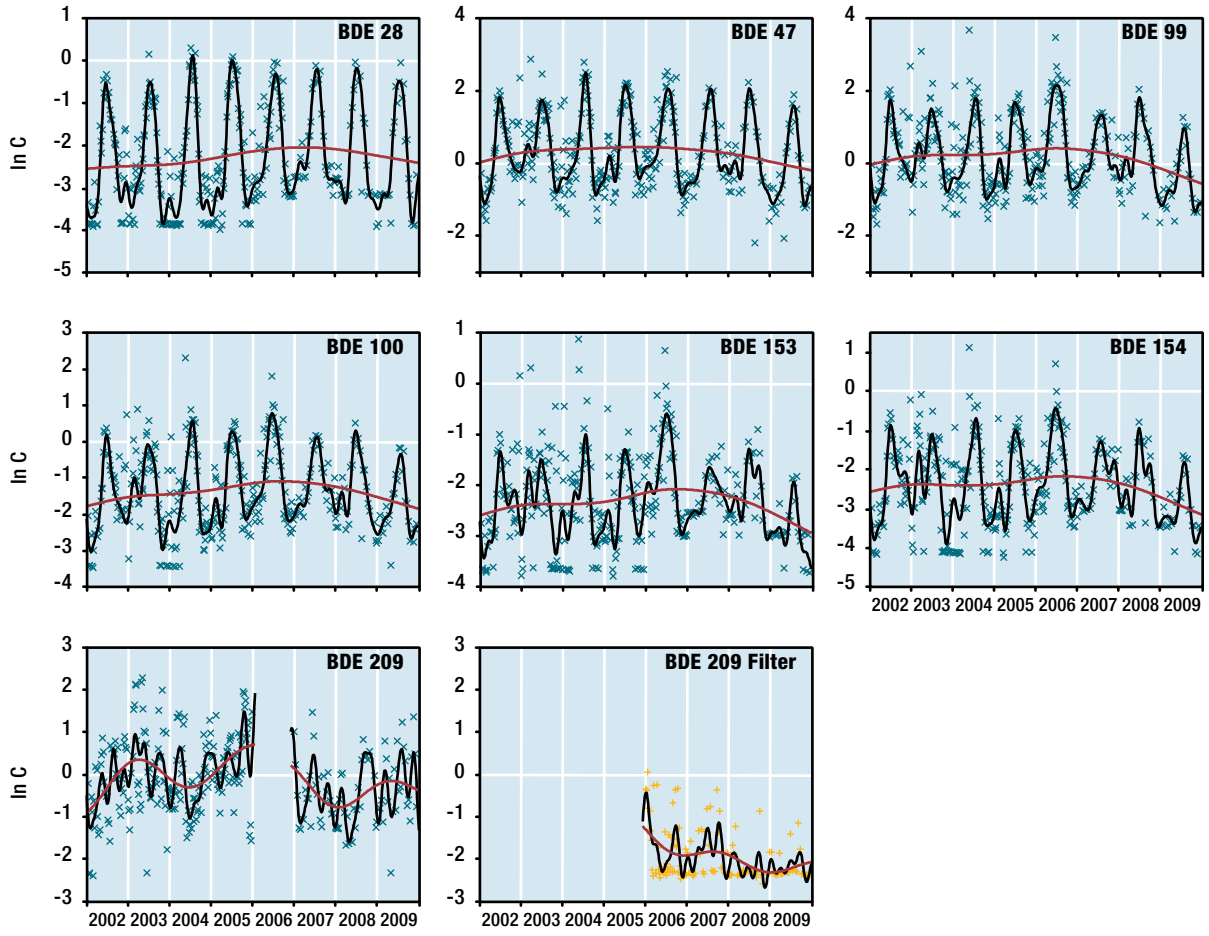

FIGURE 3.6

PBDE (gas and particle phase, pg m^{-3}) temporal trends and seasonal cycles at Alert (NU) (Note: air concentrations of BDE-209 measured in 2006 did not meet QA/QC criteria due to high PUF blanks and therefore are not shown on this plot). Particle phase concentrations of BDE-209 collected on filter only (2006–2009) are shown on the last panel. Concentration (C) is displayed using a natural log scale.

Since the filter and PUFs of each sample were extracted separately, the temporal trend of particle-bound BDE-209 can be rebuilt using particle phase concentrations only. Since the gas- and particle-phase extracts were combined for analysis between 2002 and 2005, the particle extracts need to be reanalyzed before the time trend can be reported in the future. While the air concentrations of lighter BDE congeners, such as BDE-47 and BDE-99, followed the seasonal temperature cycle well, with higher concentrations during the summer and lower concentrations in winter, higher BDE congeners, such as BDE-153 and BDE-209, do not usually show good correlations with temperatures. The difference in seasonality between lighter and higher congeners may be the result of a combination of higher input of heavier congeners bound to particles during the arctic haze season, the difference in the ability of different congeners to bind to particles, the lower volatility and the higher tendency to deposit for the higher congeners (Su et al. 2007).

Beginning in 2007, a series of "new" flame retardants (FRs) were being screened for in air samples taken at Alert (NU). These include thirteen non-PBDE FRs :

- 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE),
- 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EHTeBB),
- bis(2-ethyl-1-hexyl)tetrabromophthalate (TBPH),
- pentabromotoluene (PBTo),
- hexabromobenzene (HBB),
- pentabromobenzene (PBBz),
- allyl 2,4,6-tribromophenyl ether (ATE),
- 2-bromoallyl-2,4,6-tri-bromophenyl ether (BATE),
- tetrabromo-o-chlorotoluene (TBCT),
- 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE),
- 2,2',4,5,5'-pentabromobiphenyl (BB-101),
- pentabromobenzyl acrylate (PBBA),
- octabromotrimethylphenylindane (OBIND);

and two highly chlorinated FRs (*syn*-Dechlorane Plus (*syn*-DP) and *anti*-Dechlorane Plus (*anti*-DP)) (Xiao et al. 2011). See also Table 1.2 in Chapter 1, section 1.3.2. BTBPE, EHTeBB and TBPH were generally detected with concentrations similar to those of the dominant BDE congeners. PBTo and HBB were sometimes detected in the Alert (NU) atmosphere at slightly lower concentrations with no obvious seasonal trends or temperature correlations. All five FRs were included in the high priority list suggested by Harju et al. (2008). Parameters related to their estimated long-range transport potential are cited in Table 3.2. Air concentrations of the 3 major new FRs measured in air at Alert (NU) are shown in Figure 3.7.

Air concentrations of BTBPE at Alert (NU) ranged from 0.16 pg m^{-3} to 1.9 pg m^{-3} with no significant temperature dependence, indicating insignificant local emissions around the vicinity of Alert (NU). The concentrations found at Alert (NU) were similar to those reported in air in the Great Lakes region (0.5 pg m^{-3} to 1.2 pg m^{-3}) (Venier and Hites 2008).

TABLE 3.2. Model estimation results of long range transport potential of selected brominated flame retardants cited from Harju et al. (2008).

	log K_{OA}	log K_{AW}	Half-life in air (hours)	Half-life in water (hours)	Half-life in soil (hours)	Overall persistence (days)	CTD (km)	Φ_{Air}	Transfer efficiency in %
BTBPE	15	-5.2	8.6	4,300	8,600	520	2,800	1	12
EHTeBB[a]	12	-3.6							
TBPH	18	-6	5.9	1,400	2,900	170	2,900	1	13
PBTo	9.5	-3	690	4,300	8,600	510	6,900	0.01	
HBB	9.9	-3	11,000	4,300	8,600	520	11,000	0.023	

[a] Cited from Ruan et al. (2009), calculated from US EPA EPI Suite V3.20; Physical chemical partitioning properties and degradation half-lives were estimated using SPARC and EPI Suite, respectively. Characteristic travel distance (CTD) in km, transfer efficiency in % and the estimated particle bound fraction in the atmosphere (Φ_{Air}) are also given.

The average atmospheric concentration of EHTeBB at Alert (NU) was 0.74 pg m^{-3}, with a range from 0.16 pg m^{-3} to 2.2 pg m^{-3}. The average TBPH concentration at Alert (NU) was 0.80 pg m^{-3} with a range of 0.1 pg m^{-3} to 1.5 pg m^{-3}. EHTeBB and TBPH are two major components in Firemaster® 550 (FM 550), a replacement for PBDEs. The mass ratio of EHTeBB to TBPH in FM 550 is approximately 4 (Stapleton et al. 2008). TBPH is also added to Dechlorane Plus 45 (DP-45), a liquid flame retarded plasticizer (Andersson et al. 2006) The ratio of EHTeBB/TBPH present in the air samples from Alert (NU) varied from 0.18 to 3.4 with an average of 0.92. It is believed that the degradation rates of both EHTeBB and TBPH are slower than those of nona-BDEs (Davis and Stapleton 2009). Thus the lower EHTeBB/TBPH ratios found at Alert (NU) are unlikely to be due to the degradation rate difference. Considering that EHTeBB is presumably the more volatile of these two compounds (Ruan et al. 2009), it is reasonable to believe that the TBPH levels at Alert (NU) are partly due to sources other than FM 550.

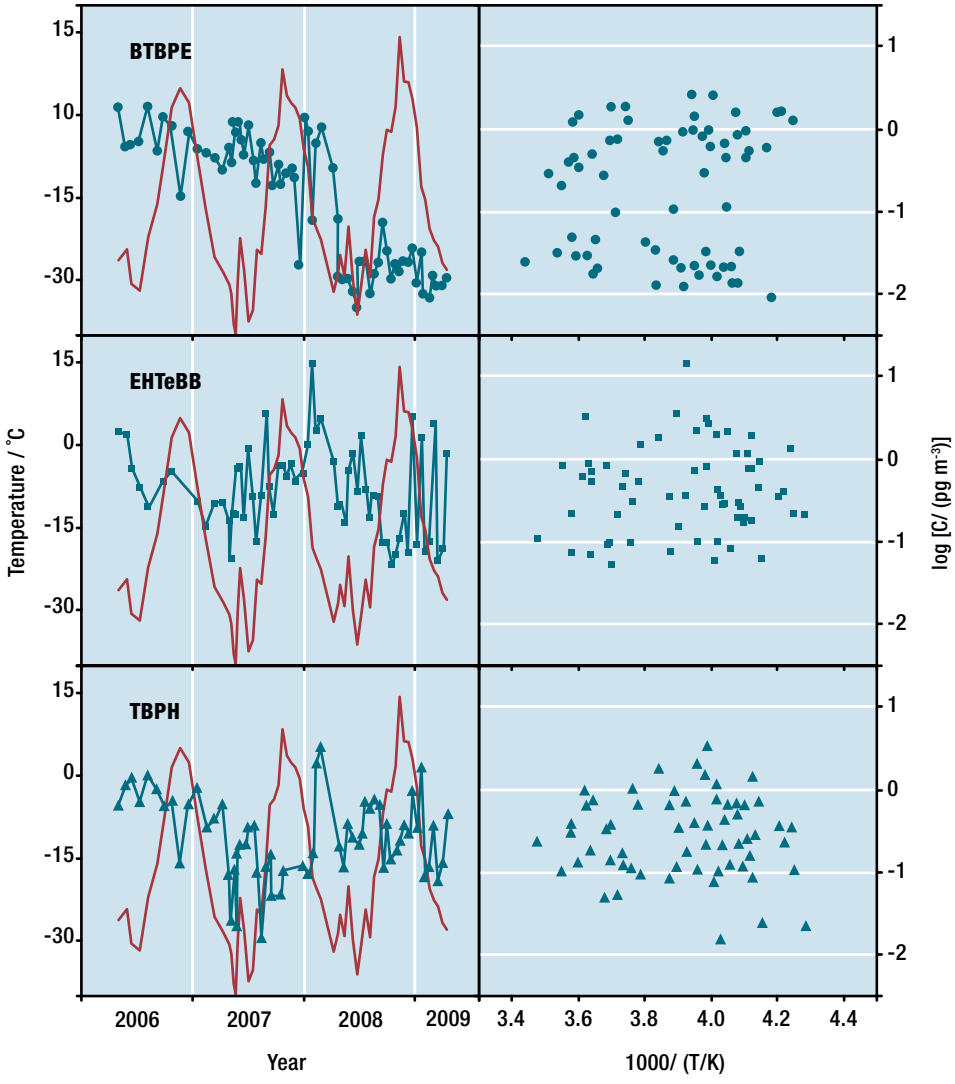

FIGURE 3.7

Seasonal variation in concentrations (pg m^{-3}) and temperature dependence of alternative BFRs at Alert (NU). The right hand panels illustrate the temperature dependence of each BFR. Temperature is shown in red.

DP was detected in 11 out of 14 Alert (NU) samples. The total DP concentrations varied from not detected (< 0.05 pg m^{-3}) to 2.1 pg m^{-3}. The *anti*-DP isomer was the dominant isomer with a concentration up to 1.9 pg m^{-3}, which is similar to the level of BDE-153 and BDE-154 found at the same site. The average concentrations for *syn*-DP and *anti*-DP were 0.18 pg $m^{-3}$and 0.57 pg m^{-3}, respectively. During a recent cruise from the East Greenland Sea to Antarctica, DP was ubiquitously present in the marine air boundary layer (Möller et al. 2010). The lowest and the highest concentrations, 0.05 pg m^{-3} and 4.2 pg m^{-3}, respectively, were detected successively near East Greenland, while the concentration range was similar to what was found at Alert (NU). The mean fractional abundance of *syn*-DP, defined as the percentage of *syn*-DP in total DP, varied from 7% to 46% with an average of 28%, which is very close to the previously reported composition of commercial DP mixtures (Tomy et al. 2007) and to what has been observed in the atmosphere of urban or source regions (Hoh et al. 2006, Ma et al. 2011, Qiu et al. 2010, Ren et al. 2008, Wang et al. 2010b). Consistent with previous studies (Hoh et al. 2006), the DP detected at Alert (NU) was primarily associated with particles.

BTBPE, EHTeBB and TBPH were detected at relatively high levels comparable to those of the PBDE congeners (see Annex Table A3-3). Their occurrence in air at the remote arctic station of Alert (NU) highlights the urgency of further investigations. Considering that the air concentrations of these new FRs are similar to those of the PBDEs, further research on their toxicology and environmental risk is called for.

Figure 3.4 shows the comparison of results reported by the FTS and the conventional Hi-Vol sampler for PBDEs and three dominant "new" BFRs, namely BTBPE, EHTeBB and TBPH. For most compounds, both the absolute levels and the trends reported by these two sampling methods generally agree well. For BDE-209, due to the relatively high PUF blank levels for the super Hi-Vol samples, no significant differences were found between the PUF samples and the corresponding PUF blanks. Only particulate concentrations derived from the filters of the super Hi-Vol samples were used for comparison with FTS results in Figure 3.4. It clearly shows that these two techniques gave very good agreement. Events of low FTS-derived air concentrations for BDE-209 were consistent with samples from the super Hi-vol that were below detection. Details on comparability between the FTS and the super Hi-Vol can be found in Xiao et al. (2012).

3.1.4.2. Polychlorinated naphthalenes in arctic air and snow

A technical review of the Polychlorinated naphthalenes (PCNs) dossier by the UNECE Task Force on POPs supported the dossier's conclusion that PCNs be considered for inclusion in the LRTAP Convention (UNECE 2006). At the Stockholm Convention COP in 2011, the EU also proposed chlorinated naphthalenes for addition to the Stockholm Convention. Like other POPs, PCNs are globally distributed. Their sources, pathways and occurrences in air and biota of polar regions have been reviewed by Bidleman et al. (2010) (see Chapter 2, section 2.3.6.2).

3.1.4.2.1 Overview of PCNs in arctic air

Atmospheric half-lives of PCNs with respect to gas-phase OH radical reaction were predicted by Puzyn et al. (2007) as: 2 days (monochloronaphthalenes, mono-CNs), 5 days (di-CNs), 10 days (tri-CNs), 19 days (tetra-CNs), 39 days (penta-CNs), 79 days (hexa-CNs), 163 days (hepta-CNs) and 343 days (octa-CN). The Stockholm Convention (Annex D) (UNEP 2001) recognizes an atmospheric half-life > 2 days as a criterion for long-range transport potential, which is exceeded by all but the mono-CNs. Several studies have measured PCNs in atmospheric samples from arctic and subarctic regions, but different numbers of homologues and congeners have been reported by various investigators, making comparison of concentrations difficult. Air concentrations of ΣPCNs, locations, homologues and congeners that were determined are summarized in Table 3.3. Spatial trends for locations where 37 or more CN congeners were measured and are illustrated in Figure 3.8.

PCNs were first quantified in arctic air by Harner et al. (1998), who collected shipboard samples in 1996 in the Barents Sea, Norwegian Sea, eastern Arctic Ocean, and in a few archived air sample extracts from 1993–1994. The latter were taken at land-based high arctic stations at Alert (NU), Canada and Dunai, Russia. Average concentrations of ΣPCNs (3–8 Cl) in air were 3.5 pg m^{-3} and 0.84 pg m^{-3} at the two land stations, while shipboard averages ranged from 7.1–40 pg m^{-3} in the three ocean regions. A follow-up study at Dunai (Russia), Alert (NU) and subarctic Tagish (YK) was done with archived air sample extracts covering a full year from 1994–1995 (Helm et al. 2004). Annual mean ΣPCNs (3–8 Cl) was 0.66 pg m^{-3} at both the Dunai (Russia) and Alert (NU) stations and was lower at Tagish (YK), 0.37 pg m^{-3}. The ΣPCNs levels at Dunai (Russia) and Alert (NU) were higher during winter, spring and fall compared to summer, while seasonal differences

TABLE 3.3. ΣPCNs in air of arctic and subarctic regions, pg m^{-3}

Location	Latitude degrees	Longitude degrees	Year	Mean ΣPCNs	Homologues	Congeners analyzed	Reference[1]
Alert, Canada	82.5N	62.3W	1993–94	3.5	3–8	40	1
Alert, Canada	82.5N	62.3W	1994–95	0.66	3–8	40	2
Alert, Canada	82.5N	62.3W	2004–05	1.2	3–8	49	3
Dunai, Russia	74.1N	124.5E	1993	0.84	3–8	40	1
Dunai, Russia	74.1N	124.5E	1994–95	0.66	3–8	40	2
Tagish, Canada	60.3N	134.2W	1994–95	0.37	3–8	40	2
Resolute Bay, Canada	74.6N	94.9W	1999	4.2	3–8	40	4
Eastern Archipelago, Canada	63.7–74.6N	68.5–94.9W	1999	7.4	3–8	40	4
Norwegian Sea	63.4–74.4N	6.3–16.0E	1996	7.1	3–8	40	1
Barents Sea	71.1–80.3N	21.6–65.7E	1996	40	3–8	40	1
Eastern Arctic Ocean	74.6–89.9N	10.9–179.9E	1996	12	3–8	40	1
Ny-Ålesund, Norway	78.5N	11.5E	2001	35	3–8	44	5
Ny-Ålesund, Norway	78.5N	11.5E	2004–05	7.6	3–8	49	3
Tromsø, Norway	69.7N	17.0E	2003	25	3–8	44	5
Ammernäs, Sweden	65.5N	43.7E	1990–91	1.6	4–6	37	6
Nuuk, Greenland	64.1N	51.4W	2004–05	0.16	3–7	13	7
Storhofdi, Iceland	63.4N	20.3W	2004–05	0.86	3–8	49	3
Barrow, USA	71.3N	156.8W	2004–05	2.3	3–8	49	3

[1]References 1: Harner et al. 1998; 2: Helm et al. 2004; 3: Lee et al. 2007; 4: Helm 2002; 5: Herbert et al. 2005b; 6: Egebäck et al. 2004; 7: Bossi et al. 2008

were not apparent at Tagish (YK). The higher concentrations of ΣPCNs at Alert (NU) and Dunai (Russia) during the cold months were in contrast to the trend for mono- and non-ortho PCBs, which showed no distinct seasonality. Helm et al. (2004) noted that the ΣPCNs appeared to follow the trend for arctic haze, which is a prominent feature of the high arctic air mass in winter and spring, and that combustion related PAHs also peaked during the haze season (Halsall et al. 1997). In the summer of 1999, Helm (2002) conducted air sampling at Resolute Bay (NU), Canada and from shipboard in the eastern Canadian Archipelago with mean ΣPCNs (3–8 Cl) concentrations of 4.2 pg m^{-3} and 7.4 pg m^{-3}, respectively. Helm (2002) observed a decrease in the ΣPCNs and the tri-, tetra- and penta-CN homologues in air with decreasing temperature at Resolute Bay. Plots of the Clausius-Clapeyron equation (ln partial pressure vs. 1/T) yielded apparent enthalpies of air-surface exchange (ΔH_{EX}) of 68 kJ mol^{-1} for the ΣPCNs and 44–91 kJ mol^{-1} for the homologues. These are similar to enthalpies of vapourization and octanol-air partitioning, which implies regional air-surface exchange, as has been noted for PCNs in temperate regions (Lee et al. 2000).

Herbert et al. (2005b) sampled air in winter months at the Norwegian arctic research station at Ny-Ålesund (Norway) during the month of April 2001 and in Tromsø (Norway) and from February to March 2003. Mean ΣPCNs (3–8 Cl) were relatively high at both stations, 35 pg m^{-3} and 25 pg m^{-3} respectively, similar to those found over the Barents Sea in 1996 (Harner et al. 1998).

Egebäck et al. (2004) collected air samples from September 1990 to March 1991 at Ammarnäs, a meteorological station in northern Sweden. The mean ΣPCNs was 1.6 pg m^{-3}, though only the 4–6 Cl CNs were determined. Parallel sampling was done at Hoburgen, a station in southern Sweden, where ΣPCNs averaged 5.1 pg m^{-3}. At a third station in southern Sweden, tri-CNs were also measured in air and deposition, and accounted for approximately 60% of ΣPCNs. Similarly high proportions of tri-CNs were found at other arctic stations (see below). With this consideration, the ΣPCNs at Ammarnäs and Hoburgen might be raised to approximately 4 pg m^{-3} and approximately 13 pg m^{-3}, respectively, to include the tri-CNs for comparison to other studies.

Bossi et al. (2008) carried out air sampling at Nuuk, Greenland during 2004–2005. The annual mean ΣPCNs

(3–7 Cl) was 0.16 pg m^{-3}. Similarly to results observed at Tagish (YK) (Helm et al. 2004), no seasonality in ΣPCNs concentrations was observed over this time frame. Since only 13 congeners were quantified, including one tri-CN, it is difficult to compare these ΣPCNs levels with those in other studies. Relationships were explored between atmospheric concentrations of semi-volatile compounds and carbon monoxide, which is considered to be an indicator of anthropogenic influence. Although significant correlations were obtained for some compounds: positive for chlordanes, *p,p'*-DDE, trifluralin and negative for γ-HCH, correlations for other organochlorine pesticides (dieldrin, endosulfan, α-HCH) and ΣPCNs were not significant.

The ΣPCNs (3–8 Cl) in pg m^{-3}, at arctic and subarctic sites in the first phase of the Global Atmospheric Passive Sampling (GAPS) study were: Alert (NU) 1.2, Ny-Ålesund (Svalbard/Norway) 7.6, Storhofdi (Iceland), 0.86 and Barrow (AK), USA 2.3. PCNs were below the limits of detection, 0.0007–0.23 pg m^{-3} per congener, at the Italian base in Antarctica (Lee et al. 2007).

Farrar et al. (2006) and Jaward et al. (2004) deployed passive air samplers across Europe to determine spatial trends of PCNs and other POPs in air. Farrar et al. (2006) used polymer coated glass slides, which were deployed for seven days in June 2002. Jaward et al. (2004) deployed GAPS PUF disk type samplers from June to July, 2002. Both groups included two arctic and subarctic stations in Ny-Ålesund and Iceland. Although these papers show relative ΣPCNs concentrations (based on analysis of 10–17 congeners) on bar graphs, neither report numerical values for most sites. Jaward et al. (2004) found no correlation between CN congeners and PAH congeners in the European air survey. Farrar et al. (2006) found a significant correlation of PCNs with only one PAH, benzo[ghi]perylene, but PCNs were significantly correlated with most PCB congeners.

3.1.4.2.2. Potential source regions

As shown in Figure 3.8, the ΣPCNs concentrations in air are much higher at most European arctic and subarctic locations than at sites in Siberia, Iceland, Alaska and the Canadian Arctic. Harner et al. (1998) noted that high concentrations in the Barents Sea were associated with five-day air parcel trajectories from Europe, while samples with lowest ΣPCNs had air mass origins over the open ocean, northern Scandinavia and Greenland. Herbert et al. (2005b) measured elevated ΣPCNs at Ny-Ålesund during a period when air trajectories originated from western Europe, the UK and Scandinavia. However, the authors could not rule out the possibility of PCN contamination from the local scientific facility

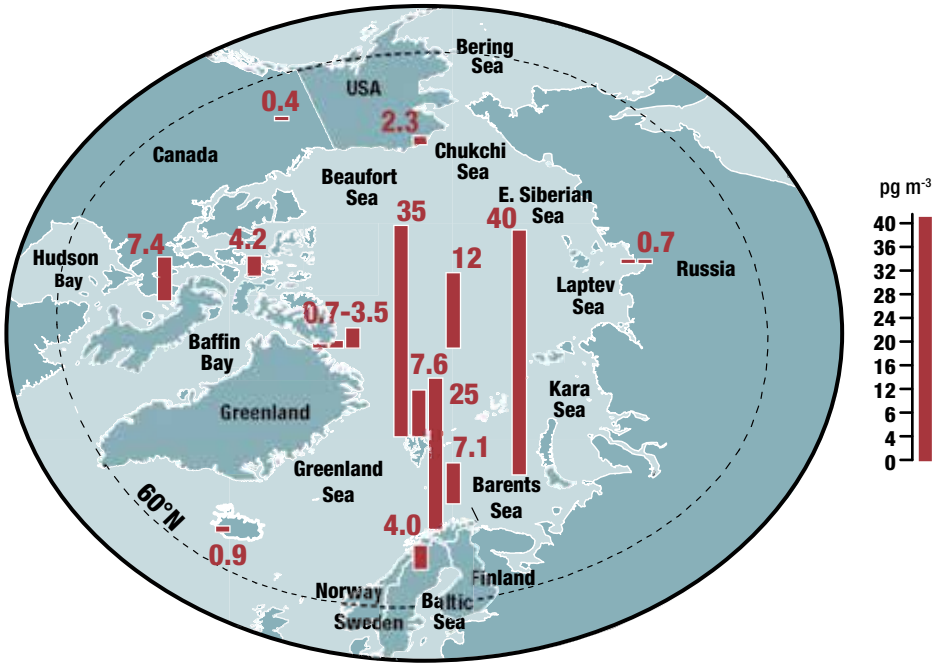

FIGURE 3.8

ΣPCNs in air of arctic and subarctic regions, pg m^{-3}. Data are included for those studies that measured 37 or more congeners (Table 3.3). The ΣPCN concentration of 1.6 pg m^{-3} in northern Sweden, based on the analysis of the 4–6 Cl homologues (Egebäck et al. 2004), was increased to 4.0 pg m^{-3} by assuming that tri-CNs accounted for 60% of ΣPCNs.

at Ny-Ålesund or the city of Tromsø. Air trajectories were examined for PCN samples collected in 1994 at Hazelrigg, a semi-rural site in northwest England. Higher levels of ΣPCNs (pg m^{-3}) were found in samples with trajectories from the UK (108 ± 115) compared to those with trajectories from other areas of Europe (74 ± 65), the North Atlantic (52 ± 17) and arctic Scandinavian regions (20 ± 13) (Harner et al. 2000b). The ΣPCNs in air at sites in England did not decline from 1994 to 2001, in contrast to declining levels of ΣPCBs over the same time period in the UK (Lee et al. 2005).

Although the ΣPCNs at Dunai (Russia), Alert (NU) and Tagish (YK) were much lower than those in the European Arctic, Helm et al. (2004) were able to make inferences about source quadrants based on five-day air trajectories. Levels at Dunai (Russia) were positively correlated ($p < 0.05$) with the fraction of time that air parcels originated over eastern and western Russia. At Alert (NU), ΣPCNs were weakly correlated ($p < 0.1$) with the time over the North Atlantic and Europe and negatively correlated ($p < 0.05$) with the percent of air masses originating from the North American sector. Tagish (YK) is a high elevation site (2200 m) and air arrived from the North Pacific for most of the period of the analysis. No relationships were found for ΣPCNs concentrations and air transport direction at Resolute Bay (NU) or the eastern Canadian Archipelago (Helm 2002).

Figure 3.8 shows 1–2 orders of magnitude difference in ΣPCNs concentrations among circumpolar arctic and subarctic stations. By comparison, the variability in median concentrations of legacy organochlorine pesticides (chlordanes, HCHs, dieldrin, *p,p'*-DDE) among circumpolar air monitoring stations is only about a factor of 2–3 (Su et al. 2006, 2008).

Concentrations of Σ_{37-49} PCNs in arctic air (0.37–40 pg m^{-3}, median 3.5 pg m^{-3}, Table 3.3) can be compared to those of ΣPCBs. A survey of 102 PCB congeners at Alert (NU), Tagish (YK) and Dunai (Russia) from 1992–1994 showed similar Σ_{10}PCBs levels at Dunai (Russia) and Alert (NU) (27 pg m^{-3} and 34 pg m^{-3}, respectively) and lower concentrations at Tagish (YK) (17 pg m^{-3}). A heavier PCB congener profile characterized the Dunai (Russia) site. The Σ_{10}AMAP PCBs at the same sites were 5.8, 8.1 and 3.7 pg m^{-3}, respectively (Hung et al. 2001, Stern et al. 1997). Reports of PCBs in 2000–2005 were only for the Σ_{10} AMAP congeners: 2.8, 8.5 and 7.4 pg m^{-3} at Alert (NU), Ny Ålesund (Svalbard/Norway) and Storhofdi (Iceland), respectively, and 6.1 pg m^{-3} for the Σ_7 congeners at Pallas (Finland) (Hung et al. 2010). Temporal trends of ΣPCNs in arctic air have not been assessed, but there are no indications of decline in UK air between the mid-1990s and 2001 (Lee et al. 2005).

3.1.4.2.3. Homologue and congener profiles

PCN homologues at Alert (NU) and Dunai (Russia) were dominated by tri-CNs, which accounted for 60% or more of ΣPCNs, followed by 20–35% contribution of tetra-CNs, with the remainder consisting of penta-, hexa-, hepta- and octa-CNs. (Harner et al. 1998, Helm et al. 2004). Tri-CNs and tetra-CNs accounted for 55% and 35–40% of ΣPCNs at Tagish (YK). Penta-CNs made up approximately 10% of, and heavier CNs < 2% of ΣPCNs (Helm et al. 2004). A similar distribution was found at Resolute Bay (NU) and in the Canadian Archipelago: 48–65% tri-CNs, 26–47% tetra-CNs, 8–10% penta-CNs and 1–2% of the heavier CNs (Helm 2002). Homologue profiles in the Norwegian Sea and eastern Arctic Ocean showed 45–50% and 35% contributions of tri-CNs and tetra-CNs, respectively, while tetra-CNs were slightly higher than tri-CNs in the Barents Sea, each homologue accounting for 40–45% of ΣPCNs (Harner et al. 1998).

Herbert et al. (2005b) found that tri-CNs contributed 65–70% and tetra-CNs 28–30% of ΣPCNs in air at Ny-Ålesund and Tromsø. The tri-CNs in snow accounted for 84% of ΣPCNs at Ny-Ålesund, but only 40% of ΣPCNs at Tromsø, where tetra-CNs dominated (54% of ΣPCNs). Lee et al. (2007) reported that tri-CNs accounted for 70–80% of ΣPCNs at Alert (NU) and Barrow (AK), but 55% of ΣPCNs at Ny-Ålesund. Tetra-CNs made up 15–20% of ΣPCNs at Alert (NU) and Barrow (AK), and 40% at Ny-Ålesund.

PCNs are released to the air by volatilization from in-use or disposed products and from contaminated soil. They are also emitted by industrial and waste incineration processes due to de *novo* synthesis as well as release from within the incinerated waste. Ongoing emissions from combustion sources contribute PCNs to the atmosphere even though industrial use of PCNs has stopped. Several CN congeners present in combustion effluents are either absent or occur at only minor levels in commercial PCN mixtures. Distinction of CNs from "combustion" vs. "evaporation" sources and identification of combustion-related CNs in arctic air is discussed in Chapter 2, section 2.3.6.2., whereas a discussion of PCNs in snow is made in section 3.1.6.3.

3.1.4.3. Poly- and perfluoroalkyl substances (PFASs)

Poly- and perfluoroalkyl substances (PFASs) are generating intense scientific and regulatory interest because of their widespread detection, persistence in the environment, potential toxicity and bioaccumulation. Among the PFASs, perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are routinely measured in humans and biota, including those from remote regions. These findings have contributed to the recent listing of PFOS as a POP under the LRTAP POPs Protocol and the Stockholm Convention (see Chapter 1). The transport pathway for PFASs is still under scientific debate, however it was hypothesized that the occurrence of PFASs in the Arctic is possibly due to two major pathways or combination of both: (1) atmospheric transport of volatile precursors which degrade to less volatile PFASs (e.g., PFOA and PFOS) and deposit via wet and dry deposition, or (2) oceanic transport of directly emitted PFASs to the Arctic. While modeling studies have predicted that the oceanic pathway is dominant, PFASs have been detected in arctic air, surface snow, ice caps, arctic lake water, sediment and fish; indicative of atmospheric deposition. Trends of PFASs in fish and wildlife are discussed in Chapter 4.

The first study to investigate the precursor compounds of PFOA and PFOS (fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs) and sulfonamidoethanols (FOSEs)) was carried out in July 2005 (Shoeib et al. 2006). Twenty, 24-hour high volume air samples (sample volumes of approximately 300 m^3 each) were collected during a crossing of the North Atlantic and Canadian Archipelago on the Oden Icebreaker. PFASs were detected above the method detection limit (MDL) in 100% of the samples. The highest concentrations (sum of gas- and particle-phase) of FTOHs were for 8:2 FTOH (5.8–26 pg m^{-3}), followed by 10:2 FTOH (1.9–17 pg m^{-3}) and 6:2 FTOH [below detection limit (BDL) to 6.0 pg m^{-3}]. For the FOSAs and FOSEs, MeFOSE was dominant and ranged from 2.6 pg m^{-3} to 31 pg m^{-3};

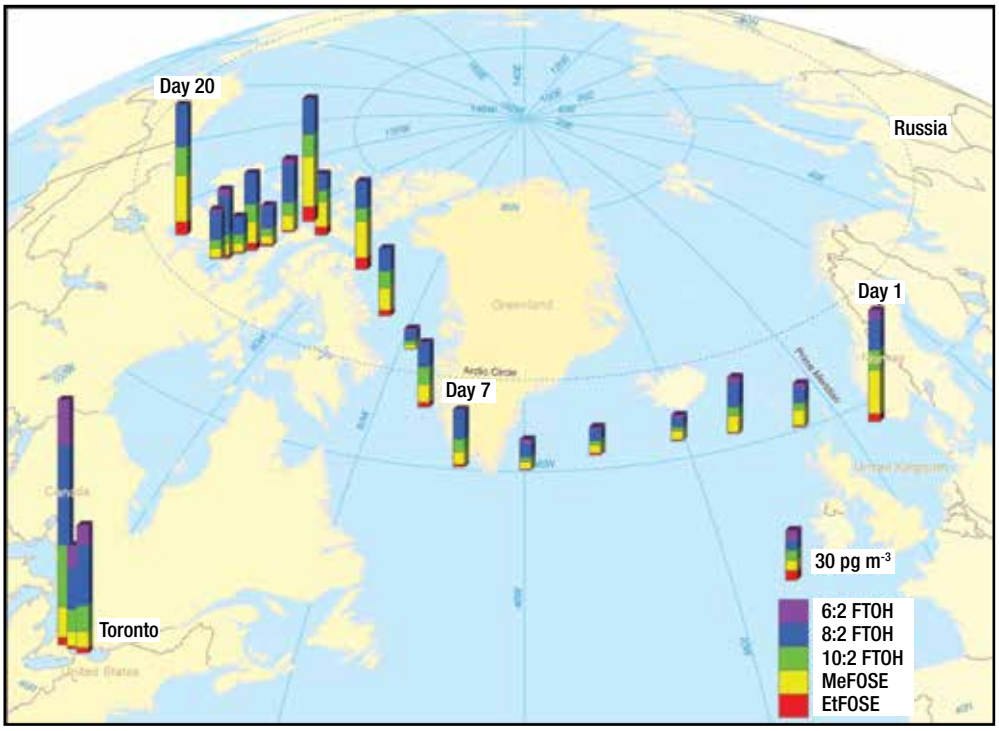

FIGURE 3.9

Total air concentrations (sum of gas phase and particle phase, pg m^{-3}) for FTOHs and FOSEs across the North Atlantic Ocean and Canadian Archipelago and in Toronto, Canada (from Shoeib et al. 2006).

EtFOSE ranged from BDL to 8.9 pg m^{-3} and MeFOSEA was BDL in all samples. The mean 8:2 FTOH concentration was only a factor of about 3 lower than for three urban samples that were collected in Toronto (ON) for comparison. Wallington et al. (2006) applied a 3D global atmospheric chemistry and transport model that predicts FTOHs (namely, 8:2 FTOH) and related degradation products are ubiquitous in the arctic region at about one-fifth the concentrations observed in source regions. The empirical data above were the first to confirm model results that predict the efficient, long range atmospheric transport and widespread distribution of FTOHs and related compounds in the arctic region. It was observed that the proportions of the two dominant PFASs changed systematically across the cruise track (Figure 3.9).

MeFOSE was dominant in the early samples in the eastern part of the North Atlantic Ocean. Air parcel back-trajectories for these samples were also more representative of the North Atlantic region. The elevated air concentrations for the first sample are consistent with air that passed over potential source regions in northern England and Ireland just prior to arriving at the ship. The samples collected west of Greenland showed a dominance of 8:2 FTOH. Back-trajectories for these samples stemmed from the Canadian Archipelago and Beaufort Sea (Shoeib et al. 2006). These results suggest a characteristic signature or composition of PFASs for different parts of the arctic region. Air parcel back-trajectories showed that the sampled air was largely representative of the arctic air mass confirming the widespread distribution of the precursor compounds in the Arctic.

The partitioning behavior of PFASs was also reported in this study. Mean particle percentages for FTOHs and FOSAs in the cruise samples (mean temperature, 5 ± 4 °C) were BDL for 6:2 FTOH, 23% for 8:2 FTOH, 15% for 10:2 FTOH, 32% for MeFOSE, and 22% for EtFOSE. Further, the partitioning to particles for MeFOSE and EtFOSE was significantly correlated with inverse absolute temperature, whereas the FTOHs did not show this trend. The Toronto samples (mean temperature, -1 ± 1 °C) showed similar particulate percentages for MeFOSE and EtFOSE; however, the FTOHs were substantially less particle-bound, consistent with other research. The high particulate percentage of 8:2 FTOH and 10:2 FTOH found in this study, was explained by a potential contribution of sea spray and/or mist aerosols. However, other ship based samples show less 8:2 and 10:2 FTOH loading on particle (Ahrens et al. 2011, Dreyer et al. 2009, Shoeib et al. 2010). Although the mechanism for this partitioning is not understood, the results do indicate the need to better account for particle phase transport when modeling the atmospheric fate of these chemicals.

The second study of PFASs in air from the arctic region was carried out at Resolute Bay (NU) (Stock et al. 2007). Ten air samples were collected in the summer of 2004 using a high volume air sampler located 1 km west of the airport and 2.5 km of the Barrow Strait on the southern coast of Cornwallis Island. Samples were analyzed for more suites of PFASs: perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs) precursor chemicals including the FTOHs, FOSAs, FOSEs, and precursor degradation products such as the fluorotelomer unsaturated carboxylates (FTUCAs).

Figure 3.10 shows the concentration of PFASs (particle and gas phases) obtained at Cornwallis. Mean values of total concentrations of FTOHs ranged from 2.8 pg m^{-3} for 10:2 FTOH to 14 pg m^{-3} for 8:2 FTOH. Mean concentration of ΣFTOHs was 28 pg m^{-3}. Although the 8:2 FTOH was the most frequently observed FTOH, the range of concentrations (not detected to approximately 20 pg m^{-3}) of the 8:2 FTOH was not significantly different from that observed for the 6:2 FTOH. Among FOSAs and FOSEs, MeFOSE was the dominant compound with the largest mean concentration (29 pg m^{-3}), observed > the method detection limit (MDL) in 60% of samples. EtFOSE, EtFOSA, MeFBSE, and EtFBSE were observed at similar concentrations (mean values of total concentrations ranged from 11 pg m^{-3} to 23 pg m^{-3}). Mean concentration of ΣFOSAs/FOSEs was 112 pg m^{-3}. Mean values of total concentrations of PFSAs were higher than the FTOHs. The concentrations of FOSAs, FOSEs and FTOHs determined in this study are similar to those reported by Shoeib et al. (2006). These results confirm that volatile precursors, such as FOSAs, FOSEs and FTOHs, reach arctic latitudes.

PFSAs and PFCAs were detected on atmospheric particles with mean concentrations that ranged from < 0.1 pg m^{-3} to 5.9 pg m^{-3}. The dominant contaminant was PFOS (mean con-centration of 5.9 pg m^{-3}), observed > the limit of quantification (LOQ) in 90% of samples. PFOS concentrations were 1–2 orders of magnitude greater than other detected PFSAs and PFCAs. PFHxS and PFDS were also observed in filter samples (mean concentrations of both 0.2 pg m^{-3}). The dominant PFCA was PFOA (mean concentration of 1.4 pg m^{-3}), observed > LOQ in 60% of samples. Longer-chain PFCAs were also observed. PFNA and PFDA were both detected at mean concentrations of 0.4 pg m^{-3}, while PFUA, PFTriA, and PFTeA were observed at

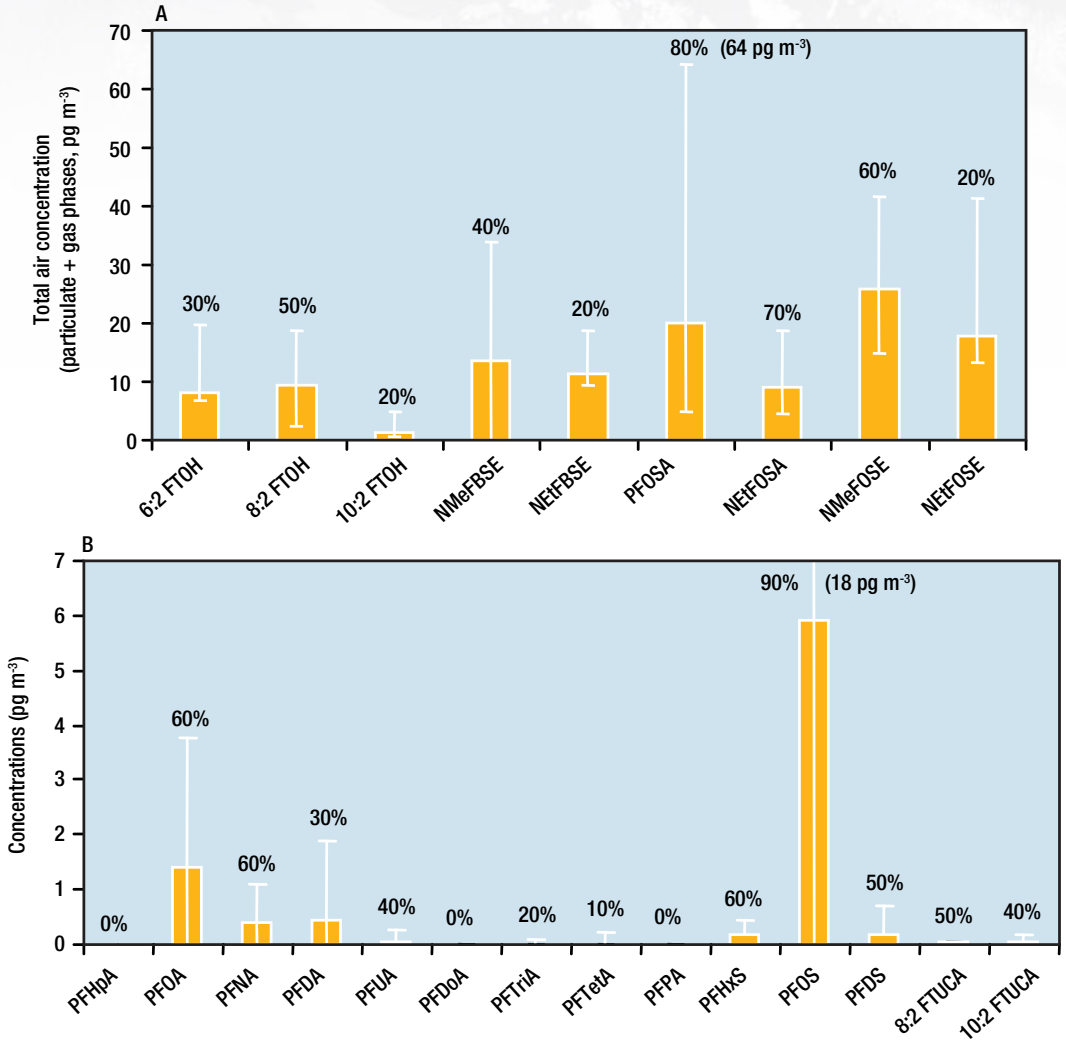

FIGURE 3.10

Mean values of (A) total concentrations (particle and gas phases) (pg m^{-3}) of FTOHs and FSAs and (B) particle concentrations of PFSAs, PFCAs, and FTUCAs, in air samples (n=10) collected at Resolute Bay (NU) in the summer of 2004 (Stock et al. 2007). Bars indicate the range of concentrations observed. Frequency of detection (%) of the individual analytes is also indicated.

mean concentrations ranging from 0.02 pg m^{-3} to 0.06 pg m^{-3}. PFHpA and PFDoA were not detected in any samples, although this may be explained by poor extraction recoveries in this study. Positive sampling artifacts were reported for PFCAs showing that vapor phase PFCAs can adsorb to glass fiber filters and the particulate matter already collected on the filter using conventional high volume sampling techniques, resulting in an overestimation of the particle phase (Arp and Goss 2008, Ahrens et al. 2011, 2012) The fluorotelomer unsaturated carboxy-lates, 8:2 and 10:2 FTUCA, were observed at mean concentrations similar to those observed for the longer-chain PFCAs (0.06 pg m^{-3} and 0.07 pg m^{-3}, respectively). The presence of PFSAs and PFCAs on atmospheric particles in the Arctic could be due to contributions from both transport hypotheses: the atmospheric oxidation of precursors and/or that the marine aerosols from the Arctic Ocean contribute to the presence of PFSAs and PFCAs in atmospheric particles.

The detection of the degradation products: FTUCAs in sediment and atmospheric particles indicate that degradation of FTOHs is occurring in the arctic abiotic environment.

Air samples were collected during a cruise onboard the *CCGS Amundsen* in the Labrador Sea and Hudson Bay in summer 2007 and in the Beaufort Sea in spring and summer 2008 as part of the International Polar Year (IPY) campaign of Circumpolar Flaw Lead Study (CFL) and annual ArcticNet expedition (Figure 3.11) (Ahrens et al. 2011). The particle and gas phases were collected

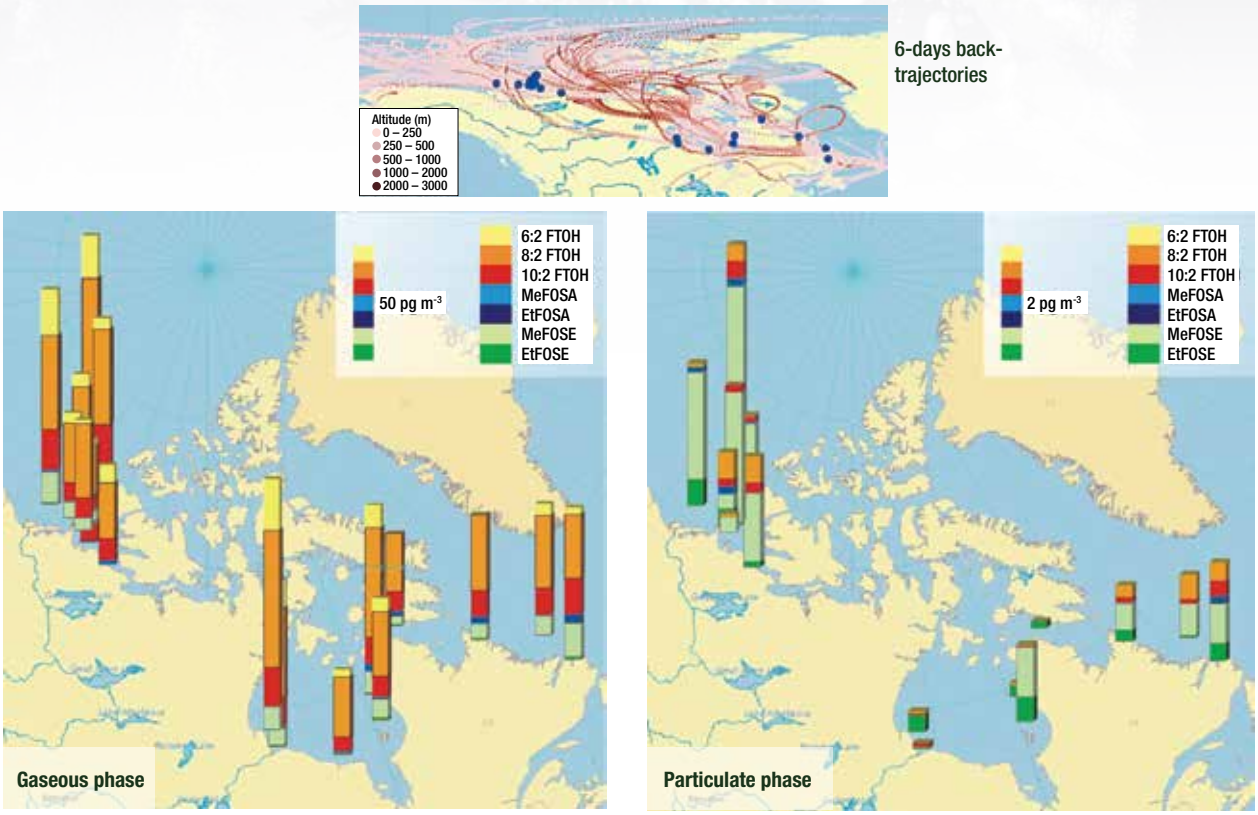

FIGURE 3.11

(A) Sampling sites and 6-day air back-trajectories for FTOHs, FOSAs, FOSEs in the Canadian Arctic atmosphere in 2007 and 2008. (B) Concentrations, pg m^{-3}, in the gas phase and (C) particulate phase.

separately by a high volume air sampler using GFFs and a PUF-XAD resin cartridge, respectively. The samples were analyzed for three FTOHs (i.e., 6:2 FTOH, 8:2 FTOH and 10:2 FTOH), two FOSAs (i.e., MeFOSA and EtFOSA) and two FOSEs (i.e., MeFOSE and EtFOSE). All PFASs were detected in the gaseous phase, while in the particle phase, the 6:2 FTOH concentrations were below the MDL.

The ΣPFAS concentration in the gas phase ranged between 43 pg m^{-3} and 162 pg m^{-3}. The highest gas phase concentrations of FTOHs was found for 8:2 FTOH (26–83 pg m^{-3}), followed by 10:2 FTOH (7.5–31 pg m^{-3}) and 6:2 FTOH (< 1.1–29 pg m^{-3}). For the FOSAs and FOSEs, MeFOSE was dominant (< 0.06–22 pg m^{-3}), followed by MeFOSA (< 0.08–3.6 pg m^{-3}), EtFOSE (< 0.06–1.4 pg m^{-3}) and EtFOSA (< 0.04–1.7 pg m^{-3}). The concentration levels in the particulate phase were about 30 times lower than in the gas phase and ranged between 0.3 pg m^{-3} and 10 pg m^{-3}. The ΣPFAS particle concentrations in the Hudson Bay and Labrador Sea ranged between 0.3 and 3.6 pg m^{-3}, while higher ΣPFAS concentrations were found in Beaufort Sea (up to 10 pg m^{-3}). The dominant PFASs were the FOSEs with MeFOSE as the dominant compound (< 0.02–7.4 pg m^{-3}), followed by EtFOSE (< 0.02–3.2 pg m^{-3}). The concentrations of the other PFASs in the particle phase were below 1 pg m^{-3}. Generally, the PFAS concentrations were about 3 times lower than in urban areas such as Toronto, Canada (Shoeib et al. 2006). Based on 6-day air back-trajectories, the air mass originated from the Arctic which indicates that background concentration levels were measured in this study (Figure 3.11).

While the PFASs were dominantly distributed in the gas phase, individual PFASs showed a different partitioning profile (Figure 3.12). The particle associated fraction (Φ) represents the fraction in the particulate phase ($c_{particle}$) in relation to the gas phase (c_{gas}) in air.

$$\Phi = c_{particle} / (c_{gas} + c_{particle})*100 \qquad \text{Eq. 18}$$

The highest particle associated fraction was observed for EtFOSEs (approximately 33%). The main influence on the partitioning is due to the functional

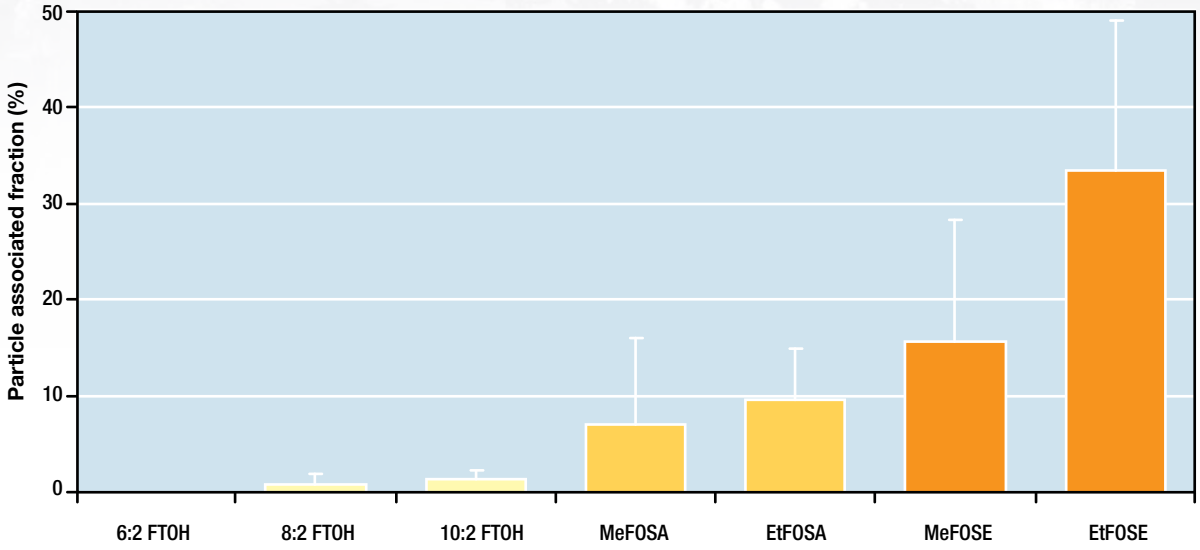

FIGURE 3.12

Particle associated fraction (ϕ) of individual PFASs in the Canadian Arctic atmosphere.

group. Thus, the particle associated fraction decreases from the FOSEs (approximately 25%) to the FOSAs (approximately 8.4%) and FTOHs (approximately 0.8%). Furthermore, the particle associated fraction increased with increasing chain length (i.e., 6:2 FTOH (0%) < 8:2 FTOH (1.0%) < 10:2 FTOH (1.4%)). Interestingly, EtFOSE concentration on particles increased with decreasing temperature ($r = 0.52$) which indicates that the temperature has an influence on the partitioning.

PFCAs and PFSAs were below MDL in the gas phase although sampling artifact has been indicated above. The longer chain PFCAs, PFDA, PFUnDA, PFDoDA and PFTeDA, were quantified in the particle phase, while the shorter chain PFCAs (C_4–C_9) and PFSAs were not detected. PFCAs were only detected sporadically with highest concentrations for PFUnDA and PFDoDA (both 0.08 pg m^{-3}). The concentrations of ΣPFCAs (< 0.04–0.18 pg m^{-3}) were much lower in comparison to ΣFTOH, ΣFOSA and ΣFOSE concentrations on particles (< 0.1–1.6 pg m^{-3}, < 0.1–0.3 pg m^{-3} and 0.3–8.6 pg m^{-3}, respectively). It is interesting to note that the average ΣPFCA concentrations over the Labrador Sea and Hudson Bay (0.09 pg m^{-3} and 0.05 pg m^{-3}, respectively) were higher than over the Beaufort Sea (0.01 pg m^{-3}), where only PFDoDA could be quantified in two samples. This is consistent with the concentrations of their potential precursor compounds, the FTOHs, which were highest in the particle phase over the Labrador Sea.

To observe how atmospheric levels of PFASs in the Canadian Arctic change in response to global emissions, atmospheric concentrations of precursor PFASs (FTOHs, FOSAs and FOSEs) have been monitored at Alert (NU) since 2006. Eighty-seven air samples were collected at Alert (NU) between August 2006 and October 2010 for the screening of 7 PFASs. Blank-corrected results revealed that 4 out of the 7 PFASs were found in 70–97% of the air samples. The dominant PFAS measured was generally 8:2 FTOH. The median total (gas and particle) concentration of 8:2 FTOH is 1.75 pg m^{-3} (mean: 2.28 pg m^{-3}; BDL–9.73 pg m^{-3}; n=84) (Figure 3.13)) which is much lower than those previously reported in arctic air in the North Atlantic and Canadian Archipelago (Shoeib et al. 2006) of 5.8–26 pg m^{-3}; and at Cornwallis Island (Stock et al. 2007) of BDL-18.6 pg m^{-3}]. Statistically significant correlations were observed between 10:2 FTOH and 8:2 FTOH ($r^2 = 0.42$, $p < 0.0001$); indicating that this pair of PFASs originated from the same source. However, no correlation was observed between EtFOSE and MeFOSE or between the FTOHs and the FOSEs; implying that different sources are responsible for these two groups of compounds in air at Alert (NU).

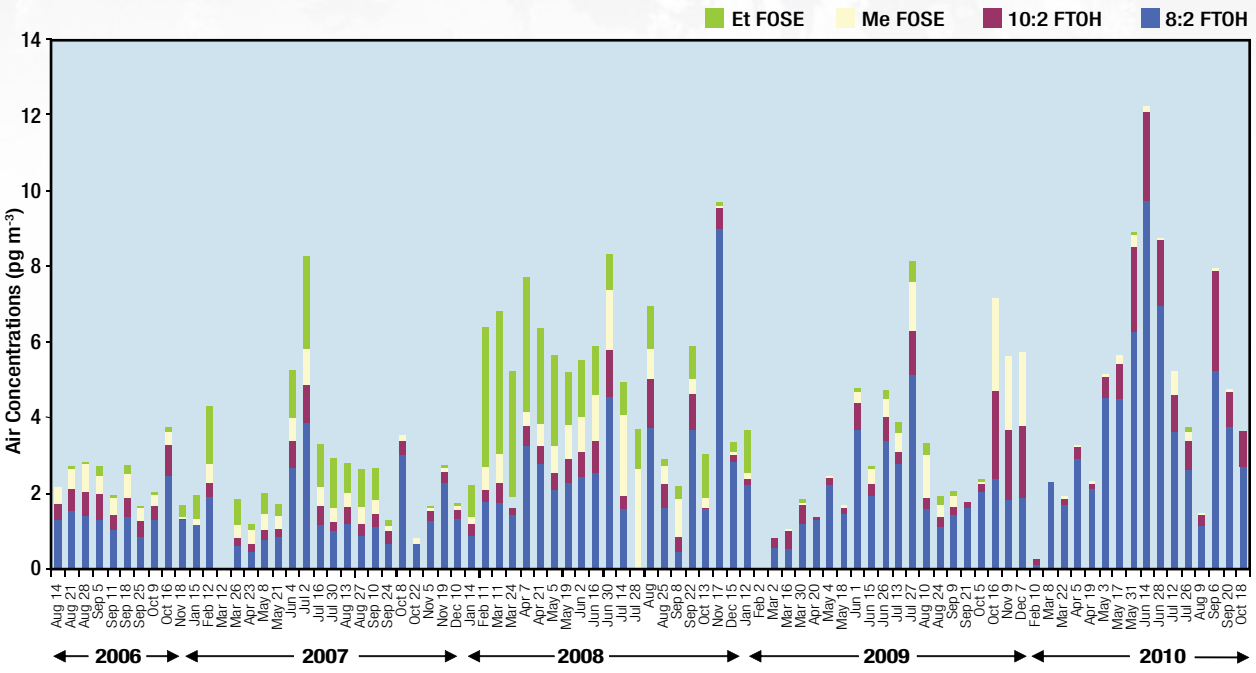

FIGURE 3.13

Atmospheric concentrations (gas and particle phase, pg m^{-3}) of PFASs measured at Alert (NU) (Aug 2006–Oct 2010) (x-axis indicates start dates of weekly-integrated sample).

Figure 3.14 shows the time trends and seasonal cycles of the FTOHs and FOSEs observed at Alert (NU). Considering about 4.5 years of data, MeFOSE and EtFOSE show decreasing tendencies. The use and release of PFOS, its salts and its precursors, are listed under the Stockholm Convention for control in June 2005. Due to such control initiatives and voluntary withdrawals of related products by manufacturers, the FOSEs, as PFOS precursors, show declining trends at Alert (NU) since 2008. On the other hand, the FTOHs that are not regulated show increasing tendencies in air at Alert (NU) during this same period of measurement. In terms of seasonality, all 4 compounds showed winter and spring maxima which may be associated with the increase in particulate input during the arctic haze season. Summer maxima are also apparent for 8:2 FTOH, 10:2 FTOH and MeFOSE which may be related to volatilization due to higher temperatures. Continuous measurements are required to examine the relative concentrations of these compounds during different seasons and determine what factors influence their transport to the Arctic.

3.1.4.4. Current use pesticides (CUPs)

Numerous CUPs are widely used around the globe. Elevated air concentrations of CUPs were reported near application source areas (Tuduri et al. 2006, Yao et al. 2008, Yao et al. 2006). Some CUPs were also found in environmental media in remote regions like the Arctic (Hoferkamp et al. 2010), although they were not applied locally. However, air concentrations of CUPs are seldom measured and reported in the Arctic (Hoferkamp et al. 2010). To address this knowledge gap, atmospheric occurrence and levels of CUPs have been regularly monitored at Alert (NU) in the Canadian High Arctic since August 2006 using a PS-1 air sampler. In total, 87 sets of samples were collected from 2006–2010, and screened for 22 CUPs. Table 3.4 lists mean, standard deviation (SD),

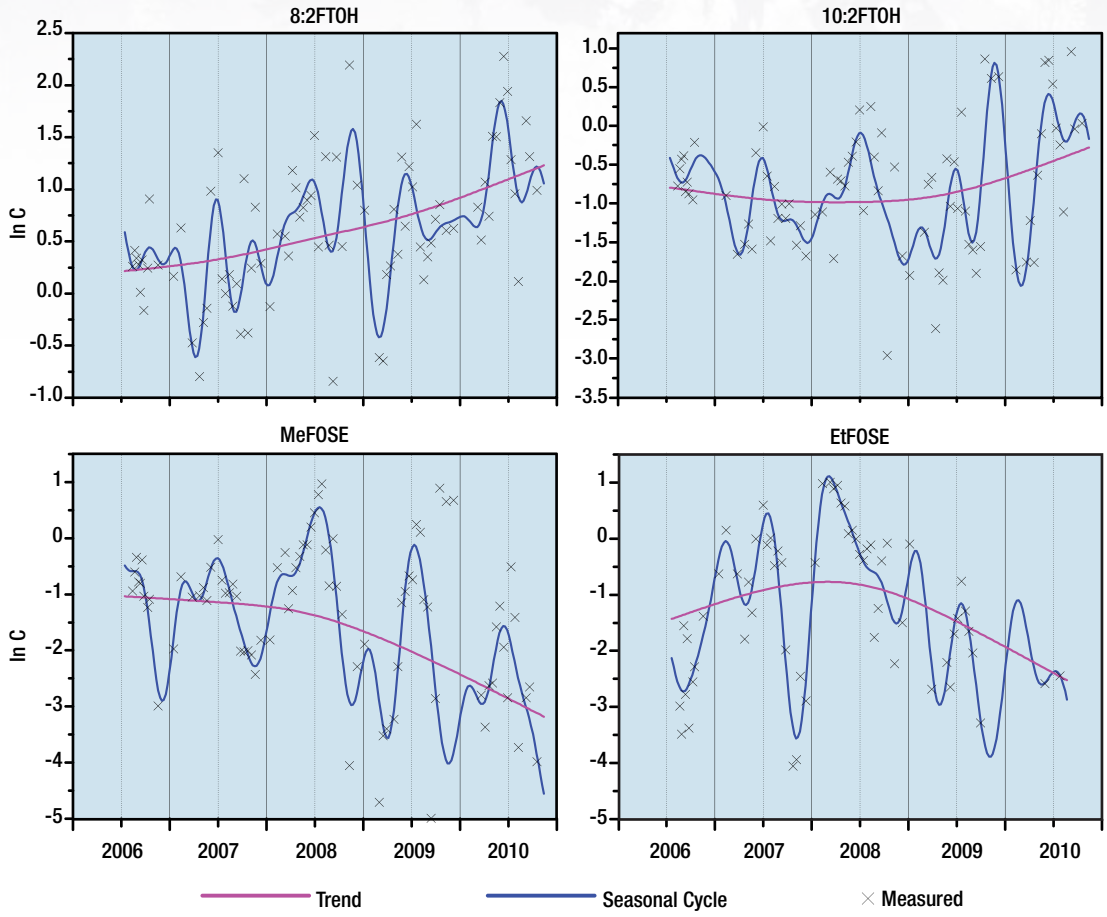

FIGURE 3.14

Interannual changes in FTOHs and FOSEs at Alert (NU) (gas and particle phase). Concentration (pg m^{-3}) is displayed using a natural log scale.

and range of 7 selected CUPs. Air concentrations of CUPs were generally low (< 1 pg m^{-3}) at Alert (NU). The concentrations given here are not blank corrected. Mean field and laboratory blank concentrations are shown in Figure 3.15 (green solid line). The 7 selected CUPs listed in Table 3.5 were above mean blanks in over 40% of samples, and the others were often not detectable.

TABLE 3.4. Mean, standard deviation (SD), and range of CUP concentrations (pg m^{-3}) at Alert (NU) in 2006–2009.

	Mean (SD, min–max)
chlorpyrifos	0.39 (0.95, BDL–7.2)
dacthal	0.048 (0.059, BDL–0.24)
α-endosulfan	3.8 (3.7, BDL–14)
endosulfan sulfate	1.5 (3.7, BDL–24)
pentachloronitrobenzene	0.25 (0.72, BDL–5.7)
tefluthrin	0.027 (0.041, BDL–0.16)
trifluralin	0.037 (0.051, BDL–0.35)

Note: BDL= Below detection limit

α-endosulfan was detected in 98% of all air samples with mean concentration 3.8 (BDL–14) pg m^{-3}. At Alert (NU), samples were collected using a super Hi-Vol air sampler (as reported above) and α-endosulfan was also analyzed. The differences between the two types of air samples ranged from 0.53–180% with median of 72%.

$$\left[\frac{|C_{PS\text{-}1} - C_{super}|}{(C_{PS\text{-}1} + C_{super}) \div 2} \times 100\%\right]$$

They are comparable to inter-laboratory variations for measuring trace organic chemicals in air samples (Su and Hung 2010). However, it should be noted that the results for super Hi-Vol are by GC-ECD which has potentially more interferences than the GC-negative ion MS method used for analysis of the lower volume CUPs samples.

Elevated concentrations of α-endosulfan were found in spring and fall, which is consistent with previous findings (Hung et al. 2010). Concentrations of dacthal and trifluralin were high in summer time, whereas in winter high concentrations for pentachloronitrobenzene (PCNB) were found (Figure 3.15). No apparent seasonality was seen for air concentrations of chlorpyrifos, endosulfan sulfate, and tefluthrin. Different seasonality of CUPs in the arctic atmosphere are likely related to their respective application patterns and subsequent long-range transport to the Arctic.

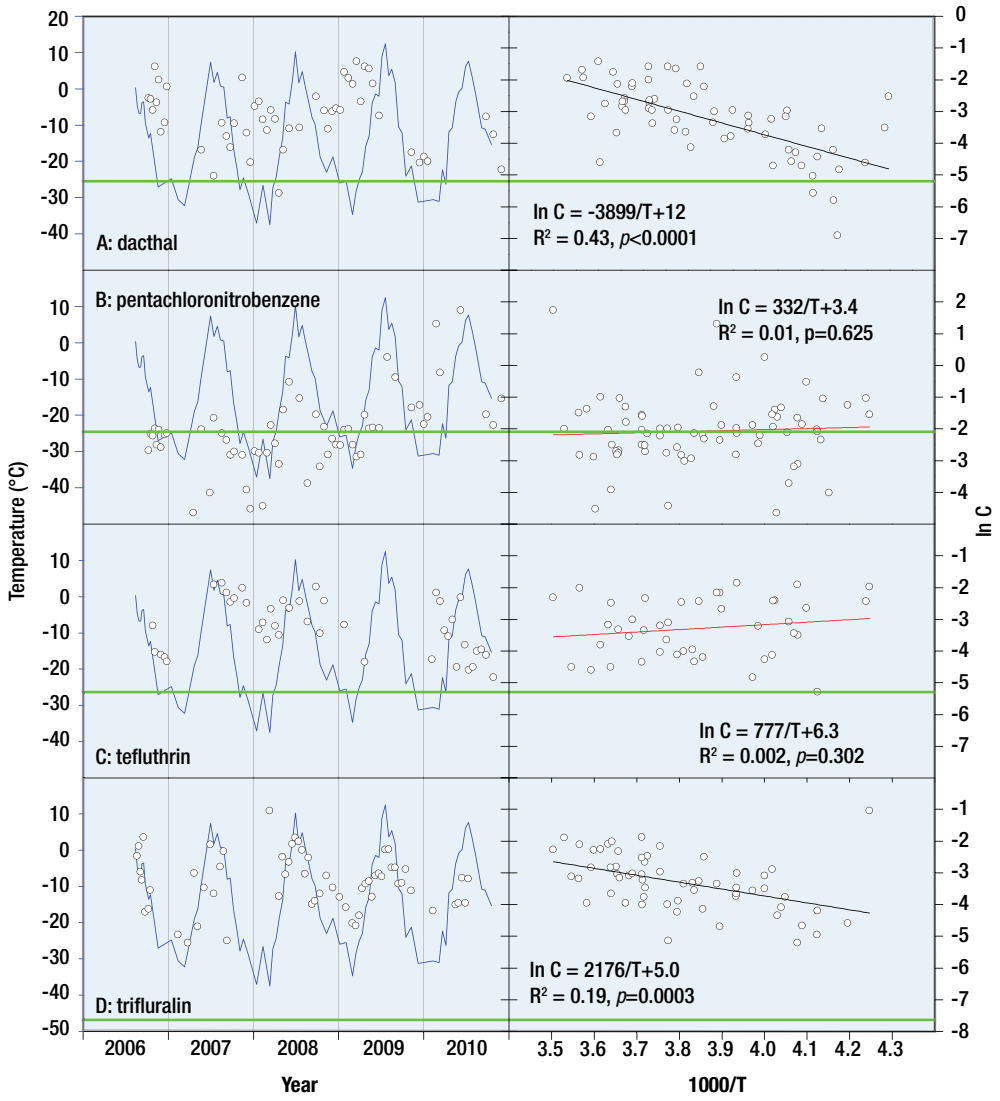

FIGURE 3.15

Seasonality of dacthal (A), pentachloronitrobenzene (B), tefluthrin (C), and trifluralin (D) and their temperature dependences at Alert (NU). Blue solid lines represent temperatures; white circles indicate air concentrations (pg m^{-3}, natural log scale); black solid lines are linear regression lines and green solid lines show mean blank concentrations.

3.1.4.5. CUPs measurements from the Canadian Archipelago cruise 2005

Samples that were collected during the crossing of the North Atlantic and Canadian Archipelago in July 2005 onboard the Oden Icebreaker were analyzed for PFASs (Shoeib et al. 2006), CUPs and OCPs (section 3.1.4.3).

Air parcel back-trajectories for the air samples are shown in Figure 3.16 and indicate that they were largely representative of the arctic summer air mass with no observed events of strong advection inputs from potential source regions to the south. Samples were analyzed for dacthal, trifluralin, chlorothalonil, metribuzin, pendimethalin, α- and γ-HCH, chlordanes (CC (*cis*-chlordane), TC (*trans*-chlordane) and TN (*trans*-nonachlor)) and endosulfans (α- endosulfan, β-endosulfan and endosulfan sulfate). Metribuzin and pendimethalin were not detected in blank samples, and were rarely detected in samples. These samples are very interesting because they represent background arctic concentrations of key pesticides during a time of the year that they might be applied (in the case of CUPs) or re-volatilized (in the case of legacy pesticides) from sources in the northern hemisphere.

The poor detection of some compounds demonstrates the challenges associated with sampling for trace contaminants in arctic air and the need for very large sample volumes to meet detection criteria–especially during times such as this when intrusion of southern air masses was minimal. During this relatively clean period, only a few of the target compounds were measured at concentrations that satisfied the MDL.

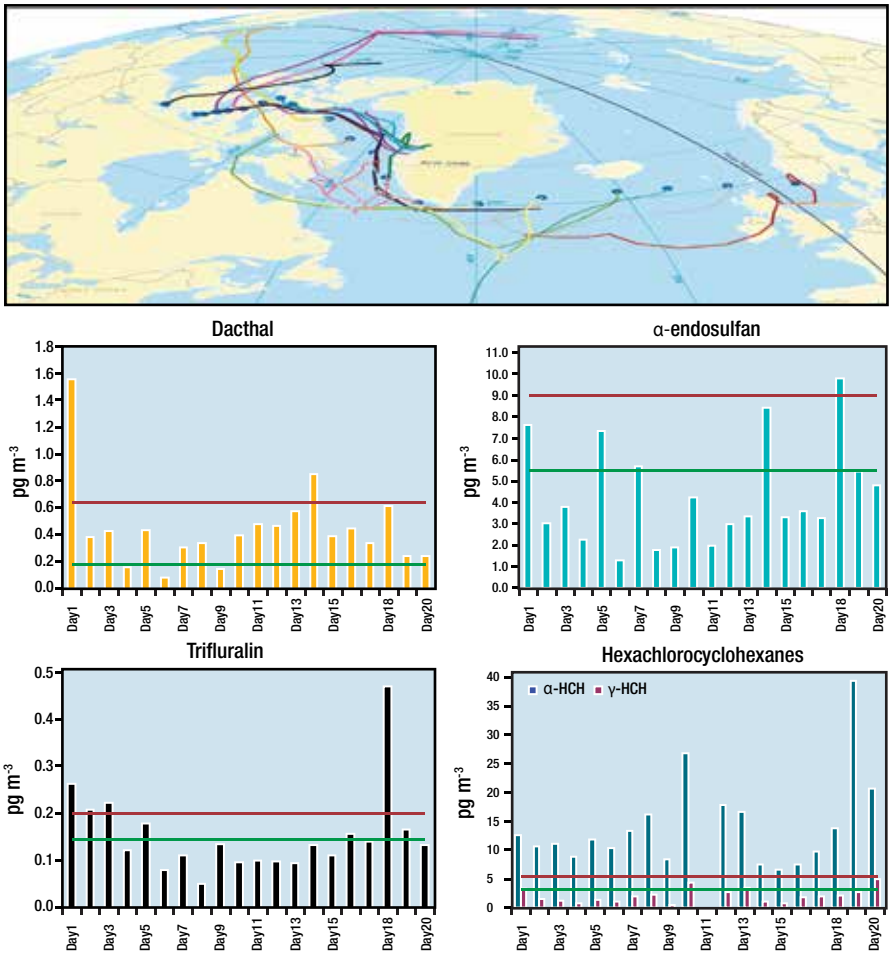

FIGURE 3.16

Oden (icebreaker) cruise track showing average 6-day air parcel back-trajectories (upper map) (at 10 m above sea level) for each sample (using different colours) and air concentrations (pg m^{-3}) for selected legacy OCPs and CUPs (lower panels). The red line indicates limit of detection (method detection limit (MDL) = average blank concentration ± 3×SD) and the green line indicates average blank concentration (n=3). For HCHs, lines are for α-HCH as γ-HCH which were not detected in blanks.

Results are highlighted in Figure 3.16 for pesticides that are of interest due to their recent attention in international review and regulatory initiatives.

Dacthal air concentrations exceeded the MDL of 0.6 pg m^{-3} in two cases. All dacthal concentrations on the cruise (Figure 3.16) were higher than those observed at Alert (NU) (Table 3.4). The elevated concentration in sample 1 is consistent with ongoing dacthal use in the United Kingdom (Ruggirello et al. 2010) and back-trajectories for this sample that stem from this region. Previous studies have indicated a high air transport potential for dacthal (Hoferkamp et al. 2010, Muir et al. 2004). The MDL for α-endosulfan was relatively high (approximately 9 pg m^{-3}) and only one sample (Day 19) was above this limit. Air concentrations of β-endosulfan (not shown) tracked the results for α-endosulfan but with concentrations about five times lower, including a lower MDL value of 1.8 pg m^{-3}. The back-trajectory for the sample on Day 19 showing highest air concentrations of endosulfans was extended to an additional 5 days to investigate potential source regions but the results were inconclusive. Endosulfan sulfate was not detected in any of the samples. Air concentrations of trifluralin were quite low and only exceeded the MDL (0.2 pg m^{-3}) a few times—at the beginning of the study (indicating potential UK or European sources) and again on Day 19, when α-endosulfan was also elevated. All dacthal concentrations on the cruise (Figure 3.16) were higher than those observed at Alert (NU) (Table 3.4). Lindane was detected in all but one sample (IDL = 0.48 pg m^{-3}) but was not detected in blanks; α-HCH was above the MDL (5.4 pg m^{-3}) in all samples. The sustained high air concentration of α-HCH is believed to be linked to ocean-air transfer from the large reservoir of historically deposited chemicals (Halsall et al. 1998, Hargrave et al. 1997). Air concentrations of α-HCH are consistent with measurements at Alert (NU) (Figure 3.15) and with earlier measurements, e.g., in the Canadian Archipelago (Hargrave et al. 1997; Jantunen et al. 2008; Wong et al. 2011); Russian Arctic or Norway (Halsall et al. 1998); High Arctic station in Alert (NU) (Halsall et al. 1998, Hung et al. 2005); and in Greenland (Bossi et al. 2008). Not shown in Figure 3.16 are the air concentrations for CC, TC and TN, that hovered around the MDL values (pg m^{-3}) of 0.44, 0.43 and 0.030 respectively, for the duration of the cruise, and showed good correlation with each other and with dacthal.

3.1.5. Global atmospheric passive sampling (GAPS) network: Legacy and new POPs

The GAPS Network is the only global-scale program reporting air concentrations of POPs under the global monitoring plan (GMP) of the Stockholm

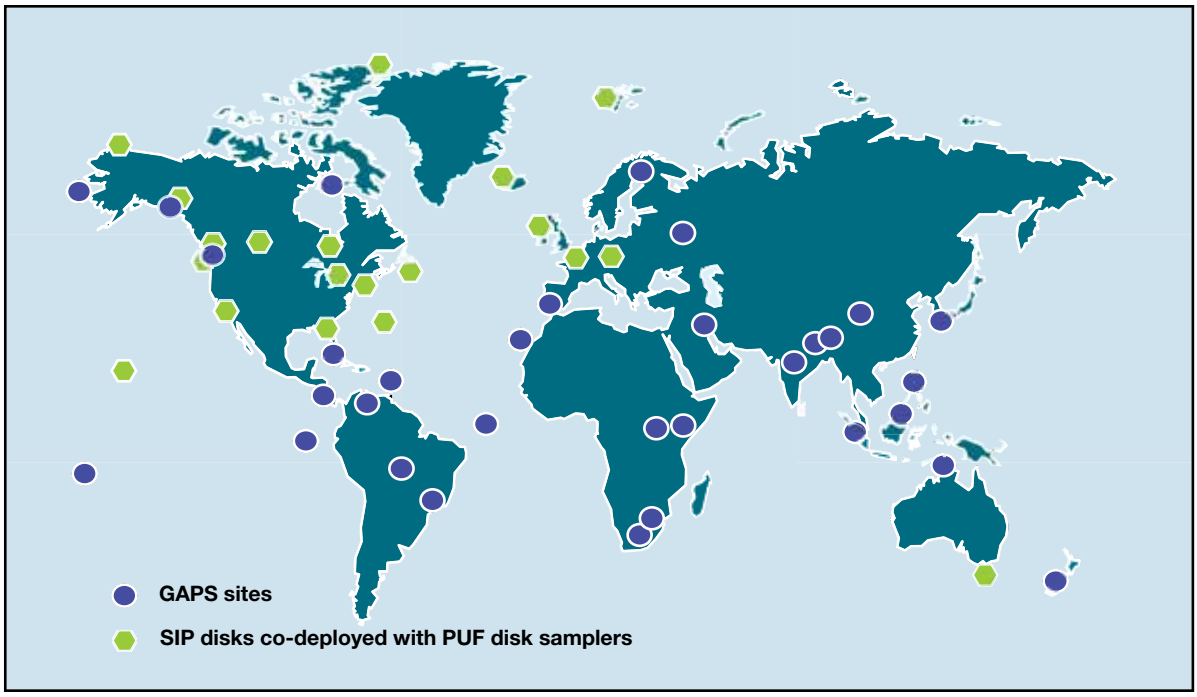

FIGURE 3.17

Map showing location of GAPS Network sites.

Convention. This program was initiated in December 2004 as a two-year pilot study (Harner et al. 2006) before evolving into a network, and now consists of more than 60 sites on seven continents (Pozo et al. 2009, Pozo et al. 2006, Shunthirasingham et al. 2010). Passive air samplers (PAS) are advantageous because of their low cost, simple construction and electricity-free operation. PAS are therefore very useful in overcoming some of the logistical challenges in air sampling over large spatial scales in the largely undeveloped arctic region. PAS used under GAPS include the PUF disk sampler (3-month deployment), the XAD-sampler (1 year deployment) and currently, testing of the new sorbent impregnated polyurethane (SIP) disk sampler (3-month or longer deployments) (Genualdi et al. 2011, Genualdi et al. 2010). Thus unlike high volume samplers that can provide air concentrations of POPs over short time resolutions (days to weeks), PAS provide time-weighted information over longer periods and cannot be used to evaluate the gas-particle partitioning of a chemical. However, the spatial information provided by PAS allows for new approaches for interpreting data and improved integration with transport models and emissions information. Of the approximately 60 sites currently part of the GAPS network (Figure 3.17), several of them are in the arctic and subarctic region (7). These include: Alert (NU); Barrow (AK); Dyea (AK); St. Lawrence Island (AK); Little Fox Lake (YK); Storhofdi (Iceland); and Ny-Ålesund (Norway). The remaining non-arctic sites provide useful context for comparing and assessing the global spatial distribution of POPs and long range atmospheric transport to the Arctic.

The first 1–2 years of results from PUF disk samplers show seasonally resolved concentrations of several POPs including α- and γ-HCH, chlordanes, heptachlor, dieldrin, DDTs, endosulfans (Figure 3.18), and PCBs (Pozo et al. 2009). As a result of their current and widespread use, globally, endosulfan exhibited the largest range in air concentrations with a strong seasonality in source

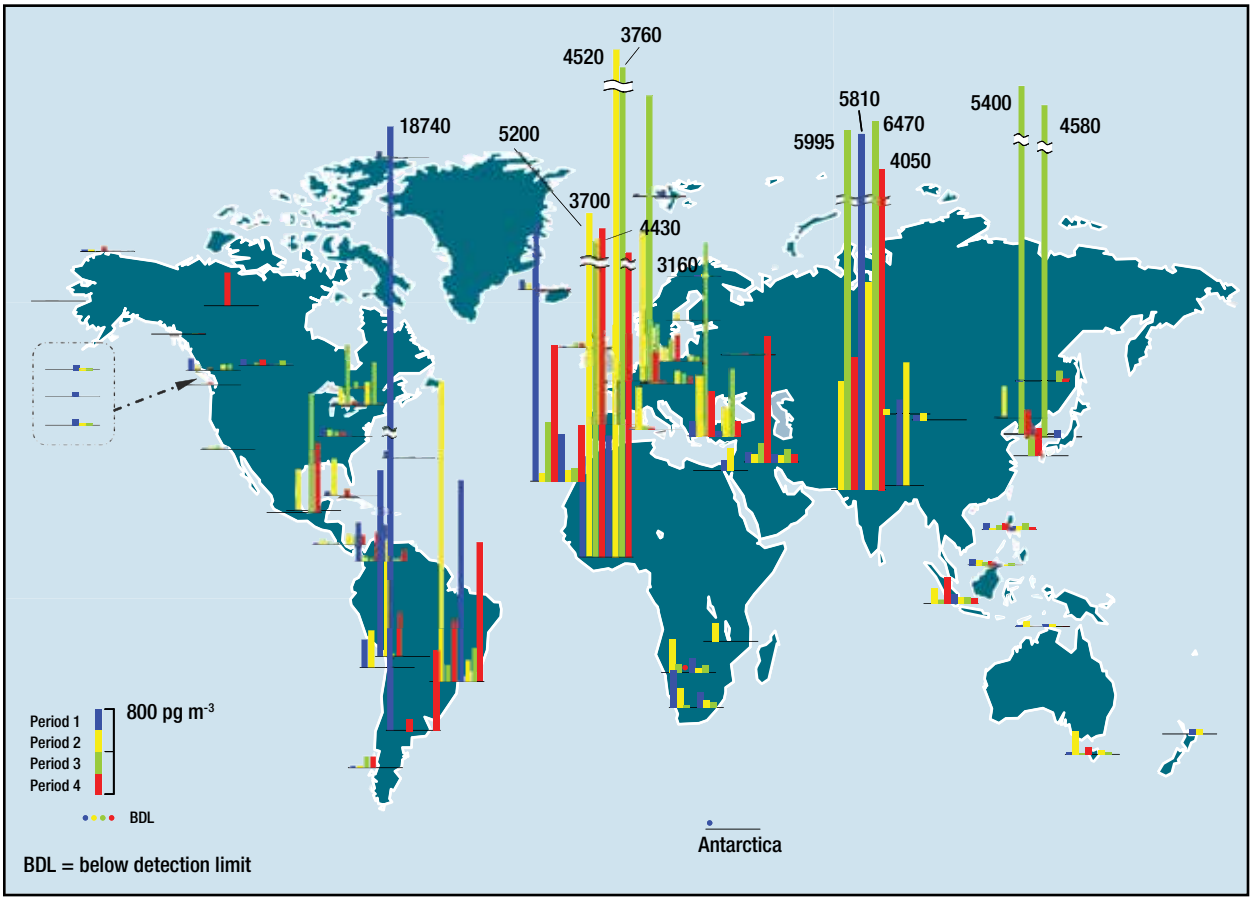

FIGURE 3.18

ΣEndosulfan concentrations in air on a quarterly (seasonal) basis at GAPS Network sites during 2005 and 2006. (ΣEndosulfans = α-endosulfan + β-endosulfan + endosulfan sulfate).

regions and low concentrations at background sites including arctic and subarctic sites. PBDEs were also determined but were generally below the detection limit of 3.7 pg m^{-3} at all arctic sites with the exception of Ny-Ålesund (Norway), in period 4 (2005) where ΣPBDEs was 32 pg m^{-3}. Efforts are underway to improve detection limits for PBDEs that are currently limited by blank contamination. First year samples were also analyzed for new classes of flame retardants and results are summarized in Table 3.5 The widespread detection of these compounds in the global atmosphere identifies another research and monitoring need for future work. As many of the new flame retardants have low vapour pressures they will exist in the atmosphere mainly associated with particles and it will be important to characterize particle phase sampling rates for passive air samplers. Harner et al. (2013) recently showed that for PUF disk passive air samplers, the sampling rates for particle phase polycyclic aromatic compounds (PACs) were the same as for gas-phase compounds. These results are being tested and confirmed for other compound classes, including flame retardants.

TABLE 3.5. Detection of alternative flame retardants in GAPS Network samples from October–December, 2005. Approximately 50 sites were included in the sampling (Lee et al. 2013).

	Detection frequency (%)				
Compound[1]	North America (n=9)	Central and South America (n=6)	Europe (n=9)	Africa (n=3)	Asia and Australia (n=10)
BTBPE	100	100	100	100	100
HBCDD	89	100	100	100	100
HBB	89	100	100	100	90
TBB	89	100	78	67	100
TBPH	100	100	90	67	70
PBBz	89	50	100	100	70
TBCT	89	100	100	33	90
ATE	67	67	78	67	60
PBEB	67	67	89	33	80
PBTo	67	67	78	33	90
DPTE	11	17	67	0	60
pTBX	56	0	78	33	20
PBBA	11	33	22	33	70
BB-101	33	17	33	0	80
BATE	33	17	44	0	30
DBDPE	11	0	0	0	0
OBIND	0	0	0	0	0
Legend					
n=number of sites					
Detection frequency		<10%		50–90%	
		10–49%		>90%	

[1] BTBPE- 1,2-*bis*(2,4,6-tribromophenoxy)ethane; HBCDD-hexabromocyclododecane; HBB-hexabromobenzene; TBB- 2-ethylhexyl-2,3,4,5-tetrabromobenzoate; TBPH- *bis*(2-ethyl-1-hexyl)tetrabromophthalate; PBBz-pentabromobenzene; TBCT-tetrabromo-o-chlorotoluene; ATE- allyl 2,4,6-tribromophenyl ether; PBEB- pentabromoethylbenzene; PBTo- pentabromotoluene; DBTE- 2,3-dibromopropyl-2,4,6-tribromophenyl ether; pTBX- 2,3,5,6-tetrabromo-*p*-xylene; PBBA- pentabromobenzylacrylate; BB-101- 2,2',4,5,5'-pentabromobiphenyl; BATE- 2-bromoallyl 2,4,6-tribromophenyl ether; DBDPE- decabromodiphenylethane; OBIND- octabromotrimethylphenylindane

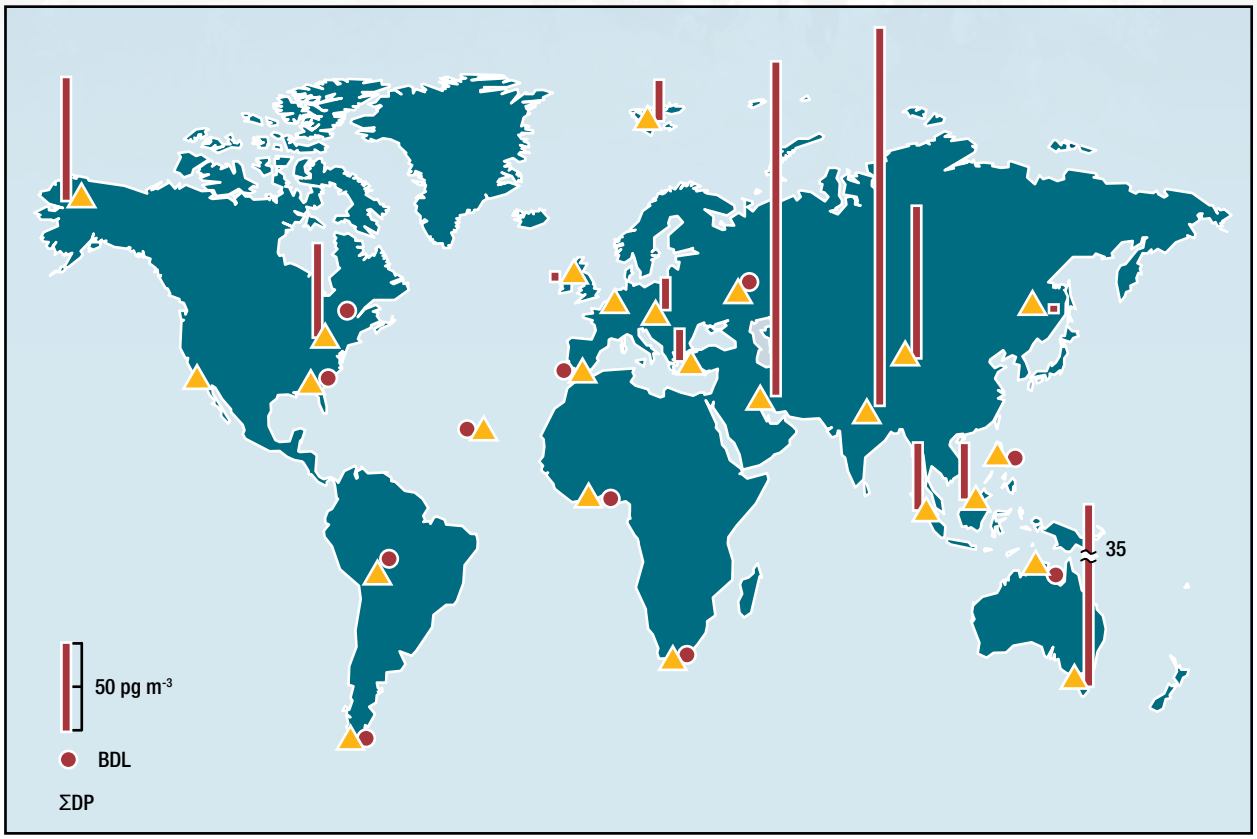

FIGURE 3.19

Dechlorane Plus (DP) concentrations on global background air from the Global Atmospheric Passive Sampling (GAPS) study (Sverko et al. 2010).

More global background data is becoming available from special studies under the Global Atmospheric Passive Sampling (GAPS) Network (Sverko et al. 2010), such as results showing relatively high DP air concentrations at selected sites in southern Asia and North America (Figure 3.19), suggesting potential sources in these regions. Some surprisingly high values of DP will be validated using later year samples from these sites (e.g., the high value at Cape Grim, Australia).

Results for yearly deployed XAD samples are available for a large subset of GAPS sites for years 2005, 2006, 2007 and 2008. The data show distinct spatial patterns and temporal tendencies for some of the legacy and new POPs (Shunthirasingham et al. 2010) (Figure 3.20). Whereas OCPs such as α- and γ-hexachlorocyclohexane, endosulfan, DDT and its metabolites, and chlordane-related compounds tend to be more prevalent in developing countries, especially in Asia, concentrations of current use pesticides such as trifluralin and chlorothalonil are often higher in Europe and North America.

The data generated by the GAPS network is "comparable" in the sense that samples deployed at sites all around the world are prepared and returned for analysis to the same laboratory at Environment Canada, in the case of PUF disk samplers, and at the University of Toronto, for the XAD samplers. Such data are invaluable for investigating relative differences in air concentrations between regions and for developing and validating long-range transport models. Samples from the GAPS Network are also archived for future retrospective analysis.

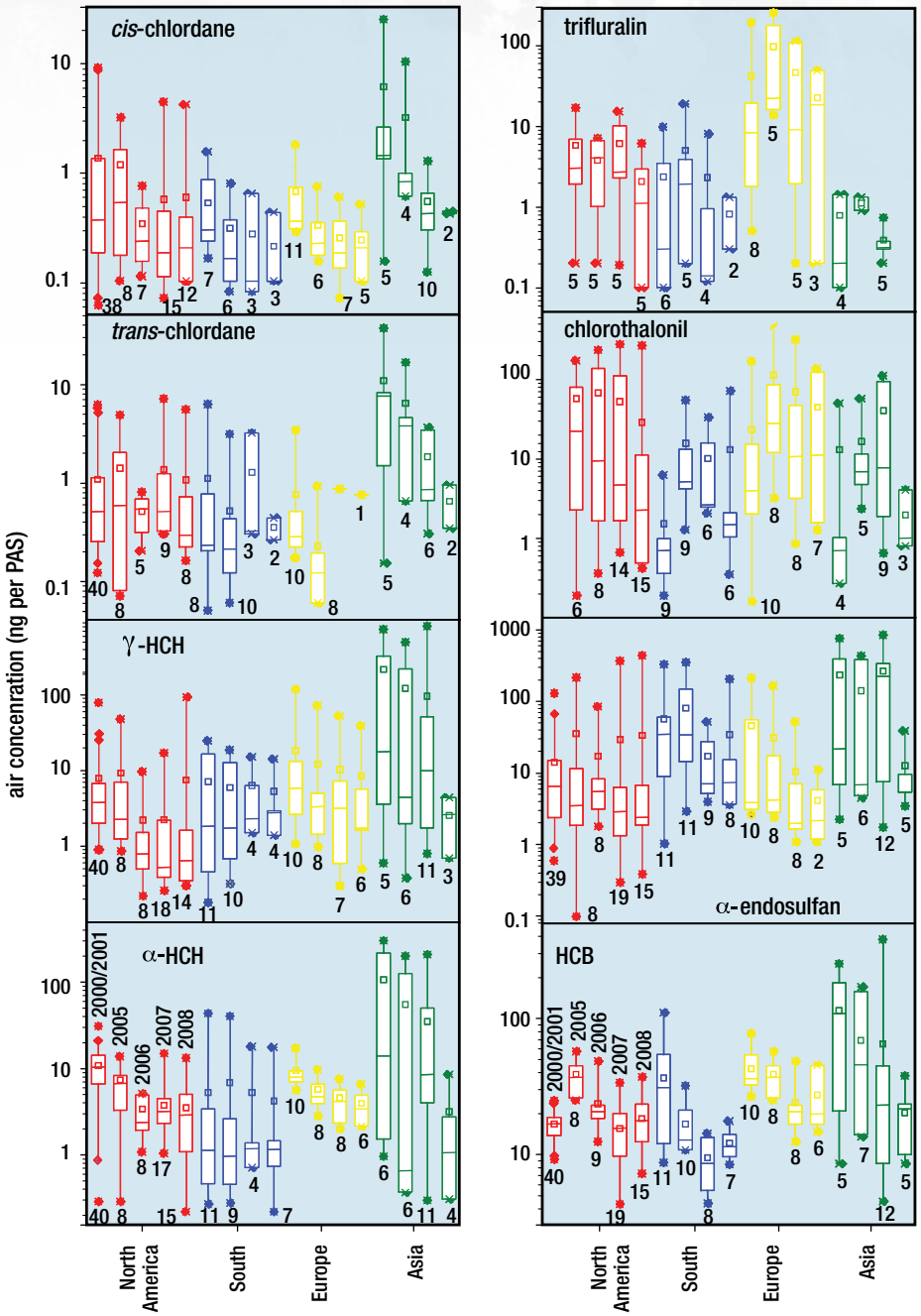

FIGURE 3.20

Box and whisker plot of the concentrations of organochlorine pesticides (left) and current use pesticides (right) in major world regions (ng per passive air sampler). Four entries for each pesticide and region represent the data for the first four years of the GAPS study. The 2000 and 2001 data for North America are from Shen et al. (2004, 2005). The number below each box indicates the number of sampling sites. (Shunthirasingham et al. 2010).

3.1.5.1. SIP disk pilot study Phase 1 results: PFASs and siloxanes

3.1.5.1.1. Global and arctic PFASs

In a global pilot study, volatile and ionizable PFASs were measured using sorbent-impregnated polyurethane foam (SIP) disk passive air samplers during the 2009 spring sampling period (April to June) of the GAPS Network (Genualdi et al. 2010). This study complemented other high volume atmospheric measurements of PFASs at Alert (NU), at Resolute Bay (NU), and on ocean cruises (section 3.1.4.3). Among the 20 sites in the pilot, four polar sites were included in this study: Alert (NU), Canada; Barrow (AK), USA; Ny-Ålesund (Norway) and Storhofdi (Iceland). The sampling locations consisted of 12 background, 4 polar, 1 subpolar, 3 urban, and 1 agricultural site. The SIP disk samplers consisted of PUF disks impregnated with finely ground XAD-4 resin. The addition of XAD-4 greatly improves the sorptive capacity of the PUF disk samplers for more volatile compounds such as FTOHs, and polar chemicals. It also allows for extended sampling times during which the sampler remains in the linear region of the uptake curve and thus provides time-weighted average air concentrations for these compounds over deployment periods of several weeks or more. Precursor PFASs (FTOHs, FOSAs and FOSEs) and seven ionizable PFASs (C4, C6, C8 PFSAs, C8-C11 PFCAs) were measured in these samples. Results are summarized in Figure 3.21 (Genualdi et al. 2010). Among the FTOHs, 8:2 FTOH was the dominant compound with air concentrations (pg m^{-3}) of 6.4 at Alert (NU) and 6.8 at Barrow (AK). EtFOSA and MeFOSA were below detection at the four polar sites, whereas MeFOSE and EtFOSE were only detected at Barrow (AK) with air concentration (pg m^{-3}) of 0.54 and 0.44 respectively. Ionizable PFASs were quantifiable only at the Alert (NU) site. PFOS was the dominant compound with air concentration of 2.0 pg m^{-3}. Shorter chain PFSAs were also detected at the Alert (NU) site with air concentrations of 0.77 pg m^{-3} and 0.087 pg m^{-3} for PFBS and PFHxS respectively. Ionizable PFASs, such as PFOS, are expected to be relatively involatile and exist mainly on aerosols in arctic air with the exception of low pH aerosol (typical of urban air) that would favour transition to the neutral forms with potential for volatilization into the gas phase (Ahrens et al. 2012).


Photo: Rick Massie

The dominance of FTOHs over the FOSAs and FOSEs observed in this study is consistent with active air sampling at Alert (NU) (section 3.1.4.3) although concentrations of 8:2 FTOH in the SIP disks were lower than the range observed with high volume sampling. For comparison, air concentrations reported from one-day and two-day ship based samples for a transect from Longyearbyen, Svalbard to Kiel, Germany (Dreyer et al. 2009) showed high levels of FTOHs, with 8:2 FTOH ranging from 11 pg m^{-3} to 50 pg m^{-3}, while MeFOSE and EtFOSE ranged from 0.4 pg m^{-3} to 1.9 pg m^{-3} and 0.5 pg m^{-3} to 2.5 pg m^{-3}, respectively.

The presence of neutral PFASs in arctic air supports their potential long range transport from source regions. However, it is unclear whether the ionizable PFASs (e.g., PFOS) arrive via long-range atmospheric transport or if they are formed in the arctic from neutral precursor PFASs (Ellis et al. 2004; Schenker et al. 2008). Ocean transport also plays an important role in the conveyance of ionizable PFASs (Prevedouros et al. 2006; Wania, 2007).

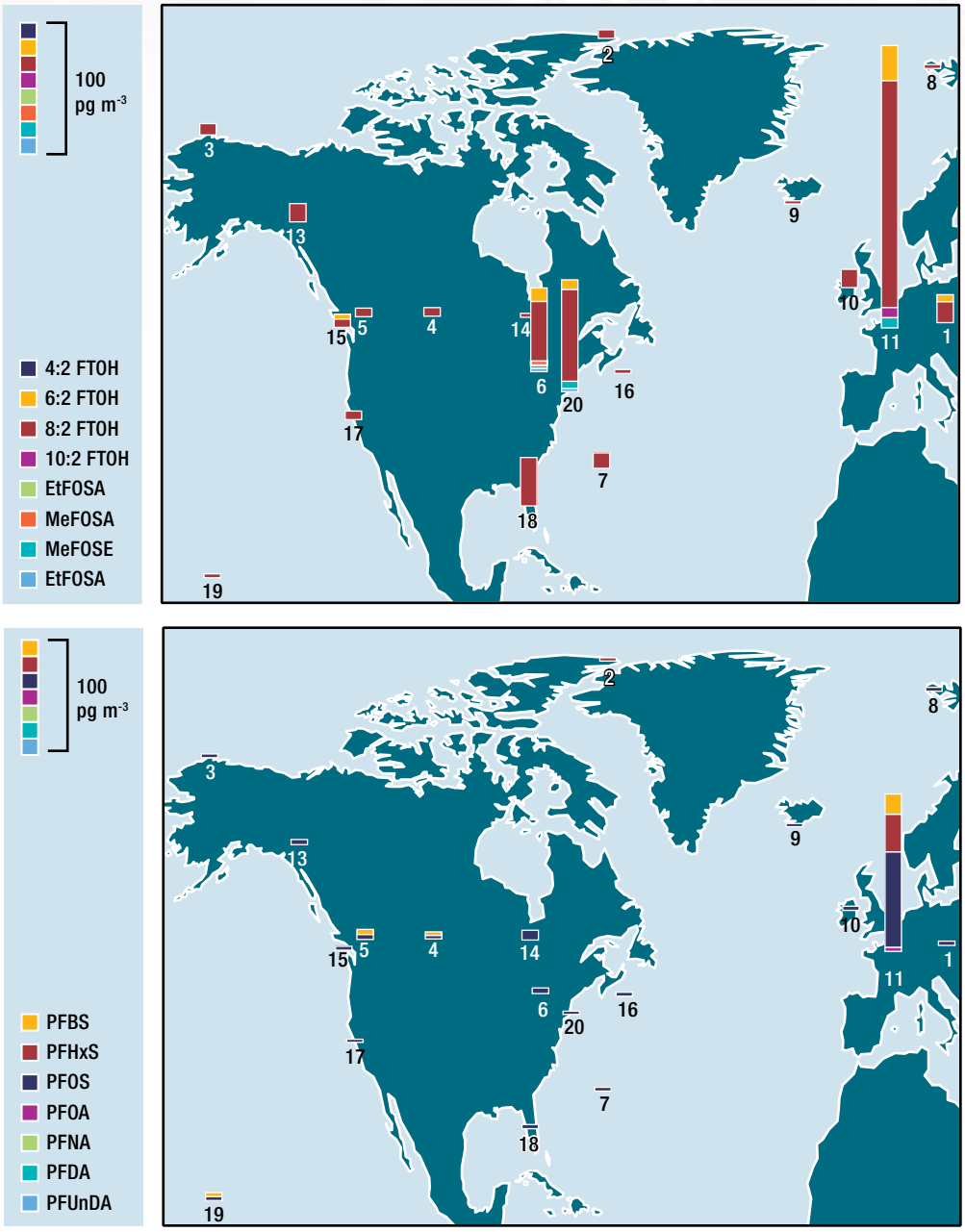

FIGURE 3.21

Neutral per- and polyfluorinated alkyl substances (A) and ionizable PFASs (B) measured in air (pg m^{-3}) using SIP disk air samplers (March–June 2009). Sites 6, 11 and 18 are urban sites. (Genualdi et al. 2010).

3.1.5.1.2. Global and arctic measurements of volatile methyl siloxanes

In a related study using SIP disks, volatile methyl siloxanes (see Glossary for full names) were measured as shown in Figure 3.22 (Genualdi et al. 2011). The dominant siloxanes were D3 (38%), D4 (28%) and D5 (29%), while the content of the linear-siloxanes was lower than 0.3%. This pattern is different to measurements in ambient air on and around wastewater treatment plants and landfill sites where D5 dominated (66% and 58%, respectively) (Cheng et al. 2011).

Highest Σsiloxane concentrations were found at the sites in Groton (CT, USA), Sydney (FL, USA), Hilo (HI, USA), Whistler (BC, Canada), and Downsview (ON, Canada) ranging from 67–177 ng m^{-3}, while the concentrations at the other sites ranged between

2–40 ng m^{-3}. These concentrations were generally 1–2 orders of magnitude lower than near-waste sector "background sites" (i.e., wastewater treatment plants and landfills). Interestingly, three locations at the east coast of North America (Downsview, ON, Canada: Groton, CT, USA: Sydney, FL, USA), shows a dominance of the D5 siloxane whereas west-coast samples and arctic samples show higher proportions of D3 and D4. This may reflect a common source region for the west coast and arctic samples. Phase 2 of the SIP disk pilot study was initiated in January 2011 and at all GAPS sites and will provide a more complete global picture of siloxane concentrations in air.

Concentrations of D5 measured in phase 1 of the SIP disk pilot study were compared to results from two chemical fate and transport models, the Danish Eulerian Hemispheric Model (DEHM) (Hansen et al.

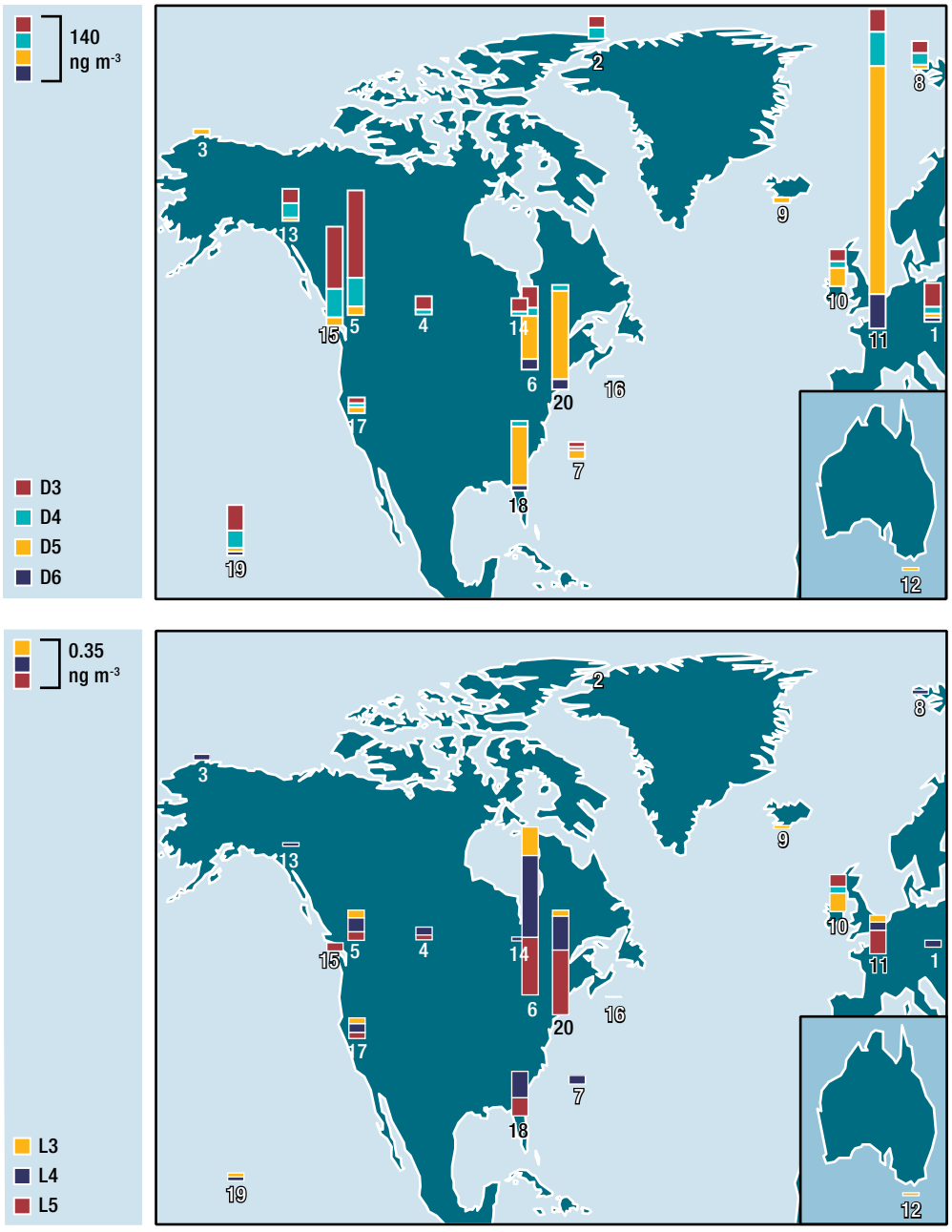

FIGURE 3.22

Siloxanes measured in air (ng m^{-3}) using SIP disk air samplers (March–June, 2009). Urban sites have black numbers and background are white numbers. Sites 6, 11 and 18 are urban sites. Redrawn from Genualdi et al. (2011).

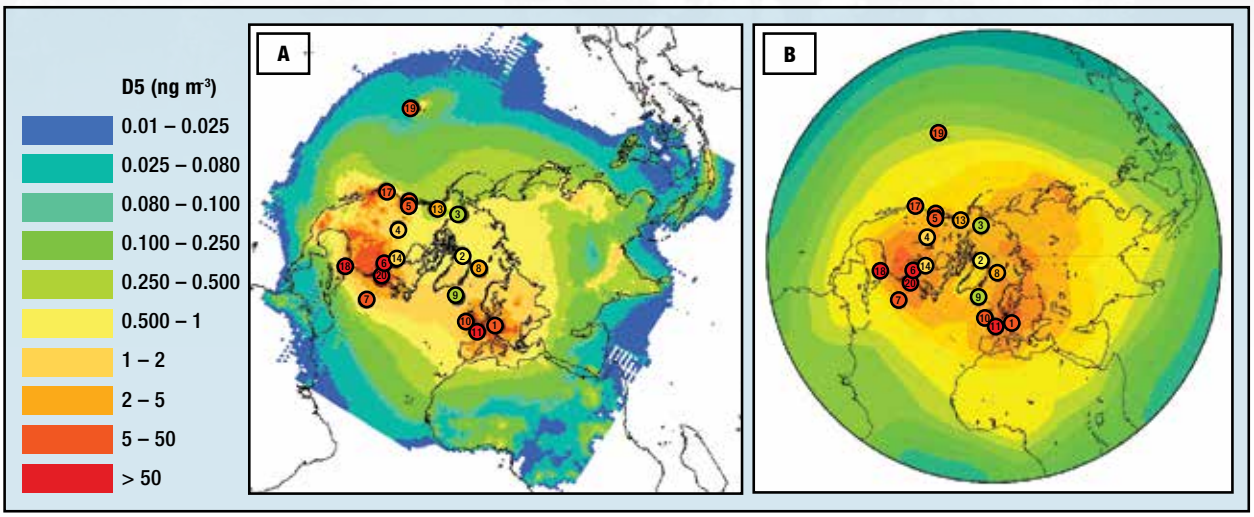

FIGURE 3.23

Overlay of measured and modeled results for decamethylcyclopentasiloxane (D5) using the (A) DEHM and (B) BETR models. The different coloured circles with site numbers correspond to concentrations at GAPS sampling locations (Genualdi et al. 2011).

2008a) and the Berkeley-Trent Global Contaminant Fate Model (BETR Global) (MacLeod et al. 2005) (Figure 3.23). These models use spatially-resolved emission estimates and physico-chemical properties of D5 as inputs to calculate concentrations in the atmosphere. The correlation coefficients between the measured and modeled results were 0.73 and 0.58 for the DEHM and BETR models respectively. Agreement between measurements and models indicate that the sources, transport pathways, and sinks of D5 in the global atmosphere are fairly well understood.

The cyclic volatile methyl siloxanes (cVMS) are currently under consideration for regulation in Canada and Europe because of concerns about persistence, toxicity and potential for bioaccumulation in aquatic food chains. Levels in air at the five monitoring sites in the Arctic are in the nanogram per cubic meter range, i.e., 1–2 orders of magnitude higher than atmospheric concentrations of polychlorinated biphenyls (PCBs) and hexachlorocyclohexanes (HCHs), which are regulated internationally under the Stockholm Convention. Determining whether the relatively high exposure of the arctic atmosphere to cVMS translates into risks to the ecosystem and/or human health will require further assessment of the impacts associated with exposure by inhalation and potential for deposition. In addition, the possible impacts of the silanols, formed by degradation of cVMS by hydroxyl radicals, which are expected to be rapidly scavenged from the atmosphere, should be examined.

In summary, in addition to generating first global-scale data for several classes of chemicals, another important outcome of the phase 1 SIP disk pilot study of 2009 was the demonstration of good agreement in derived air concentrations between co-deployed PUF disk and SIP disk samplers for PCBs (Genualdi et al. 2010).

3.1.5.2. Outlook for the GAPS network

The GAPS Network is currently in its 9th sampling year (i.e., 2013). Monitoring of legacy POPs and surveillance of new POPs continues through the core program using seasonally deployed PUF disk samplers, yearly deployed XAD-type samplers, and more recently, through pilot studies testing the versatile SIP disk samplers. These data sets will allow for analysis of spatial trends and temporal tendencies that may be associated with, and inform international regulation efforts on POPs. The data will be submitted to the second global monitoring plan (GMP) report of the Stockholm Convention, due in 2015. This will contribute to Canada's reporting obligations under the Convention. It will also address the more fundamental obligations to assist developing regions with implementation of new air monitoring programs. Data from the GAPS Network and related off-shoot regional passive sampling networks is providing the necessary spatial resolution that will revolutionize the role of measurements and the "integration" of measurements with global transport models and emissions inventories, with the aim to improve understanding of the sources,

transport, and fate of POPs and related chemicals. A higher level of understanding is required if we are to evaluate the effectiveness of control measures on observed concentrations of POPs. This is particularly relevant for the arctic region due to the complexity of sources and interactions with POPs in this environment. One of the challenges associated with the future use of passive samplers is characterizing the sampling rates of high K_{OA}, mainly particle-bound chemicals and/or developing alternative passive particle samplers.

3.1.6. POPs in snow and ice

3.1.6.1. Atmosphere-snowpack interactions

The influence of the snowpack on boundary layer chemistry in the polar regions has received growing scientific attention over the last 5 years, with evidence demonstrating the influence of surface snow layers on NOx and oxidant chemistry (Grannas et al. 2007), as well as Hg depletion events in the lower atmosphere (Dibb et al. 2010) , Johnson et al. 2008). Similarly, for semi-volatile chemicals, like POPs, the extensive snowpack over the Arctic serves as an important repository for these chemicals and can influence their seasonal behavior in the overlying atmosphere (Hansen et al. 2008b, Meyer and Wania 2008).

Snowfall is highly efficient at removing both particle-bound and vapour phase POPs from the atmosphere. Vapour scavenging is a function of the specific surface area (SSA) of the snow and is predicted to be most pronounced for snow possessing high SSA (e.g., 1,000 $cm^2\ g^{-1}$) and at cold temperatures (< -10 ^oC), resulting in scavenging ratios for semi-volatile chemicals being generally higher than those predicted for rain (by over an order of magnitude in some cases) (Lei and Wania 2004). The snowpack, therefore, has a high capacity for semi-volatile contaminants and can accumulate chemicals through successive snowfall events. The amount of chemical deposited is unlikely to be the quantity released during seasonal melt, as a significant fraction of relatively volatile, hydrophobic chemicals can be re-released to the atmosphere during snow compaction and ageing. Herbert et al. (2005a) demonstrated that the rapid loss of organochlorine pesticides and PCBs measured in fresh snowfall in the Norwegian Arctic was empirically related to increases in snow density (and presumably snow surface area) as the fresh snow underwent metamorphosis and compaction over a period of several days. It is probable that this loss is related to chemical volatility or, more appropriately, a snow interface/air partition coefficient, K_{IA}, although the rather low precision of chemical measurements between successive snow samples did not allow for a clear distinction between chemicals of differing physical-chemical properties. Similarly, a study conducted on separate snowfall events in the Turkey Lake watershed (east of Lake Superior) related changes in POP concentrations to the snow aging process, with loss of PCBs and OC pesticides of the same order of magnitude as the corresponding reduction in the specific snow surface area. Again, in this study, no relationship between the extent of loss and the K_{IA} of the chemical was apparent, although other factors such as air and snow temperatures and water content of the separate snowfall events played an important role in contaminant behavior (Burniston et al. 2007).

Measurements of POPs in snow reveal a wide range in concentrations which are largely dependent on the physical characteristics of the snow such as its density, surface area, as well as the particle and organic matter content (Meyer and Wania 2008). In this context, the snow surface area, expressed as a surface area index—the vertically integrated surface area of snow crystals to ground area ($m^2\ m^{-2}$)—is a useful measure of the ability or capacity of a snowpack to sorb vapour-phase pollutants. For example, the high arctic snowpack presents a higher surface area index (approximately 2500 $m^2\ m^{-2}$) than subarctic regions (approximately 1,000 $m^2\ m^{-2}$), therefore providing a greater capacity to retain snow-sorbed contaminants removed from the atmosphere, relative to subarctic regions. Warming of the High Arctic will modify snowpack structure and reduce this index, altering the sorptive capacity of snow and reducing the efficiency of air-to-surface transfer for more volatile pollutants (Dominé et al. 2007, Taillandier et al. 2006). How this change in snowpack structure would be offset against predicted increases in snowfall for some parts of the Canadian Arctic is unclear. Nonetheless, changes to both seasonal and permanent snowpacks will affect contaminant dynamics, influencing the timing and extent of release of chemicals both back to the air and to marine-freshwater systems following melt. Enhanced seasonal melt of permanent snowpacks and ice caps may lead to significant re-mobilization of accumulated persistent chemicals, depending on the exact circumstances of melting and the properties of the contaminant in question. Some evidence of

this is available from Antarctica, where the lack of decline in ΣDDT levels in Adélie penguins (*Pygoscelis adeliae*) coupled with the presence of *p,p'*-DDT (indicating a current source of DDT) are most likely attributable to the release of DDT residues in glacier meltwater following glacier ablation in coastal regions (Giesz et al. 2008). In the Arctic, levels of several perfluorinated chemicals measured in surface marine waters of the Greenland Sea were found to be significantly higher in the coastal areas of East Greenland (specifically for several PFCAs including PFHpA and PFOA) as a result of snow and ice meltwater runoff (Busch et al. 2010).

Modeling the seasonal evolution of the arctic snowpack has demonstrated the role it plays in affecting atmospheric concentrations of α-HCH and other POPs and helps to explain seasonal variations observed in atmospheric levels observed at a number of monitoring stations, including Alert (NU) (Hansen et al. 2006, Hansen et al. 2008c). Fresh snowfall and diffusive vapour exchange are processes which will both add and remove chemical contaminants to the surface snowpack, resulting in a highly dynamic system of contaminant exchange with the lower atmosphere, driven by physical changes to the evolving surface snowpack. Figure 3.24 illustrates the time-series of measured α-HCH air concentrations at Alert (NU) over a retrospective period including modeled concentrations generated both with and without the seasonal arctic snowpack included in the model. The stronger agreement between observed data and modeled results with the snowpack included, indicates the importance of snowpack chemical transfer in influencing vapour phase contaminant levels in the lower atmosphere.

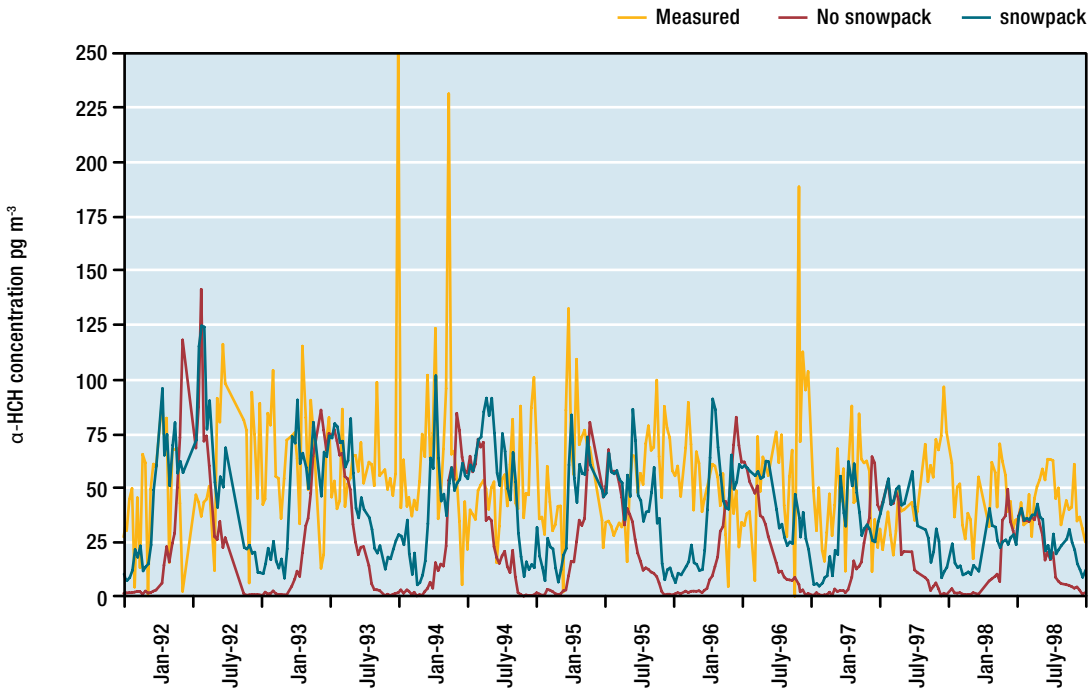

FIGURE 3.24

Measured and modeled concentrations of α-HCH in the atmosphere at Alert (NU). The modeled concentrations were determined using the Danish Eulerian Hemispheric Model (DEHM); an atmospheric chemistry-transport model incorporating a single-layer seasonal snowpack (Hansen et al. 2008c).

3.1.6.2. Perennial snowpack and ice-core studies

Several field studies conducted since NCP-II have demonstrated the presence of POPs in snow at a number of locations in the Canadian Arctic. These include studies conducted on the sea-ice snowpack and in the snowpack of ice caps; the latter allowing for an accumulation time-series from the mid-1990s to mid-2000s.

3.1.6.2.1. PFASs in Canadian Arctic snow and ice caps

Perfluorinated alkyl acids have been analyzed in snow sampled on various ice caps across the Canadian Archipelago with concentrations of PFOA and PFOS in surface-snow on the Agassiz, Meighen and Melville ice caps ranging from 5.0–12.1 and 13.1–53.7 pg L^{-1} respectively, with ΣPFCAs ranging from 20.7–75.4 pg L^{-1}. On the Devon Island ice cap, concentrations of the PFOS in snow (average for the 0–100 cm depth) were similar to other ice caps (4.9 pg L^{-1}) while ΣPFCAs were higher (121 pg L^{-1}) (Young et al. 2007). In northern Ellesmere Island, snow sampled within the Lake A watershed, had PFOA concentrations ranging from 199–239 pg L^{-1} and PFOS from 14–70 pg L^{-1} (Veillette et al. 2012). The concentrations in high arctic snow were 2–3 orders of magnitude lower than those measured in precipitation at lower latitudes by Scott et al. (2006b). These concentrations are comparable to levels observed for "legacy" POPs in previous arctic snow studies, and their presence in remote snowpacks demonstrates the atmosphere as an important source of these chemicals.

Sampling of the perennial snowpack on the Devon Island ice cap allowed for the generation of a time-series of concentrations from 1996 to 2005. Snow density-corrected concentrations of PFOS showed a significant decline over this period, while a similar trend was not observed for the PFCAs, with the later years (2004–2005) displaying some of the highest concentrations of PFOA and PFNA (> 100 pg L^{-1}) and reflecting ongoing emission and use of these chemicals or their precursors over this time period. The time series of PFCA and PFOS concentrations are displayed in Figure 3.25. The derivation of deposition fluxes, scaled up for the entire area of the Arctic > 65°N, based on the average concentrations in snow at the various ice caps are in reasonable agreement to modeled fluxes developed from an atmospheric chemistry transport model (within a factor of approximately 2). The model-derived fluxes are based on the oxidation of 8:2 FTOH (the volatile precursor to PFOA) and its subsequent deposition (Wallington et al. 2006). For example, the average flux of PFOA to arctic surfaces, determined from the 2005 snow layer, was 271 kg y^{-1} compared to the modeled flux of 400 kg y^{-1}, indicating that the atmosphere is an important contemporary source of PFCAs in arctic terrestrial surfaces.

Photo: Derek Muir

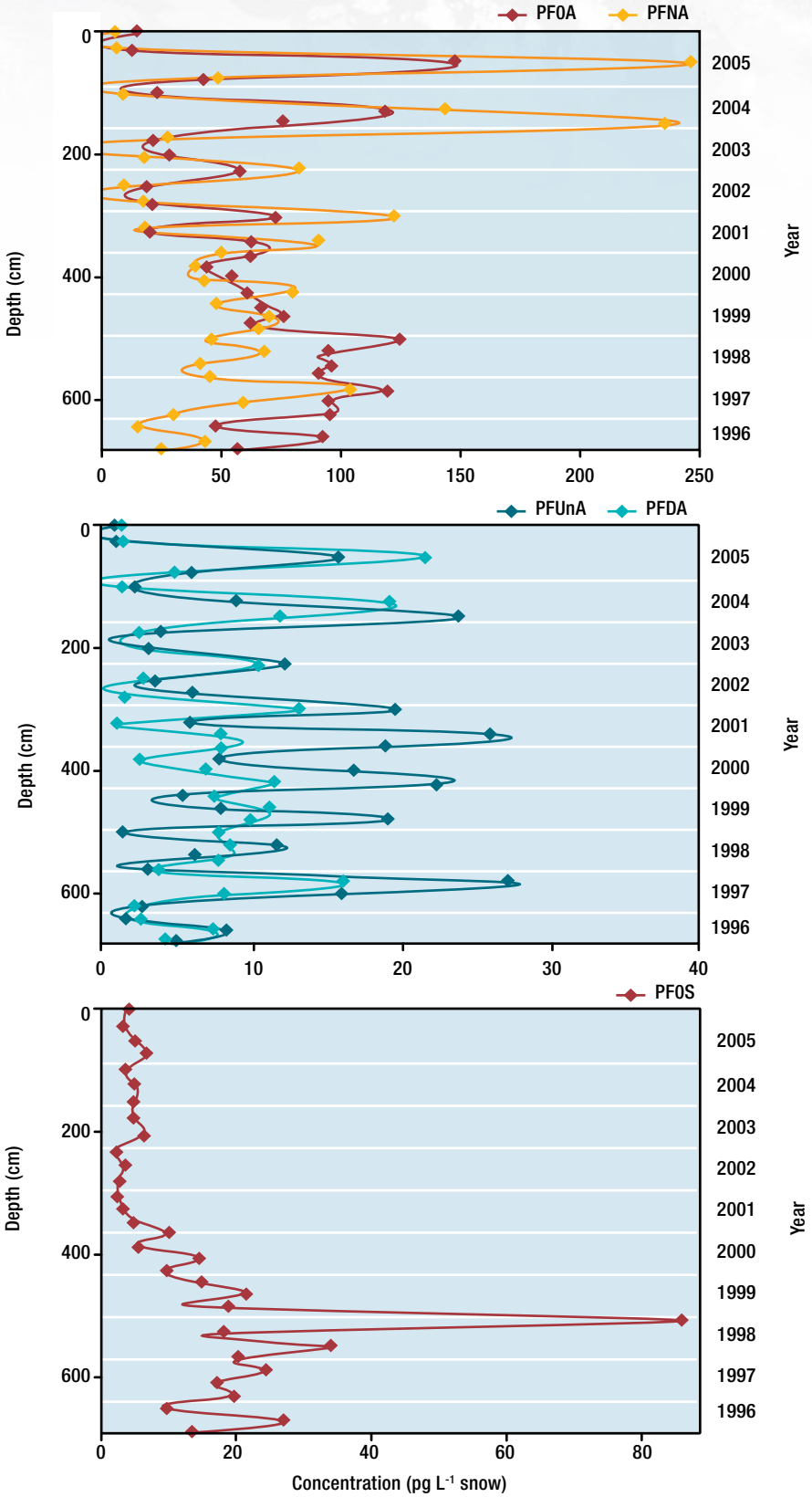

FIGURE 3.25

Accumulation time-series of perfluorocarboxylic acids (perfluorooctanoic acid, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA)) and perfluorooctane sulfonate (PFOS) concentrations in the perennial snowpack of the Devon Ice Cap, Devon Island (NU) (Young et al. 2007). Note that the high concentration of PFOS in the 1998 layer could be partly attributable to meltwater percolation from overlying snow layers affected by the warm summer of 2001, although this was not apparent for the PFCAs.

3.1.6.2.2. BFRs in the Devon ice cap

PBDEs and other BFRs have also been measured in the snowpack of the Devon Island ice cap, over approximately the same accumulation period as the PFASs (Meyer et al. 2012). Snow was collected from snow pits dug near the summit of the Devon ice cap in 2005, 2006 and 2008. The collection in 2008 involved sampling continuous segments of the pit wall, whereas sampling in 2005 and 2006 involved an 8 cm diameter core taken every 25 cm. Thus the 2008 results are thought to be more representative of fluxes of PBDEs and other BFRs. Dating using annual snow accumulation data, ion chemistry and density measurements established that the pits covered the period from approximately 1993 to spring 2008. Samples were extracted under clean room conditions, and analyzed using GC-negative ion MS for 26 tri- to decabromodiphenyl ethers (BDEs), as well as other BFRs, non-brominated flame retardants, and industrial chemicals. Decabromodiphenyl ether (BDE-209) was the major congener present in the samples followed by nona-BDEs, both accounting for 89% and 7% of total BDE, respectively. BDE-209 concentrations were remarkably high compared to other POPs with concentrations ranging from 9.5 ng L^{-1} to 100 ng L^{-1} in 2008 and in the same range in 2005 and 2006. BDE-209 was, in most cases, significantly correlated ($p < 0.05$) to tri- to nona-BDE homologues, and the strength of the correlations increased with increasing degree of bromination. This implied that the octa- and nona-BDEs were likely formed by debromination of deca-BDE. The nona-BDEs/deca-BDE ratio was 0.07 compared with 0.01–0.04 in technical deca-BDE products (de Wit 2002). In contrast, concentrations for the penta-BDE (sum of BDE-47, BDE-99 and BDE-100) ranged from 0.06–1 ng L^{-1}. Fluxes of BDE-209 ranged from 100–2000 pg cm^{-2} y^{-1} in the 2008 snow pit with no clear temporal trend over the 15 year depositional period (Figure 3.26).

Concentrations for the penta-BDE and octa-BDE in the 2002–2007 snow layers were approximately 150–800 pg L^{-1} and 50–200 pg L^{-1} (snow water equivalent) respectively, while levels of the deca-BDE were much higher exceeding 100 ng L^{-1} for the 2005 and 2006 snow layers. The relatively higher levels of deca-BDE, essentially a particle-bound compound, may reflect the lack of post-depositional loss of this chemical from fresh snowfall as well as its ongoing worldwide use. The fluxes of BDE-209 on the Devon Island ice cap were comparable to a flux of 322 pg cm^{-2} y^{-1} derived from an ice layer

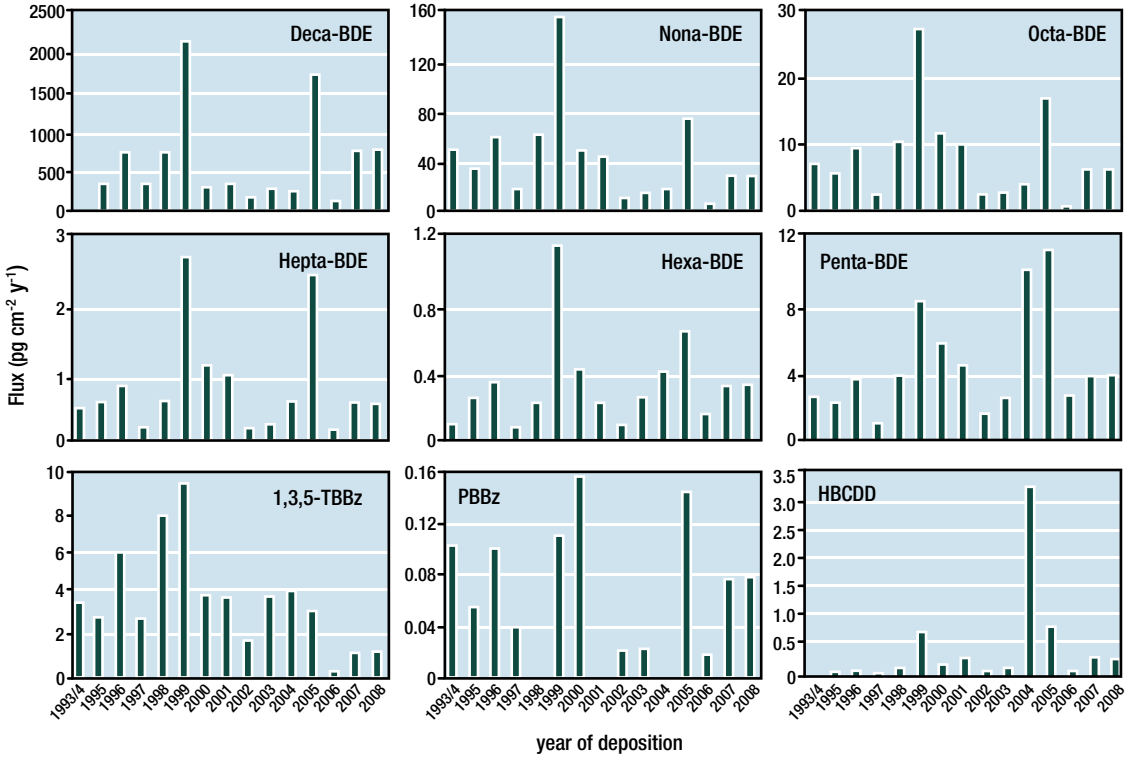

FIGURE 3.26

Fluxes of deca-BDE (BDE-209) and total nona-, octa-, hepta-, hexa- and penta-BDEs along with 1,3,5-tribromobenzene, pentabromobenzene and HBCDD in the Devon ice cap (Meyer et al. 2012).

corresponding to the accumulation period 1995–2005, taken from the Holtedahlfonna Ice Cap, Svalbard (Hermanson et al. 2010). In both studies, other brominated flame retardants were also detected including HBCDD and BTBPE. The accumulation flux of HBCDD to Holtedahlfonna for the 1995–2005 ice-layer was approximately 950 pg cm^{-2} y^{-1}.

However, the accumulation of HBCDD on the Devon ice cap was much lower, approximately 0.2–3.0 pg cm^{-2} y^{-1} over the annual layers (1995–2007) in the snow. This discrepancy may be partly due to the influence of different source regions, with HBCDD use in Europe accounting for the relatively high accumulation flux of this chemical in Svalbard. Both locations showed increasing concentrations of HBCDD over time. However, background HBCDD concentrations reported for the ice core analyzed by Hermanson et al. (2010) were elevated (7.5 ng L^{-1}) indicating some HBCDD was introduced during sampling or extraction and thus the estimates for Svalbard are uncertain. Background concentrations for the Devon snow samples were at detection limits. Other non-BDE flame retardants and industrial chemicals found in the snow pits included 1,3,5-tribromobenzene and pentabromobenzene (Figure 3.26) as well as hexabromobenzene and pentabromoethyl benzene.

3.1.6.3. Air-surface exchange and PCNs in snow

Atmospheric deposition of POPs takes place by precipitation scavenging of particulate and gaseous compounds and the two-way exchange of gaseous compounds between water, ice and snow, and soil. The relative loadings of PCNs to arctic ecosystems by these processes depend on their distribution between the particle and gas phases in the atmosphere. The apparent phase distribution of PCNs in arctic air was investigated by Harner et al. (1998, 2004), using the concentrations of PCNs trapped in a glass fiber filter and a backup polyurethane foam adsorbent as measures of particle-bound (C_p, pg m^{-3}) and gaseous (C_g, pg m^{-3}) compounds. Heavier CN congeners with lower liquid-phase vapour pressures (P_L, Pa) and higher K_{OA} were preferentially associated with particles. Helm and Bidleman (2005) measured the apparent particle-gas distribution for PCNs, non-ortho PCBs and mono-ortho PCBs in a larger set of winter and spring air samples from Alert (NU) and Dunai (Russia). Percentages of CN homologues on particles ranged from < 5% for tri-CNs and tetra-CNs, 20–30% for penta-CNs, 75% for hexa-CNs and > 90% for hepta-CNs and octa-CN. About 50–60% of CBs 77, 114, 118 and 105 were associated with particles, increasing to 75–85% for CBs 126 and 156. Harner et al. (1998) correlated the log C_p/C_g ratio to log K_{OA} ($r^2 = 0.837$) for a single winter sample taken at Alert. Egebäck et al. (2004) found similar correlations ($r^2 = 0.854–0.896$) for air samples collected at Hoburgen and Ammarnäs in southern and northern Sweden. Helm and Bidleman (2005) used sulfate as a surrogate for total suspended particles (TSP, µg m^{-3}) and calculated a particle-gas partition coefficient, $K_p = C_p/(C_g \times TSP)$, for a suite of PCN and mono-non-ortho PCB congeners which was correlated to K_{OA} or P_L. Comparisons were made of measured and predicted K_p, using three models, the Junge-Pankow adsorption model (Pankow 1987), which uses P_L and aerosol specific surface area as correlating parameters, an absorption model (Finizio et al. 1997, Harner and Bidleman 1998), which is based on K_{OA} and the fraction of aerosol organic matter, and a dual model which considers adsorption to black carbon and absorption to organic matter (Dachs and Eisenreich 2000). The Junge-Pankow model using P_L overestimated observed K_p, while good agreement was found using the K_{OA} absorption model and aerosol organic matter fractions of 7–12%. Surprisingly, inclusion of black carbon generally did not improve the estimates of K_p, suggesting that partitioning of PCNs to arctic aerosols occurs mainly to the organic fraction. Other studies have found that planar chlorinated aromatic compounds are strongly associated with black carbon in water and sediments (Jonker and Koelmans 2002, Lohmann 2003, Persson et al. 2002, Persson et al. 2005).

Herbert et al. (2005b) sampled air and snow at Ny-Ålesund (Norway) during April 2001 and in Tromsø (Norway) from February to March 2003. The ΣPCNs concentrations in snow meltwater spanned a wide range from 60–1100 pg L^{-1} with means of 350 pg L^{-1} and 240 pg L^{-1} at Ny-Ålesund and Tromsø, respectively. Bulk densities ranged from 0.01–0.3 kg L^{-1} for snows of different types. The highest meltwater concentration was found in an event of fresh snow with dendritic crystals and low density. Scavenging of gaseous POPs by snow is favoured in high specific surface area (SSA) (Burniston et al. 2007, Herbert et al. 2005c, Lei and Wania 2004). An empirical relationship in which snow bulk density was inversely proportional to SSA was found by Legagneux et al. (2002). Herbert et al. (2005b) found that the PCN concentrations in meltwater were correlated inversely to snow density at $p < 0.01$ for tetra-CNs and penta-CNs and < 0.1 for tri-CNs.

Atmospheric deposition of gaseous POPs to water surfaces can be estimated from concentrations in air, but a description of two-way gas exchange requires that dissolved phase concentrations in water be

known. Very few measurements of dissolved PCNs in water have been made, and none in arctic and subarctic waters. Persson et al. (2005) measured dissolved and particulate PCNs in the Grenlandsfjords, southern Norway, but the data were only presented in the form of the particle/dissolved ratio. Measurement of gaseous PCNs in air and dissolved PCNs in water allowed air-water exchange to be assessed for Lake Ontario (ON), with the result that tri-CNs were undergoing net volatilization whereas tetra-CNs were close to air-water equilibrium (Helm et al. 2003). PCNs have not been reported in the Arctic Ocean; however, reports of dissolved and particulate PCBs in the Arctic Ocean (Sobek and Gustafsson 2004) suggests that PCNs would also be present. The occurrence of dissolved PCNs at some level in subarctic Bothnian Bay (the northernmost part of the Baltic Sea) is implied, as they were found on suspended particles (Lundgren et al. 2002).

3.1.6.3.1. Toxic equivalents of PCNs in arctic air

Some studies report tetrachlorodibenzo-*p*-dioxin (TCDD) toxic equivalents (TEQ) in arctic air due to PCNs and "dioxin-like" PCBs (DL-PCBs). Assessments of PCNs TEQ in the studies cited below were based on those penta-, hexa- and hepta-CNs for which relative potencies (H4IIE-REPs) have been estimated (CNs 52, 54, 56, 57, 60, 61, 63, 64, 66, 67, 68, 69, 70, 71, and 73) (Blankenship et al. 2000, Villeneuve et al. 2000) and which were found in samples. The TEQ due to DL-PCBs were based on non-ortho CBs 77, 81, 126, and mono-ortho PCBs 105, 114, 118, and 156.

Harner et al. (1998) reported ΣTEQ (PCNs + DL-PCBs, fg m^{-3}) for air samples collected in the Barents Sea (2.0), eastern Arctic Ocean (0.81), Norwegian Sea (≤ 0.36), Alert (0.41) and Dunai (Russia) (0.60). These can be compared to the much higher ΣTEQ in Chicago (11.6). The PCNs TEQ at arctic and subarctic sites accounted for 13–67% of ΣTEQ due to PCNs + DL-PCBs. Helm et al. (2004) reported that the ΣTEQ (PCNs + DL-PCBs) at Alert (NU), Dunai (Russia) and Tagish (YK) ranged from 0.006 fg m^{-3} during the warm period to 0.061 fg m^{-3} during the cold period. During winter, PCNs contributed 71–75% of ΣTEQ at Alert (NU) and Dunai (Russia), but only 30% at Tagish (YK). In summer, DL-PCBs accounted for 65–98% of the ΣTEQ at all three sites.

No studies have been done in which PCNs, DL-PCBs and PCDD/Fs have all been measured in arctic air at the same time. Harner et al. (1998) noted that the TEQ due to PCDD/Fs (1.7 fg m^{-3}) were higher than for DL-PCBs (0.019 fg m^{-3}) in two air samples collected at Ny-Ålesund by Schlabach et al. (1996). During winter 2000–2001, PCDD/Fs TEQ at Alert (NU) averaged 0.4 fg m^{-3} (Hung et al. 2002), which Helm et al. (2004) recalculated to 0.8 fg m^{-3} using HII4E-REPs. Thus, the various studies indicate that PCDD/Fs dominate ΣTEQ in some cases and in others are rather similar to the TEQ contributions from the other two compound classes.

3.1.6.4. Contaminant occurrence and processing in the sea-ice snowpack and sea-ice

Relatively few studies have examined the occurrence of organic contaminants in the sea-ice system, largely due to practical issues of inaccessibility and other logistical difficulties. However, research conducted in the Canadian Arctic during the Canadian Circumpolar Flaw Lead system study (CFL) as part of the International Polar Year (IPY) has yielded new information regarding the accumulation of chemicals in the sea-ice snowpack and the effects of sea-ice on contaminant dynamics in the surface marine environment.

OC pesticides, PBDEs, PCBs and PFASs were measured in air and the sea-ice snowpack in the Amundsen Gulf and western Beaufort Sea of the Canadian Arctic between October 2007 and June 2008 (Codling et al. 2012, Pućko et al. 2010b, Wong et al. 2011) and a summary of measured concentrations is provided in Table 3.6.


Photo: Crispin Halsall

TABLE 3.6. Persistent organic pollutants measured in the sea-ice snowpack of the Amundsen Gulf, Canada (March–June 2008). Chemical concentrations expressed as pg L^{-1} snow-meltwater (POP samples *n*=11; PFAS *n*=15). Samples collected between 69–74°N and 119–126°W.

Chemical	Mean	range
cis-chlordane	4.9	ND–12.4
trans-chlordane	3.92	ND–9.8
HCB	81.1	<MDL–247.9
p,p'-DDE	3.96	ND–21.0
α-HCH	23.5	2.5–37.2
γ-HCH	52.1	12.9–78
PCBs		
18	25.4	4.67–78.0
28/31	59.2	<MDL–158
52	11.5	1.32–45
95	8.6	<MDL–23.5
90/101	10.7	<MDL–20.4
153/132	8.51	<MDL–15.9
149	10.9	1.80–20.1
151	3.56	<MDL–8.5
174	0.92	ND–3.82
183	0.64	ND–2.54
187	0.97	ND–3.11
Σ_{12}PCB	140	43.1–354
PBDE		
17	1.66	<MDL–3.21
28	2.2	0.88–5.21
47	40.2	11.8–68.8
99	31.6	0.81–54.0
100	3.5	ND–6.50
Σ_5PBDE	79.5	13.5–138
PFASs		
PFOS	2.83	8.43–22.3
PFOA	348	17.3–1140
PFNA	185	79.0–614
PFDA	77.4	10.1–180
PFUnDA	44.5	9.20–142

For several of the lower molecular weight compounds, the range in concentrations is relatively high, reflecting the different physical characteristics of the snow sampled over the winter period at various locations during the CFL campaign. Significant inverse relationships were evident between chemical concentrations and snow density for HCB and the PCB congeners, 18 and 28/31 (r^2=0.7–0.8, $p < 0.05$) with a weaker relationship apparent for α- and γ-HCH and *cis*- and *trans*-chlordane, and no relationship for the remaining chemicals including the PBDEs and PFASs. The highest snow densities (0.44–0.48 kg L^{-1}) were measured in the late-season for older, often partially-melted snow with correspondingly lower concentrations for the lower MW compounds compared to lower density snow, recorded. Significant loss of α- HCH and γ-HCH (by approximately 40%) from fresh snowfall via re-volatilisation was observed when windy conditions were encountered on the sea-ice, and attributed to the rapid increase in snow density and reduction in the SSA over

relatively short time periods (< 24 hours) (Pućko et al. 2011). In general, the late winter sea-ice snow pack is relatively shallow (< 1 m), comprising of hard, wind-pack slabs overlying layers of well-faceted crystals and depth hoar; snow that has undergone considerable metamorphosis. Deeper snow (> 1 m) occurs as drifts around the edges of ice floes and ice pressure ridges.

Figure 3.27 presents a non-systematic time-series of contaminant concentrations (HCB, α- and γ-HCH and PFASs) measured in the ice snowpack and air from late April to early June. The average daily air temperature fluctuated around 0 ºC from mid-May onwards, resulting in a notable reduction in the snowpack and the occurrence of melt-ponds on the sea-ice surface by late May. By early June, ice-cover in the Amundsen Gulf had decreased to < 40%, compared to approximately 98% prior to May. Concentrations of HCB and HCHs in the snow appear to decline from mid-May onwards accompanied by increasing concentrations in air. For α-HCH, increasing concentrations in overlying air as the melt season progresses are shown to be affected by increased volatilisation from surfaces, particularly open seawater. Evidence for this comes from the signal of the enantiomeric fractions (EF) of α-HCH, which in air increasingly reflect the EF signal (< 0.5) of α-HCH observed in surface seawater during this period (Wong et al. 2011). The fraction of contaminants retained in the aged, melting snowpack are therefore likely to be lost to surface marine waters during ice-floe breakup.

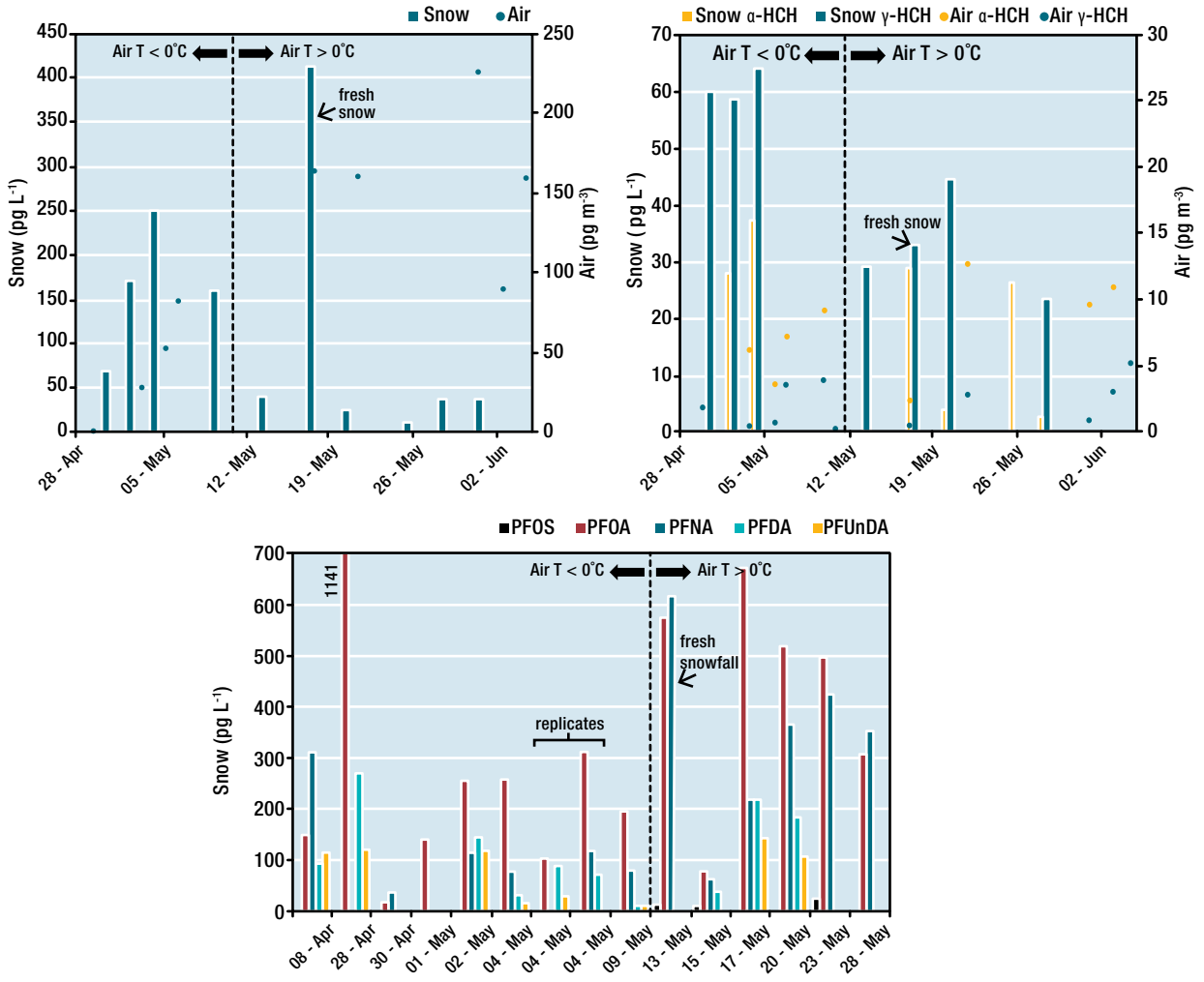

FIGURE 3.27

Time-series of HCB (A), α and γ-HCH (B) and selected PFASs (C) in the sea-ice snowpack of the Amundsen Gulf region of the Canadian Arctic (April–June 2008). The vertical dashed line approximately denotes the period when average air temperatures were at or above 0ºC. HCB and HCH concentrations in air are shown on the secondary y-axes. Note that PFAS data is for snow collected at different locations compared to A and B. Data from Codling et al. (2012); Bertrand et al. (2013).

Evidence demonstrating this is presented in Figure 3.28, which shows concentrations of PCBs, α- and γ-HCH and HCB in air, snow, sea-ice and surface seawater on 5 May 2008 and then later on 15 May 2008 in the Amundsen Gulf. An increase in concentrations in seawater is clearly apparent in the results for 15 May 2008, although the geographic sampling locations for the respective dates are different. Older, multi-year sea-ice sampled during July–August 2001in the Barents Sea marginal-ice zone, showed very low levels of PCBs, with a significant particle-bound fraction present in both aged-snow and ice and is indicative of significant contaminant processing and loss following earlier spring melt (Gustafsson et al. 2005).

The sea-ice provides a highly dynamic compartment for the accumulation and possibly "amplification" of organic contaminants. Measurements during the CFL campaign revealed mean α-HCH concentrations of 0.642 ± 0.046 ng L^{-1} in new and young ice (< 30 cm), 0.261 ± 0.015 ng L^{-1} in first-year ice (30–200 cm) and 0.208 ± 0.045 in old ice (> 200 cm). Mean γ-HCH concentrations were 0.066 ± 0.006 ng L^{-1} in the new and young ice, 0.040 ± 0.002 ng L^{-1} in first-year ice and 0.040 ± 0.007 ng L^{-1} in old ice (Pućko et al. 2010b) (Pućko et al. 2011). In general, α-HCH and γ-HCH concentrations and vertical distributions were highly dependent on the initial entrapment of brine in young ice and the subsequent desalination process. α-HCH and γ-HCH levels decreased exponentially with increasing sea-ice thickness following the sea-ice desalination curve (Figure 3.29). The correlations between Log[HCH] and Log[salinity] and between Log[HCH] and Log[thickness] in the sea-ice were significant for the α- ($r^2 = 0.84$; $p < 0.01$ and $r^2 = 0.70$; $p < 0.01$, respectively) and γ-isomers ($r^2 = 0.39$; $p < 0.01$ and $r^2 = 0.40$; $p < 0.01$, respectively). The correlations suggest that brine rejection is accompanied by HCH rejection. During the initial stage of ice formation, the growth velocity is relatively high and considerable amounts of brine are trapped in the sea-ice. As the thickness of the ice increases, the growth velocity decreases and less brine is trapped. Laboratory experiments suggest that gravity drainage is the main desalination mechanism for first-year sea-ice that is growing, with the rate dependent on the temperature gradient within the ice. This could explain the gradual decrease in desalination amounts observed in thicker ice.

Photo: Martin Fortier/ArcticNet

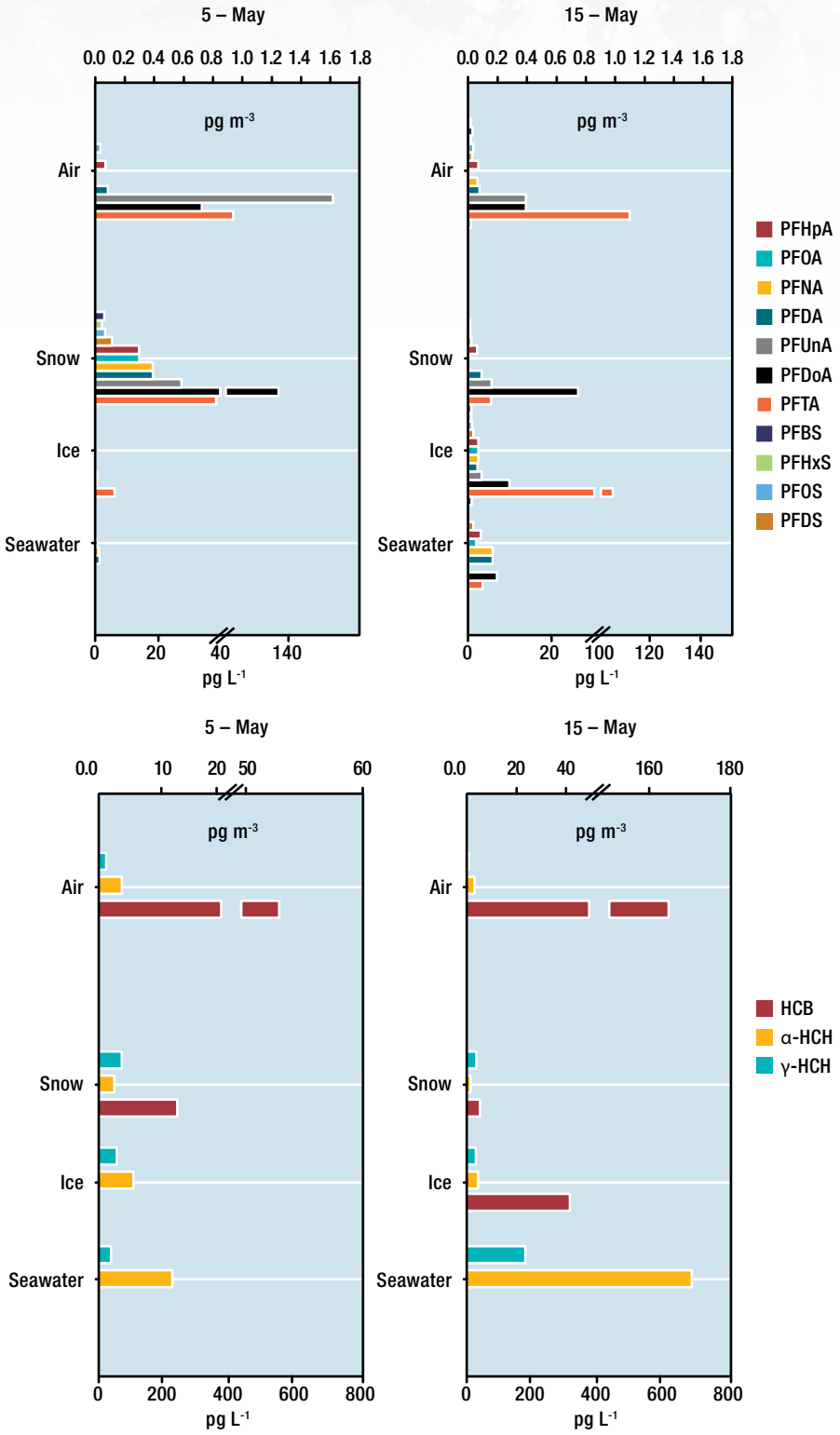

FIGURE 3.28

Concentrations of PCBs, OC pesticides and HCHs measured in the sea-ice snowpack, sea-ice, seawater and overlying air on the 5 and 15 of May 2008, respectively, in the Amundsen Gulf, Canada. Note that the sampling location on the 5 May was 71° 10' N, 126° 57' W and on the 15 May was 69° 56' N, 126° 10' W.

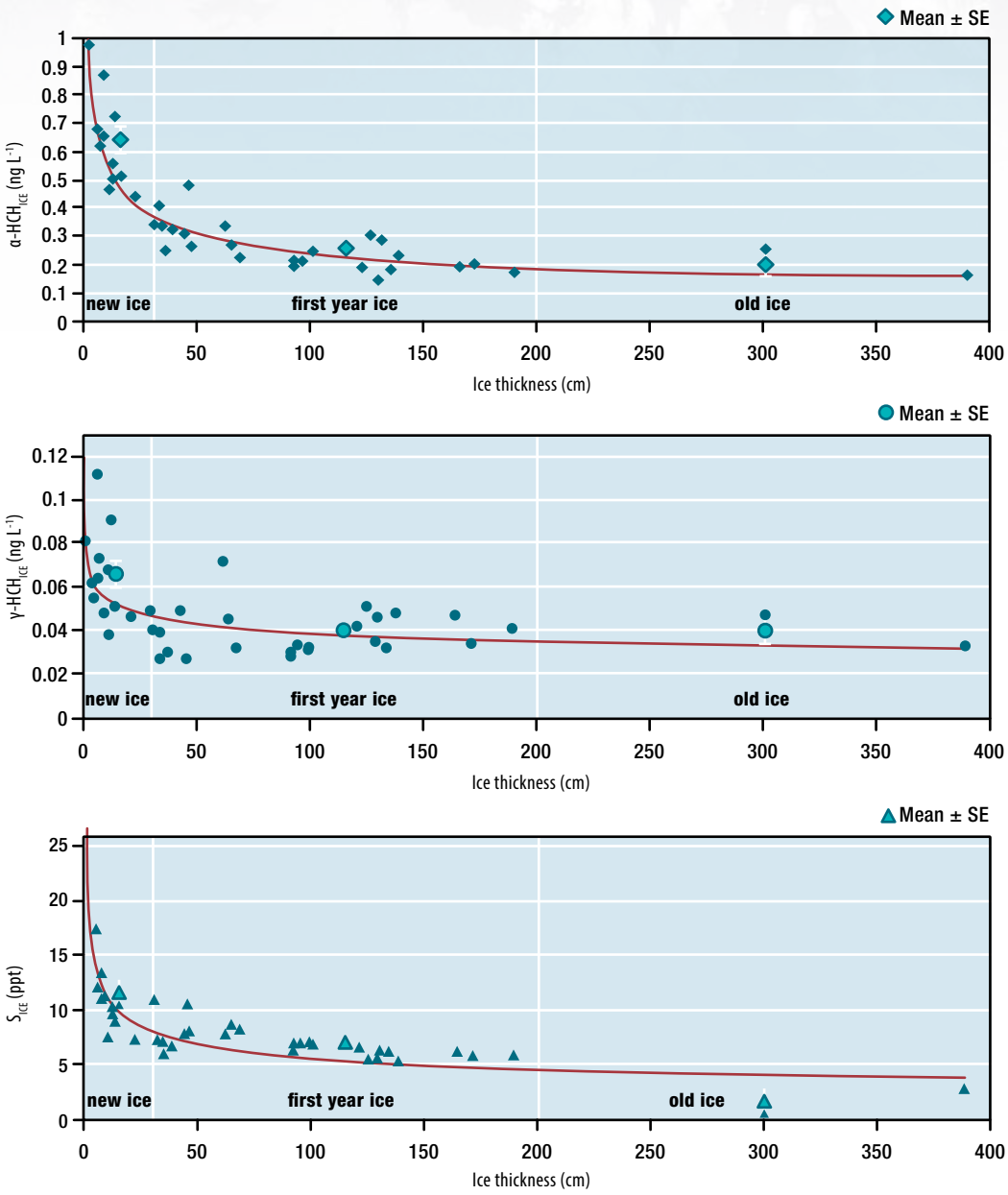

FIGURE 3.29

Dependence of α-HCH (top panel) and γ-HCH (middle panel) concentrations and salinity (S) on the sea-ice thickness.

Holes partially augered into first-year sea-ice (sumps) were used to determine α- and γ-HCH concentrations in sea-ice brine during January 2008 (Pućko et al. 2010b). HCH levels in the brine in the winter were approximately 13 times higher than in bulk ice, reaching 4.013 ± 0.307 (SE) ng L^{-1} for α-HCH, and 0.423 ± 0.013 (SE) ng L^{-1} for γ-HCH. Brine contained within sea-ice currently exhibits the highest HCH concentrations in any abiotic arctic environment, exceeding under-ice water concentrations by a factor of approximately 3 in the spring. Sea-ice brine pockets comprise an extreme-environment habitat, the function of which in polar marine environments remains unclear. The present high levels in brine, which imply former concentrations during the period of peak loading (1980–1990) of perhaps 10 times greater, therefore pose a risk to the sea-ice biota inhabiting the bottom of the ice in spring, or living within brine channels throughout winter. In the central Arctic, ice algae are thought to contribute up to 57% of the primary production (water column and sea-ice), again emphasizing the potential importance of the brine-concentration process in amplifying lower

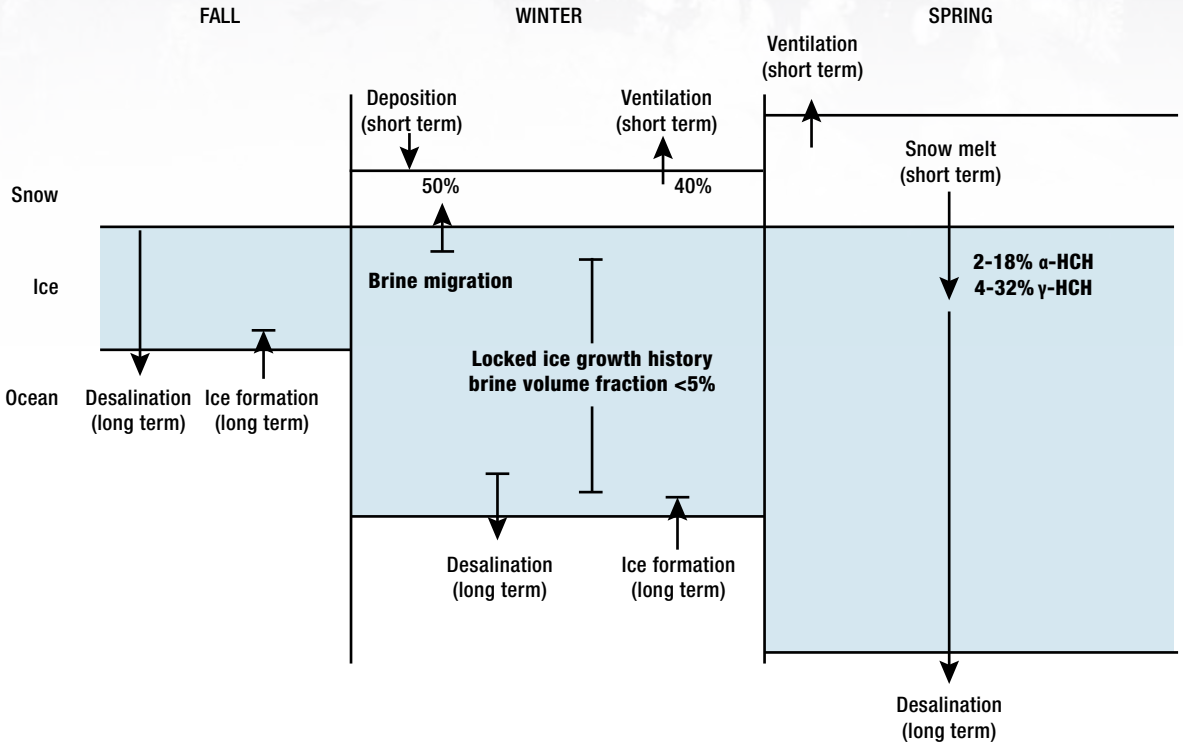

FIGURE 3.30

Schematic diagram of atmosphere to snow to sea-ice to ocean processes affecting HCH concentrations in various compartments of the arctic environment during various seasons.

food web exposure, which then translates into higher biological exposures all the way up through the arctic marine food web.

The physical processes, which depend strongly on the season, and the chemical exchanges, which depend on snow and ice physical characteristics, atmospheric conditions, and age of the snow, are summarized in a schematic diagram (Figure 3.30). Using HCH as a representative POP, concentrations in newly-forming sea-ice during the fall, depend primarily on the rate of ice formation (HCH accumulation) and desalination (concurrent HCH rejection) until the combination of declining atmospheric temperature and increasing insulation by a thickening ice cover permit the ice to cool sufficiently for its brine volume fraction to drop below 5%. In the winter, most of the ice column exhibits a brine volume fraction below 5%; throughout this time the accumulating HCH concentrations at the bottom of the ice will become locked as the ice grows, thereby reflecting the HCH concentration of the water beneath the ice. After the first snow deposition, upward migration of brine from the surface of the ice will affect levels of salt and HCHs in the snow by diffusion out of the shallow "slush" layer, which maintains a brine volume fraction greater than 5%. In contrast, and as stated above, ventilation under windy conditions will lead to a decrease in HCH concentrations in the snow pack due to the loss of snow surface area. The atmospheric environmental conditions discussed above, clearly have a significant influence on HCH variability in snow. The extent to which snow can affect HCH levels in sea-ice is significantly smaller and restricted to a short period in spring when the ice warms enough for its brine volume fraction to exceed 5%. Changes in the perennial vs. annual types of sea-ice will affect the temperature distribution at the surface of the ice, making the interaction of new snow cover and young sea-ice more widespread in the Arctic, both geographically and seasonally, and this could be most pronounced for chemicals which are not readily lost from the snowpack through changes in density and snow surface area.

3.1.7. Assessment

- Many legacy POPs including OC pesticides and PCBs are declining in the arctic atmosphere, although in some cases the rates of decline have slowed or levels increased.
- A wide range of new, potentially persistent and bioaccumulative chemicals have been detected in the arctic atmosphere over the past 10 years.

- While temporal trend studies of legacy POPs are now very strong datasets, spatial and temporal atmospheric trends of emerging chemicals of concern for the Arctic are more limited or lacking.
- There are also limited measurements of these contaminants in environmental matrices, that are in contact with the atmosphere i.e., snow-wet precipitation, water, ice caps, soils.
- In addition to the parent compounds, there is little knowledge about the occurrence of and the risk associated with their transformation products, including their atmospheric reaction and degradation products generated during transport and deposition.
- The time required for the target chemical to reach the Arctic is influenced by the location of the source, the chemical's transport pathways and its physical chemical properties. A non-declining atmospheric trend may not necessarily indicate ineffectiveness of control.
- Given the stronger winds at the higher atmospheric level that favor atmospheric transport and large cloud covers over the Arctic, wet deposition of POPs likely plays a more important role in the POPs accumulation of POPs in arctic surface compartments, particularly since the levels in arctic air have exhibited a declining trend.
- There are limited measurements and a lack of time trends of atmospheric POPs in the western and eastern Canadian Arctic. Short-term measurements have been conducted at the satellite stations of Tagish and Little Fox Lake in the Yukon and Kinngait on Baffin Island. However, with limited measurements, it is difficult to assess intercontinental transport, i.e., trans-Pacific transport to the western Arctic and trans-Atlantic transport to the eastern Arctic, as well as long-range transport from southerly sources to the lower Canadian Arctic.
- Screening for "new" flame retardant related chemicals in air samples taken at Alert (NU) has shown the presence of a range of brominated and chlorinated chemicals. BTBPE, EHTeBB and TBPH were generally detected with concentrations similar to those of the dominant BDE congeners.
- The presence of neutral and ionic PFASs and the cyclic methyl siloxanes at Alert (NU) supports their atmospheric long range transport.
- Perfluoroalkyl substances and BFR, are present in the seasonal and perennial snowpacks in the Canadian Arctic at levels akin to the legacy POPs. The accumulation of some of these chemicals, particularly PFOS and the penta-BDE, show some evidence of a decline from the mid-1990s to mid-2000s, although this is not apparent for the PFCAs and deca-BDE reflecting their ongoing global use, with long-range atmospheric transport an important source.
- The processing of POPs and other organic contaminants in the sea-ice system of the Beaufort Sea and Amundsen Gulf region is complex, but sea-ice, particularly first-year ice, shows an "enrichment" in hydrophobic POPs such as HCHs in the ice-brine, with explusion of ice-brine during the winter resulting in elevated concentrations of these chemicals in the beneath-ice environment. This process is likely to be exacerbated in a warmer Arctic which will be dominated by fresh and first-year sea-ice which have higher levels of brine relative to multi-year ice.
- Low volatility chemicals such as PFOS and the PFCAs are present in the sea-ice snowpack and sea-ice, and unlike more volatile POPs, do not decline in the snowpack due to evaporative loss during late winter. Spring melt of the ice-rafted snowpack will therefore provide an additional source of these chemicals to surface marine waters. This may account for the elevated levels of PFCAs observed in the polar mixed layer of the western Beaufort Sea and Amundsen Gulf which are comparable to, or higher than, levels observed in North Atlantic surface water.

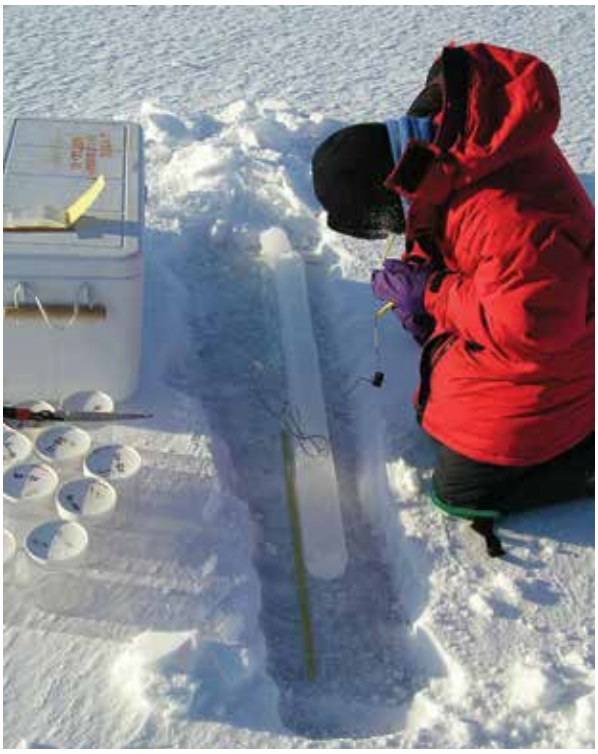

Photo: Shelly Carpenter/ArcticNet

3.2. Occurrence of Legacy and New POPs in Arctic Seawater and Lake Water

Contributors: Lutz Ahrens, Liisa Jantunen, Derek Muir, and Mahiba Shoeib

3.2.1. Introduction

Marine biota have historically received the most attention with regard to persistent organic pollutants in the arctic environment, where the level of research has continued to out distance research efforts in the freshwater and terrestrial ecosystems. This is clearly due to the higher levels observed in the marine system and the role of marine organisms in northern societies. Accumulation of POPs in marine biota starts with water, yet since NCP-II, only a few studies, mainly as a result of scientific cruises organized by circumpolar countries, have reported measurements of POPs and emerging chemicals in seawater in the Canadian Arctic and circumpolar Arctic (Table 3.7).

More measurements of HCHs have been made in arctic waters than for other organic contaminants. This is because HCH concentrations are sufficiently high that only approximately 10 L of seawater is required for analysis. The highest levels of HCHs in the world's oceans are found in the Arctic Ocean, especially in the Beaufort Sea and Canadian Archipelago probably due to the combined effect of permanent ice cover and circulation of older water within the Beaufort Sea. Results of mass balance modeling of HCH suggest that the Arctic Ocean is exporting α-HCH and β-HCH (Chapter 2, section 2.3.5.4.(Li et al. 2004). Larger volumes, on the order of 80–100 L, have been collected for other legacy and current use pesticides (CUPs) and ultra-high volumes up to approximately 1,000 L, have been sampled for PCBs and brominated flame retardants. Table 3.7 summarizes concentrations of OCPs and CUPs from sampling locations shown in Figure 3.31, and other chemicals found in arctic seawater are discussed in the text.

TABLE 3.7. Mean concentrations of legacy POPs and CUPs in arctic seawater and lakes, reported since 2001 (pg L^{-1}) [1]

Location	Year	ΣHCH	ΣCHL	HCB	Dieldrin	ΣDDT	DAC	CPY	ΣENDO	Σ_NPCB [11]	Ref
Hudson Bay Labrador Sea	2007 2007	806 [2] 615 [2]	1.8 [4] 1.5 [4]	6.4 5.1	33 34		29 35	6.7 7.6	10 [9] 8.2 [9]		1,2
Banks Island	2008	1190 [2]	2.3 [4]	5.2	27		14	23	4.3 [9]		1,2
Banks Island	2007 and 2008	1050 [2]									3,4
Banks Island	2007 and 2008									0.2–3.6	5
Banks Island	2007–2010						4–17	0.2–0.4	2.5–6.5		6
Eastern Arctic	2004	18 [2]	0.14 [5]	4.6		0.45 [7]				1.2(6)	6, 7
Eastern Arctic Eastern Arctic Chukchi Sea W-Archipelago Baffin Bay Russian Arctic	2001 2001 2005 2005 2005 2008									0.99(12) 1.4(12) 2.5(13) 2.6(13) 5.7(13) 3.4(13) [12]	8 9 9 9 9 9
Kara Sea	2003–2005	291 [3]	4.2 [6]	9.1	5.8	2.9 [8]			4.4 [10]	12(10)/59(209)	10
Yenisei Bay	2003	213 [3]	3.5 [6]	9.6	5.9	11.1 [8]			8.2 [10]	11(10)/61(209)	10
Gulf of Ob White Sea	2005 1999–2000	350 [3] 840 [3]	6.6 [6] 7[6]	11.1	7.0	15.5 [8] 5 [8]			7.2 [10] 3.4 [10]	16(10)/78(209) 37 (10)	10 10
Char	2006						10–12	<0.1	35–40		11
Hazen	2005						7–15	2–6	13–37		11

[1] Abbreviations : HCH = hexachlorocyclohexane, CHL = chlordane, HCB = hexachlorobenzene, DDT = dichlorodiphenyltrichloroethane and metabolites, DAC = dacthal, CPY = chlorpyrifos, ΣENDO = endosulfan isomers, PCB = polychlorinated biphenyls. (Wong et al. 2011); 2(Jantunen et al. 2011); 3 (Pućko et al. 2010a); 4 (Pućko et al. 2010b); 5 (Macdonald et al. 2009); 6 (Morris et al. 2011) 6 (Lohmann et al. 2009); 7 (Gioia et al. 2008); 8 (Sobek and Gustafsson 2004); 9 (Carrizo and Gustafsson 2011); 10 (Carroll et al. 2008); 11 (Muir et al. 2007)

[2] α-HCH + γ-HCH.

[3] α-HCH + β-HCH + γ-HCH.

[4] *cis*-chlordane + *trans*-chlordane + *trans*-nonachlor.

[5] *cis*-chlordane + *trans*-chlordane.

[6] *cis*-chlordane + *trans*-chlordane + *cis*-nonachlor + *trans*-nonachlor + heptachlor + heptachlor epoxide + oxychlordane.

[7] *p,p'*-DDT + *p,p'*-DDE + *p,p'*-DDD

[8] *p,p'*-DDT + *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *o,p'*-DDE + *o,p'*-DDD

[9] α-endosulfan + β-endosulfan

[10] α-endosulfan

[11] (N) = number of congeners included in Σ_NPCBs.

[12] One sample of 21 pg L^{-1} removed from the average.

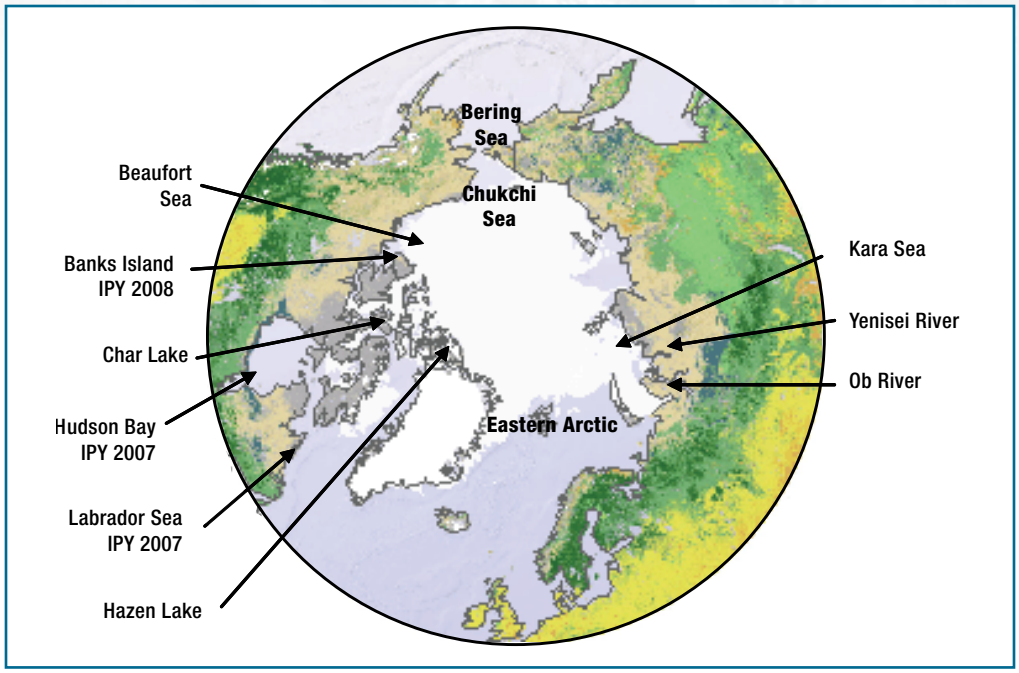

FIGURE 3.31

Map of seawater and lake water sampling locations in the Arctic (2003–2010).

3.2.2. Legacy chemicals in arctic seawater

3.2.2.1. Chlorobornanes

Chlorobornanes (CHBs, e.g., toxaphene) are typically the most abundant OCP in Canadian arctic biota particularly in marine mammals (see Chapter 4, section 4.1.5.3). There have been few studies of CHBs in arctic seawater. The ΣCHB concentrations, in decreasing order are in Baffin Bay > Beaufort Sea > Canadian Archipelago > White, Bering and Chukchi Seas (Bidleman et al. 2003, Hoekstra et al. 2002). This is consistent with air pathways from the southern US, which travel northeast and sweep over the Great Lakes and eastern Canada (Ma et al. 2005a, Ma et al. 2005b). Recent water samples from the Canadian Archipelago in 2008 show that CHB levels have dropped to or below the detection limit of approximately 5 pg L^{-1} (Jantunen et al. 2011). For the period 1993–1999, proportions of some labile CHB congeners were more abundant in archipelago seawater samples than in the Laurentian Great Lakes and southern US soils, but the source is unclear (see Chapter 2, section 2.2.1.2. for further discussion of CHB congeners).

3.2.2.2. Cyclodienes

Cyclodiene pesticides include chlordanes, nonachlors, heptachlor (HEPT), aldrin, dieldrin, endrin, endosulfan and the metabolites photoheptachlor, heptachlor exo-epoxide (HEPX) and oxychlordane (OXY). As with CHBs, very few reports of cyclodienes in Arctic Ocean water are available, especially for more recent years. Surface water samples were taken during the International Polar Year in 2007–2008 from the Canadian Archipelago (seeTable 3.7). Cyclodienes found were HEPX, *trans*- and *cis*-chlordane (TC, CC), *trans*-nonachlor (TN), dieldrin. *Cis*-nonachlor (CN), found in previous investigations in the Archipelago (Jantunen et al. 2011), was below detection (< 0.1 pg L^{-1}) in 2007–2008. Other cyclodiene OCPs sought but below detection (< 1 pg L^{-1}) in the Archipelago were HEPT and aldrin. The relative abundance of quantifiable cyclodienes in surface water during IPY in 2007–2008, was in the order dieldrin > HEPX > TC + CC > TN and the average TC/CC ratio was 0.5. Levels of TC + CC and TN (1.5 pg L^{-1} and 0.55 pg L^{-1}, respectively) were close to 2-fold lower than samples taken during Tundra North-West in 1999 (Jantunen et al. 2011). In the eastern Arctic, TC and CC were determined in surface waters between Svalbard and Greenland. Concentrations ranged from 0.02–0.2 pg L^{-1} for TC and 0.03–0.35 for CC. TC/CC ratios ranged from 0.1–0.9 with a mean of 0.5 (Lohmann et al. 2009). HEPX, a metabolite of HEPT, averaged 26 pg L^{-1} in IPY 2007–2008, higher than the previously reported levels in the Arctic (Jantunen and Bidleman 1998). The dieldrin level was higher in the Archipelago during IPY 2007–2008 (mean 30 pg L^{-1}) than

during TNW-99 (mean 15 pg L^{-1}), in contrast to the chlordanes, which were higher in 1999 than 2007–2008 (see above).

The sum of the chlordanes (TC, CC, TN, CN, HEPT, HEPX and oxychlordane) in the Russian Arctic ranged from 3.5–6.6 pg L^{-1}, where HEPX was the dominant compound (3.4–3.9 pg L^{-1}) (Carroll et al. 2008). Dieldrin level was also determined, ranging from 5.8–7.0 pg L^{-1}.

3.2.2.3. DDTs

p,p'-DDT and its metabolites *p,p'*-DDE and *p,p'*-DDD were detected in the dissolved phase in most seawater samples collected between Svalbard and Greenland (Lohmann et al. 2009). ΣDDT concentrations ranged from 0.17–0.69 pg L^{-1} (average 0.45 pg L^{-1}) and did not show a spatial trend, but *p,p'*-DDT did show a decreasing trend from near Europe (mean of 0.2 pg L^{-1}) northward to < 0.1 pg L^{-1}. Concentrations found in the Lohmann et al. (2009) study are lower than previous studies (Macdonald et al. 2000, Strachan et al. 2001).

In the Russian Arctic, lower levels of ΣDDT (*p,p'*- and *o,p'*- isomers of DDT, DDE and DDD) were found in the Kara Sea (2.9 pg L^{-1}) and the White Sea (5 pg L^{-1}) than in the Gulf of Ob (16 pg L^{-1}) and the Yenisei Bay (11 pg L^{-1}) (Carroll et al. 2008).

3.2.2.4. Hexachlorocyclohexanes

HCHs are the most abundant OCPs in Arctic Ocean water and the most studied (AMAP 2004, Bidleman et al. 2003). Mass budgets of HCHs in the Arctic Ocean have been reported by Barrie et al. (1992), Wania and Mackay (1999), Wania et al.(1999), Macdonald et al. (2000), Li et al. (2002, 2004), Toose et al. (2004) and Mackay and Reid (2008) (Chapter 2, section 2.3.4). Historically, the largest α-HCH loadings to the Arctic were from atmospheric deposition followed closely by ocean currents and rivers but currently, ocean transport is dominant (Li et al. 2004). For β-HCH, ocean transport has always been the dominant pathway (Li et al. 2004), see Chapter 2, section 2.3.5.4.). Currently the Arctic Ocean is experiencing a net loss of HCHs, where the largest removal mechanism is microbial degradation followed by ocean currents and transport to deep water (Li et al. 2004, Macdonald et al. 2000).

It has been known since the early 1990s that spatial variations exist for HCHs in Arctic Ocean surface waters. Lowest levels of α-HCH occur in the eastern Arctic Ocean, Russian Arctic and its subarctic seas (AMAP 2004, Harner et al. 1999, Lakaschus et al. 2002) as well as the Greenland Sea, while the highest levels are in the Beaufort Sea and the western Canadian Archipelago (Bidleman et al. 2007).

Photo: Martin Fortier/ArcticNet

Intermediate concentrations occur in the Bering and Chukchi Seas and northern Canada Basin (AMAP 2004, Hoekstra et al. 2002, Iwata et al. 1993, Jantunen and Bidleman 1996, Macdonald et al. 2000). These concentration gradients were created and maintained by the complex circulation in the Arctic Ocean and lack of horizontal and vertical mixing. Pacific water entering the Bering Strait was impacted by atmospheric deposition and ocean transport from high usage areas in Asia during years when the emissions were highest. Figure 2.31 (Chapter 2, section 2.3.4.1) shows that Eurasian sources contributed the bulk of α-HCH to different arctic regions. This water, containing the highest concentrations of α-HCH, is currently circulating around the Beaufort Gyre under a cap of ice. The ice cap reduces removal by volatilization. The main outflow pathway of HCHs from the Arctic Ocean is the percolation of Beaufort Sea water through the Canadian Archipelago. Advection of water from Baffin Bay westward into the Archipelago and up to the Barrow Strait creates a decreasing west to east concentration gradient (Bidleman et al. 2007, Wong et al. 2011). Outflow also takes place via the East Greenland current (Li et al. 2004, Macdonald et al. 2000).

HCHs have recently been determined in water from the Canadian Archipelago (Pućko et al. 2010b, Wong et al. 2011) and the eastern Arctic Ocean (Lohmann et al. 2009) (Table 3.7). As seen previously, concentrations of α-HCH were higher in the western Canadian Archipelago than in the eastern portion (Pućko et al. 2010b, Wong et al. 2011), and averaged 1,120 pg L^{-1} in the west and 710 pg L^{-1} in the east. Concentrations in the Archipelago, Beaufort Sea, Bering and Chukchi Seas have dropped since the 1990s. The mean concentration of α-HCH in the southern Beaufort Sea during 1999 (4,700 pg L^{-1}) was nearly five times higher than in 2007–2008 (922-964 pg L^{-1}). Less difference was seen for γ-HCH between 1999 (310 pg L^{-1}) and 2008 (129-200 pg L^{-1}). Lohmann et al. (2009) also observed declining concentrations of HCHs from west to east in the eastern (European) Arctic in 2004.

3.2.2.5. Enantiomers of chiral organochlorine pesticides in seawater

Many of the abundant organochlorine pesticides and their metabolites in the arctic food web are chiral: α-HCH, HEPT, HEPX, TC, CC, other chlordanes, some nonachlors, oxychlordane, *o,p'*-DDT and CHBs. These chemicals were manufactured with a 1:1 (racemic) proportion of enantiomers. Upon being released into the environment, enantioselective accumulation and metabolism leads to nonracemic residues in the arctic food web (Fisk et al. 2001, Hoekstra et al. 2003, Hoekstra et al. 2002, Moisey et al. 2001, Ross et al. 2008, Warner et al. 2005, Wiberg et al. 2000). The enantiomer composition of chiral organochlorines in seawater is determined in order to investigate sources and pathways (Chapter 2, section 2.3.6) and it is a starting point to follow enantioselective accumulation through the food web.

Most studies of chiral organochlorines in seawater have been done with α-HCH. Microbial degradation of HCHs in the water column is one of the largest loss mechanisms (Harner et al. 2000c, Li et al. 2004, see also Chapter 2, section 2.3.5.5) and for α-HCH can be traced by determining the proportion of its (+) and (–) enantiomers. Preferential loss of (+)-α-HCH increases with depth in the Arctic Ocean. This was first noted by Jantunen and Bidleman (1996, 1998), who collected samples at different depths in the central Arctic Ocean and regional seas in 1993–1994. Harner et al. (2000a, 1999, 2000c) used profiles of decreasing concentrations and enantiomer fractions, EF = (+)/[(+) + (–)], with depth in the Barents Sea and eastern Arctic Ocean to calculate the pseudo first-order microbial degradation rate constants of α-HCH enantiomers. Estimated half-lives due to microbial degradation were 5.9 years, 23 years and 19 years for (+)α-HCH, (–)α-HCH and γ-HCH, respectively. These are shorter than half-lives due to base hydrolysis in seawater (Harner et al. 2000a, 1999, 2000c). Enhanced enantioselective degradation of α-HCH occurs at the bottom of sea-ice in spring, and has even been observed in brine pockets within older ice, presumably due to microbial activity (Pućko et al. 2010b). Under-ice EFs measured from March–May 2008 ranged from 0.416–0.451 and averaged 0.438. Enantioselective degradation of (+) α-HCH in surface seawater was observed during the trans-archipelago expedition TNW-99, with EFs decreasing from 0.452 in the east to 0.436 in the west (Bidleman et al. 2007). EF = 0.450 was reported in the NOW Polynya in 1998 (Moisey et al. 2001). In July and August of 2007, EFs were 0.425 in the Labrador Sea and 0.447 in Hudson Bay, and in May–July 2008 EFs off Banks Island averaged 0.459 (Wong et al. 2011). Hoekstra et al. (2003) reported nearly racemic (EF of approximately 0.5) α-HCH in surface water off Barrow (AK) and Point Lay (AK). In the early 1990s, EFs in the Bering and Chukchi Seas were > 0.5, indicating enantioselective degradation of (–)α-HCH, while preferential degradation of (+)α-HCH (EFs < 0.5) was found further west in the Canada Basin (Jantunen and Bidleman 1996, Jantunen and Bidleman 1998). A few stations in the transition zone showed EFs of approximately 0.5. Perhaps the EFs of approximately

0.5 observed by Hoekstra et al. (2003) were the result of mixing of water masses with opposite α-HCH enantiomer degradation preferences.

On TNW-99, EFs of α-HCH in air sampled from shipboard were correlated with EFs in the surface water for events over open water. EFs in air were not correlated with EFs in surface water when air sampling was done over ice covered areas (Jantunen et al. 2008). In the TNW-99 (Jantunen et al. 2008) and IPY (Wong et al. 2011) studies, a rise in α-HCH concentration in air following ice breakup was accompanied by a drop in EF as revolatilized α-HCH from the sea mixed into the air boundary layer (Chapter 2, section 2.3.6.2). EFs in the eastern Arctic Ocean water measured in 2004 ranged from 0.43–0.50, with two lower EF (0.31 and 0.37) samples from the East Greenland Sea (Lohmann et al. 2009).

In arctic lakes, enantioselective and non-enantioselective microbial degradation are important loss processes. The (+) enantiomer of α-HCH is preferentially degraded in the High Arctic (Falconer et al. 1995, Helm et al. 2000, Law et al. 2001) and Yukon (Law et al. 2001) lakes and streams with EFs in the range 0.24–0.47. In the Helm et al. (2000) study, most enantioselective degradation of α-HCH occurred during peak runoff in the streams but EFs were lowest in the lakes in late summer. A mass balance indicated that 33–61% of the α-HCH was lost within the Amituk Lake lake by microbial degradation that was not enantioselective, leading to a half life ranging from 0.61–1.44 years.

Few studies report the enantiomer composition of OCPs in seawater other than α-HCH. Racemic TC (EFs = 0.492–0.515) and CC (EFs = 0.495–0.515), and nonracemic HEPX (EFs = 0.595–0.638) were found in the northern Canada Basin in 1994 (Jantunen and Bidleman 1998). Hoekstra et al. (2003) reported racemic CC and HEPX in seawater collected off Barrow (AK) and Point Lay (AK), in 1999–2000. In the eastern Arctic Ocean between Greenland and Svalbard, dissolved CC was close to racemic (EFs = 0.487–0.519), except for one sample (EF = 0.474), and the range of HEPX EFs was 0.60–0.66 (Lohmann et al. 2009).

3.2.2.6. Bromoanisoles: Dibromoanisole (DBA) and tribromoanisole (TBA)

Concentrations of 2,4-dibromoanisole (DBA) and 2,4,6-tribromoanisole (TBA) in seawater collected on the 2007–2008 ArcticNet and IPY expeditions were 8.5–38 pg L^{-1} and 4.7–163 pg L^{-1}. The highest levels were seen in the Labrador Sea compared to the western Archipelago near Banks Island (Wong et al. 2011).

Bromoanisoles are formed naturally from reactions between haloperoxidase and humic substances in oceans (Vetter et al. 2009). They are found in marine algae (Howe et al. 2005, Whitfield et al. 1999) and sponges from the Great Barrier Reef (Vetter et al. 2009) and from Antarctica (Vetter and Janussen 2005). Führer and Ballschmiter et al. (1998) reported that high levels of atmospheric bromoanisoles were associated with regions with high primary productivity off the west coast of Africa. They are also formed by biomethylation of bromophenols, which are produced anthropogenically as fumigants, wood preservatives, industrial intermediates and as by-products in chlorination of water containing bromide ions (Howe et al. 2005, Sim et al. 2009). Bromophenols have been suggested as natural precursors of brominated dibenzo-*p*-dioxins, identified in fish from the Baltic Sea (Haglund et al. 2007). Half-lives of DBA and TBA in air due to OH radical reactions are 50 hours and 100 hours respectively based on the atmospheric oxidation model in EPI Suite software (US EPA 2009), which exceeds the 2 day half life criterion for long-range transport according to the Stockholm Convention. Hence, bromoanisoles measured in the Arctic may have been produced locally or have been advected from other locations.

3.2.2.7. Hexachlorobenzene (HCB)

Sources of HCB include re-emissions from soils and sediments, new emissions and incomplete combustion from by-products of chlorinated chemicals (Bailey 2001) and several currently used pesticides (where it is a contaminant). HCB is regulated under the Stockholm Convention, and its production peaked in the 1970s and early 1980s (Barber et al. 2005). The long-range transport potential for HCB is very high and given it disperses via the atmosphere quickly (Beyer et al. 2000).

Few recent measurements of HCB in arctic water have been reported. In 2007–2008 Wong et al. (2011) determined HCB in Canadian Archipelago water averaged 5.4 ± 2.0 pg L^{-1}, with a narrow range from 4.0–6.4 pg L^{-1}. Unlike other OCPs, no significant east-west spatial variations were observed. Similar values of 4.6 pg L^{-1} were seen in the North Atlantic and eastern Arctic Ocean in 2008 (Lohmann et al. 2009). These values were comparable to 5–6 pg L^{-1} in the southern Beaufort Sea and White Sea in 1999–2000 (Strachan et al. 2001), lower than 9–11 pg L^{-1} observed in the Kara Sea, White Sea, Gulf of Ob and Yenesei Bay in 2003–2005 (Carroll et al. 2008) and also lower than 14–18 pg L^{-1} found in the central Archipelago at Resolute Bay (NU) in 1993

(Hargrave et al. 1997). In the eastern Arctic Ocean, dissolved HCB concentrations increased with latitude and ranged from 1–2 pg L^{-1} between 62–72°N; approximately 2–5 pg L^{-1} between 75–78°N and 4–10 pg L^{-1} between 79–85°N. HCB was also detected in the particulate phase at lower concentrations ranging from approximately 0.1–0.3 pg L^{-1} (Lohmann et al. 2009).

3.2.2.8. Polychlorinated biphenyls (PCBs)

Determination of PCBs in seawater is a challenge because of low levels and the possibility of contamination. A critical review of older measurements and a comparison of methodologies has demonstrated the need to use "ultra-clean techniques" for the collection of seawater samples for PCBs (AMAP 2004). A set of five samples of arctic seawater was collected using ultra-clean techniques during IPY 2007–2008 near Banks Island, in the western Canadian Archipelago. After correcting for blanks, Σ_{33}PCB concentrations in water was estimated to range from 0.2–3.6, resulting an upper estimate to the inventory of PCBs in the surface ocean of the Canada Basin of approximately 3,000 kg (Macdonald et al. 2009). These levels are lower than most of the reported levels in the Canadian Arctic which were not measured using ultra-clean methods (Bidleman et al. 2003).

PCBs were sampled in 2001, 2005 and 2008 throughout the Arctic using ultra-clean techniques (Carrizo and Gustafsson 2011). Concentrations of Σ_{13}PCBs ranged from 0.13–21 pg L^{-1}, the highest being in the shelf regions of the East Siberian Sea and Laptev Sea and the lowest in the Central Arctic Ocean (Figure 3.32). Homologue distributions in the eastern Arctic were dominated by the lighter tri-chlorinated congeners, presumably derived from atmospheric deposition. Ocean transport was a more important transport pathway to the central Arctic where heavier hexachlorinated PCBs were found. The authors estimated that the Σ_{13}PCBs in the mixed polar layer of the Arctic Ocean was 0.39 tonne.

Other data are available for PCBs in the eastern Arctic that were obtained using clean methods with low blank values. In 1999, Borgå and Di Guardo (2005) reported the Σ_6PCBs in water to be 0.3 pg L^{-1} in the Barents Sea near Svalbard. The Σ_{12-15}PCBs in the Barents Sea and North Pole area ranged from 0.13–2.6 pg L^{-1} in a cruise in 2001 (Gustafsson et al. 2005, Sobek et al. 2004, Sobek et al. 2010, Sobek et al. 2006). Fractionation of the congener groups was found by Sobek and Gustafsson (2004), and they concluded that the relative contribution of trichlorinated PCBs to the total PCB concentration increased with latitude, the tetrachlorinated

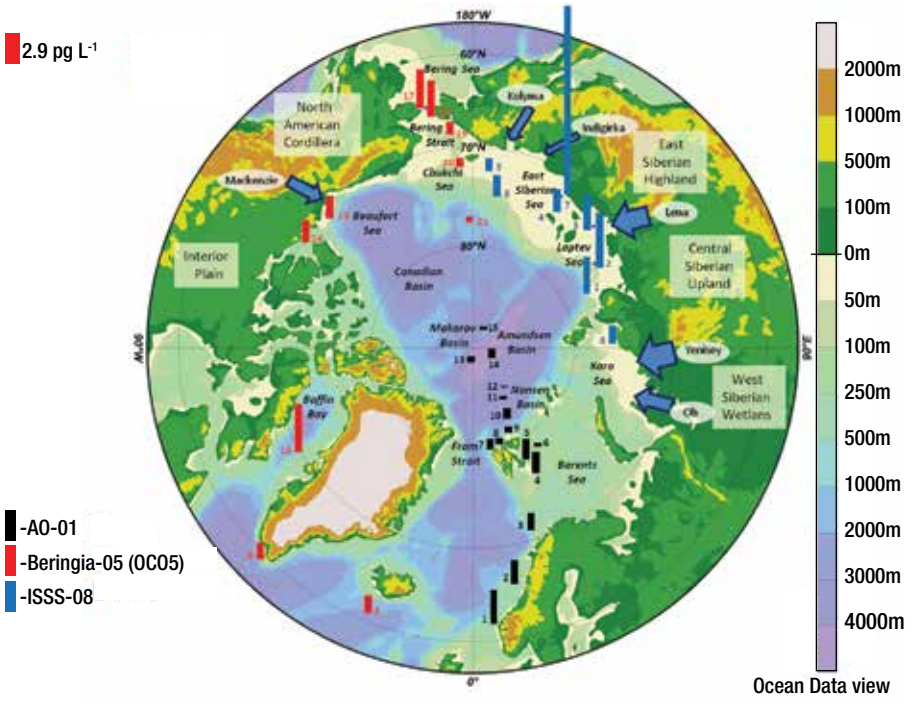

FIGURE 3.32

Concentration of PCBs in seawater in the Arctic (Carrizo and Gustafsson 2011) (reprinted with permission, copyright 2011 American Chemical Society).

homologue did not show any correlation to latitude and that the relative contribution of heavier congeners decreased with latitude. In 2004, the reported concentration of Σ_6PCBs between Greenland and Svalbard was approximately 1 pg L^{-1} with a dominance of PCBs 28/31 and 52 (0.1–0.44 pg L^{-1}) (Gioia et al. 2008). On a transect from Germany to the Arctic, Gioia et al. (2008) observed fractionation for PCBs in seawater with the relative abundance of PCBs 28 and 52 increasing and the heavier congeners decreasing with latitude. PCBs were reported in the Russian Arctic (Gulf of Ob, Yenisei Bay and Kara Sea) in 2003–2005. Concentrations of Σ_{10}PCBs ranged from 11–16 pg L^{-1} (Carroll et al. 2008).

3.2.3. New and emerging chemicals

3.2.3.1. Seawater

3.2.3.1.1. Current use pesticides

An increasing number of CUPs have been detected in arctic waters over the period 2003–2010. CUPs so far reported in arctic seawater are dacthal (a.k.a. DCPA, chlorthal dimethyl), chlorpyrifos, pentachloronitrobenzene (aka quintozene), endosulfan isomers and endosulfan sulfate, trifluralin and chlorothalonil. All of these CUPs are currently used in Canada and the United States, although dacthal has limited usage in Canada but heavier application in the USA. Seawater samples were taken in the Canadian Archipelago during the Tundra-Northwest'99 (TNW-99) expedition, during the IPY 2007–2008 as a part of ArcticNet, and the Canadian Flaw Lead Study at Barrow Strait (Table 3.7)

Chlorothalonil averaged 8.1 ± 4.0 pg L^{-1} on TNW-99 with uniform distribution from east to west. During IPY, chlorothalonil was only measured off Banks Island in 2008. Concentrations were higher, averaging 77 ± 74 pg L^{-1} but also variable ranging from 29–233 pg L^{-1}. Morris et al. (2011) did not detect chlorothalonil in Barrow Strait. Dacthal distributions were uniform with no marked difference between the east and west. Mean ± SD concentrations in the Archipelago were 16 ± 8 pg L^{-1} in 1999 and 24 ± 12 pg L^{-1} for the period 2007–2008. Morris et al. (2011) reported lower concentrations in the Barrow Strait in June 2007 under ice (4–17 pg L^{-1}). Chloropyrifos was only sought in 2007–2008 and the mean concentration was higher in the west compared to the east, 23 ± 13 pg L^{-1} vs. 7.2 ± 3.0 pg L^{-1}. Chlorpyrifos ranged from < 0.8–67 pg L^{-1} in the surface water of the Bering and Chukchi Seas in 1993 and was also detected in ice and fog condensates (Chernyak et al. 1996). Morris et al. (2011) found low concentrations of chlorpyrifos (0.2 pg L^{-1}) in the Barrow Strait in 2010 under the sea-ice. Trifluralin was also analyzed in the IPY 2007–2008 samples. It was found in the St. Lawrence Seaway and along the eastern coast of Canada and in water samples near Banks Island. Concentrations were approximately 2.9 pg L^{-1} for Bank Island (6 samples were detectable out of 13) while in the Barrow Strait it was undetectable (< 0.1 pg L^{-1}) (Morris et al. 2011).

Endosulfan levels found in seawater from the 1990s to 2000 was summarized by Weber et al. (Weber et al. 2010, Weber et al. 2006). Generally, levels of endosulfan were highest in the western arctic (Bering and Chukchi Seas), intermediate levels in the Canadian Archipelago and lowest in the central Arctic Ocean, with overall means of 2.3 pg L^{-1} for α-endosulfan and 1.5 pg L^{-1} for β-endosulfan (Figure 3.33).

More recent data found that mean concentrations of α-endosulfan were higher in 2007 and 2008 than in 1999, 4.8 pg L^{-1} and 1.4 pg L^{-1}, respectively. β-endosulfan was generally lower than α-endosulfan and ranged from 0.7–3.5 pg L^{-1}. Endosulfan sulfate, a degradation product of both α- and β-endosulfan , was also considered in 2007–2008. Concentrations were close to a factor of 10 greater than the parent endosulfan compounds, ranging from 5.0-45 pg L^{-1}. This is due to the water stability of endosulfan sulfate (Walse et al. 2003). α-endosulfan and endosulfan sulfate in the Barrow Strait during ice melt in mid-June 2007 averaged 1.4 pg L^{-1} and 4.6 pg L^{-1} at 2 m depth and 0.2 pg L^{-1} and 1.9 pg L^{-1} at 10 m depth (Morris et al. 2007). In the Barrow Strait, during ice melt in mid-June 2007 and 2010, α-endosulfan I was also detected in the Russian Arctic, with higher concentrations in the Yenisei Bay (7.3 pg L^{-1}) and Gulf of Ob (8.6 pg L^{-1}) than in the Kara Sea (4.4 pg L^{-1}) (Carroll et al. 2008).

Other compounds that were considered but not detected in the study by Jantunen et al. (2011) near Banks Island (2007–2008) include (detection limit for individual compounds are given in parenthesis, pg L^{-1}): quintozene (pentachloronitrobenzene (1)) and its degradation product pentachlorothioanisole (PCAn) (1), dimethoate (100), metribuzin (5), malathion (25), pendimethalin (0.5), dazomet (10), atrazine (10), simazine (10), terbufos (80), diazinon (10), alachlor (10), metolachlor (2), phorate (50) and disulfoton (10). Morris et al. (2011) detected PCNB (1.2–1.6 pg L^{-1}) in the Barrow Strait but also did not detect pendimethalin or metribuzin (both < 0.1 pg L^{-1}).

3.2.3.1.2. Trifluoroacetate

Trifluoroacetate (TFA) is a mildly phytotoxic (Thompson 1994), strong acid and is almost ubiquitous throughout the aquatic environment. Sources of TFA are thermolysis of perfluorinated compounds, atmospheric oxidation of hydrochlorofluorocarbons and hydrofluorocarbons, and fluorotelomer alcohols, in addition to natural oceanic sources, e.g., deep sea vents (Scott et al. 2005). TFA in arctic seawater samples from the Canadian Basin and Canadian Archipelago ranged from 60–160 pg L^{-1} down to 700 m. Below this depth, in waters having ^{14}C ages approximately 1,000 years levels were constant at 150 pg L^{-1}. Water returning to the Atlantic from the Arctic Ocean had constantly high values compared to water samples taken from the North and South Pacific Oceans and the Mediterranean Sea (Scott et al. 2005).

3.2.3.1.3. Flame retardants

The BFRs, PBDEs and several alternative non-PBDE, non-regulated BFRs in seawater were reported from the East Greenland Sea using ultra high volume water samples (700–1,000 L). Method detection limits (MDLs) ranged from 0.0003–0.24 pg L^{-1}. Σ_{10}PBDEs in the seawater of the eastern Greenland Sea ranged from 0.03–0.64 pg L^{-1}. The congener pattern was generally dominated by BDE-47 (<MDL–0.06 pg L^{-1}) and BDE-99 (<MDL–0.04 pg L^{-1}). Hexabromobenzene (HBB) (<MDL–0.003 pg L^{-1}) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) (<MDL–0.41 pg L^{-1}) showed similar concentrations and spatial trends as PBDEs. TBPH (bis-(2-ethylhexyl)-tetrabromophthalate) concentrations ranged from <MDL–1.3 pg L^{-1} (Möller et al. 2011). Brominated FRs inputs from Russian rivers contribute a significant freshwater input to the Arctic Ocean (Ob and Yenisei = 37%), thus are significant inputs of contaminants to the Arctic Basin. PBDEs

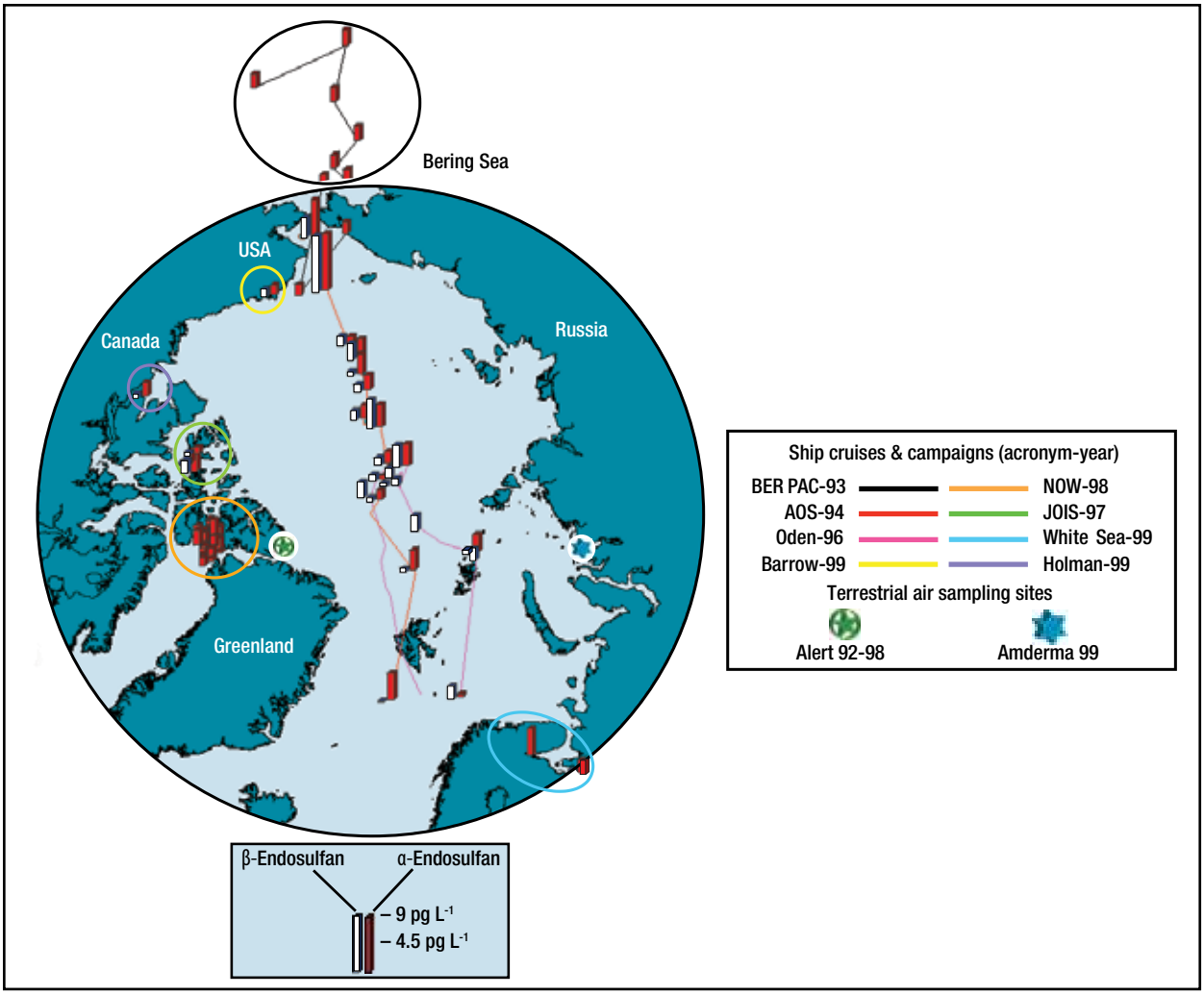

FIGURE 3.33

Surface seawater concentrations of α-endosulfan and β-endosulfan in the Arctic Ocean between 1993 and 2000 (Weber et al. 2006).

were detected at all sampling locations, predominant congeners were: BDE-38, BDE-47 and BDE-99 with proportions similar to those in the technical products DE-71 and Bromkal 70-5DE. Mean PBDE concentrations were higher in the Ob (6.7 pg L^{-1}) than the Yenisei (3.2 pg L^{-1}) but not statistically different from the Kara Sea (4.3 pg L^{-1}). Estimated fluxes of ΣPBDEs to the Kara Sea were 1.92 kg y^{-1} and 1.84 kg y^{-1} from the Ob and Yenisei, respectively. Lower brominated PBDE congeners not in the technical mixture were detected in water samples, indicating that the de-bromination of heavier congeners is occurring (Carroll et al. 2008, de Wit et al. 2010). PBDEs in seawater at Lancaster Sound were close to or at detection limits (< 1 pg L^{-1}) (Morris et al. 2011).

3.2.3.1.4. Dechlorane Plus

DP has been found in both arctic air and water samples taken between Greenland and Spitsbergen, sampling 500–2600 m^{-3} air and 300–1300 L water. Generally, DP is associated with particles in arctic air and water. MDLs for particulate species ranged from 0.0009–0.005 pg m^{-3} for air and 0.002–0.006 pg L^{-1} for water. Concentrations in water ranged from <MDL to 0.9 pg L^{-1} and in air from 0.05–4.1 pg m^{-3}, with the highest concentrations on the southern side of Greenland for air and the northern side of Greenland for water. Additionally, degradation products ($aCl_{10}DP$ and $aCl_{11}DP$) were found in arctic water ranging up to 0.07 pg L^{-1} (Möller et al. 2010).

3.2.3.1.5. Synthetic musks and phthalates

Analysis for synthetic musks and phthalates in water and air from the Greenland Sea, between Greenland and Svalbard, was made in 2004, sampling 500–1,000 L of water and 500–2,000 m^3 of air (Xie et al. 2007a, Xie et al. 2007b). Phthalates are manufactured on a global scale. They are added as plasticizers in resins and polymers and are generally not physically bound to the polymer thus can diffuse into the environment. Atmospheric deposition is a significant source to open waters (Atlas and Giam 1981, Eisenreich et al. 1981, Xie et al. 2005). The range and median concentrations of phthalates in seawater were 80–5,030 pg L^{-1} and 359 pg L^{-1}, respectively (Xie et al. 2005). The concentration of Σ_6 phthalates (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-i-butyl phthalate (DiBP), di-n-butyl phthalate (DnBP), butylbenzyl phthalate (BBP), and diethylhexyl phthalate (DEHP)) ranged from 30 pg L^{-1} to 5030 pg L^{-1} in the dissolved phase and from 1,110 pg m^{-3} to 3,090 pg m^{-3} in the gas phase. Synthetic musks are widely used as fragrances in personal care and household products. Synthetic musks considered in samples of air and water of Greenland Sea between Svalbard and Greenland in 2004 were Galaxolide (HHCB) and Tonalide (AHTN). Gas-phase concentrations in air were 1–9 pg m^{-3} HHCB and 7–25 pg m^{-3} AHTN. Although quantified in arctic air, they were below the MDL of < 0.1 pg L^{-1} in arctic seawater (Xie et al. 2007b).

3.2.3.1.6. Polyfluoroalkyl substances

PFASs are globally distributed in the marine environment (Yamashita et al. 2005). Several PFASs from various classes have been found in the pg L^{-1} range in coastal seawater (Ahrens et al. 2010) and in the pg L^{-1} range in open-ocean water (Ahrens et al. 2009, Benskin et al. 2012a, Benskin et al. 2012b, Yamashita et al. 2005). The global occurrence of PFASs in open-ocean water was first described by Yamashita et al. (2005). Overall, ocean currents and the related dilution effects have a crucial influence on the distribution of PFAS in seawater. Industrial coastal areas and atmospheric deposition are considered as sources of PFASs and ocean waters are important as sinks and for the transportation of these compounds (Ahrens et al. 2010).

Concentrations of PFOS and PFOA reported in the mid- to South Pacific Ocean, Indian Ocean and Antarctic region, were about one magnitude lower than in the North Atlantic Ocean and East Greenland Arctic Ocean (Ahrens et al. 2009, Busch et al. 2010, Rosenberg et al. 2008, Wei et al. 2008, Yamashita et al. 2005) (Table 3.8).

TABLE 3.8. Minimum and maximum PFAS concentrations in seawater, pg L^{-1} in the Canadian Arctic and North Atlantic

Location	PFBS	PFHxS	PFOS	PFOSA	PFHxA	PFHpA	PFOA	PFNA	Reference
Canadian Arctic (*n*=19)	n.a.	0.0–19	8.8–39	0.0–44	0.4–65	11–84	6.5–54	1.9–47	1
East Greenland Arctic Ocean (*n*=38)	n.a.	<9.9–14.5	<23–38.0	<36–300	<13–22.0	<5.8–26.9	<12–120	n.a.	2
North Atlantic Ocean (*n*=40)	<1.6–60	n.d.	<10–291	<17–307	<5.7–127	<5.9–104	<4.0–229	<5.1–107	3
North Atlantic Ocean (*n*=9)	n.a.	4.1–6.1	8.6–36	n.a.	n.a.	n.a.	160–338	15–36	4
Antarctic region (*n*=5)	<1(5) –2.9	<1(5)	5.1–22.6	n.a.	<5	<5	<5	<5	5

1. Benskin et al. 2012b; 2. Busch et al. 2010; 3. Ahrens et al. 2009; 4. Yamashita et al. 2005; 5. Wei et al. 2008; n.d. = not detected. n.a. = not analyzed.

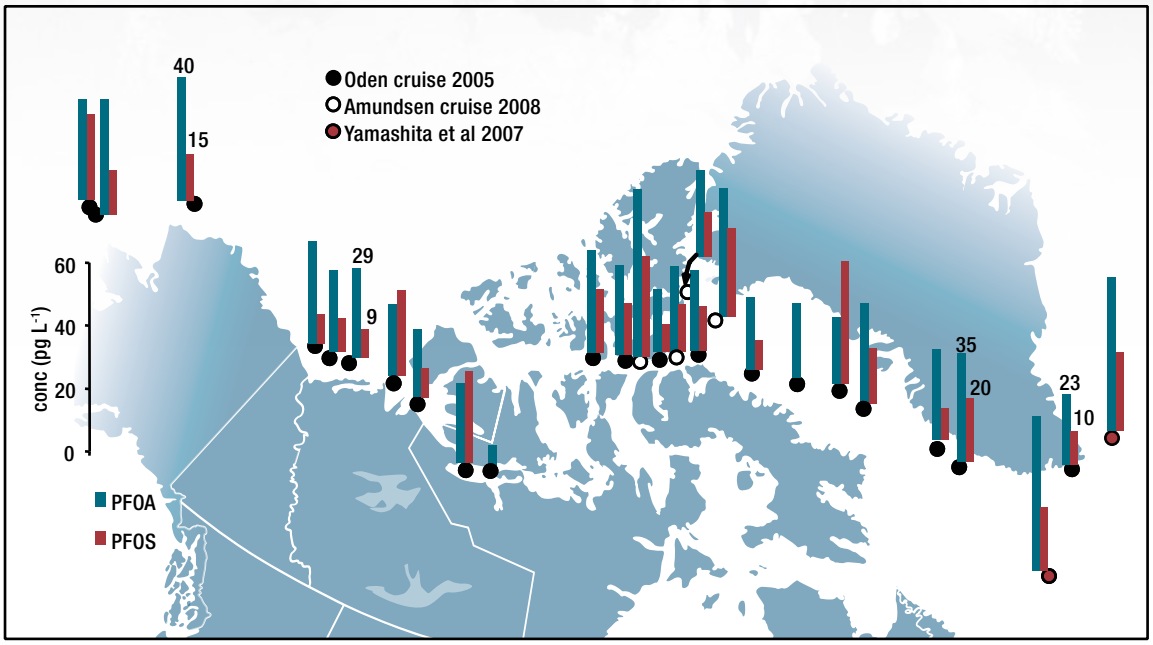

FIGURE 3.34

Concentrations (pg L^{-1}) of PFOA and PFOS in seawater from the Oden cruise (July and Aug 2005) and the Amundsen cruise (Oct 2008) (Benskin et al. 2012b, Rosenberg et al. 2008). Results from Yamashita et al. (2008) for the Labrador Sea are also shown.

Benskin et al. (2012a, 2012b) reported the first measurement of PFASs in seawater in the Canadian Archipelago, Beaufort and Chukchi Seas. The range of concentrations of major PFASs is provided in Table 3.8 and the geographical trends are shown in Figure 3.34.

PFOA, PFHpA and PFHxA were the major PFASs in waters of the Canadian Archipelago, Beaufort and Chukchi Seas. Concentrations were generally higher than in open ocean measurements in the North Atlantic (Ahrens et al. 2009, Busch et al. 2010, Yamashita et al. 2005). This may reflect the influence of freshwater inputs to these waters particularly from the Mackenzie, Coppermine and Back Rivers, which achieve maximum flows in June and July (Barrie et al. 1998, Murray et al. 1998), as well as to sampling during ice melting (the Oden cruise occurred during late July 2005).

Benskin et al. (2012a) measured the isomers of PFOA in the water samples from the Archipelago, Beaufort and Chukchi Seas (see Chapter 2, section 2.3.6.2 for background information). They found a distinct spatial trend whereby PFOA in seawater originating from the Atlantic was predominantly historic (up to 99% from manufacture by electrochemical fluorination), whereas water in the Archipelago along the ship transect from the Barrow Strait to the Bering and Chukchi Seas (Figure 3.34) had a significant telomer PFOA contribution, indicating that it was predominantly of contemporary origin (Figure 3.35 Panel A). The percent ECF was also significantly correlated with salinity ($r = 0.58$, $p < 0.01$; Figure 3.35 Panel B). This correlation suggests that water collected in the Archipelago is influenced by riverine discharges, which would presumably contain PFOA derived from an atmospheric source (i.e., linear FTOH). Summer salinity gradients in the Arctic Ocean show a major influence of freshwater inputs in the southern Beaufort Sea and in the southern Archipelago waters (Murray et al. 1998) which supports this hypothesis.

Depth profiles in North Baffin Bay and Lancaster Sound from the 2005 and 2008 cruises indicated that total PFOA and PFOS concentrations reached a maximum within 100 m and then generally decreased with increasing depth, while percent ECF of PFOA remained fairly constant with depth (Benskin et al. 2012a, Benskin et al. 2012b). Much deeper vertical profiles of several PFASs were studied in the Labrador Sea, mid-Atlantic Ocean, South Pacific Ocean and Japan Sea (Rosenberg et al. 2008, Yamashita et al. 2008). PFASs in deep ocean water from the mid-Atlantic Ocean, Japan Sea and South Pacific Ocean were not detectable or very low, which

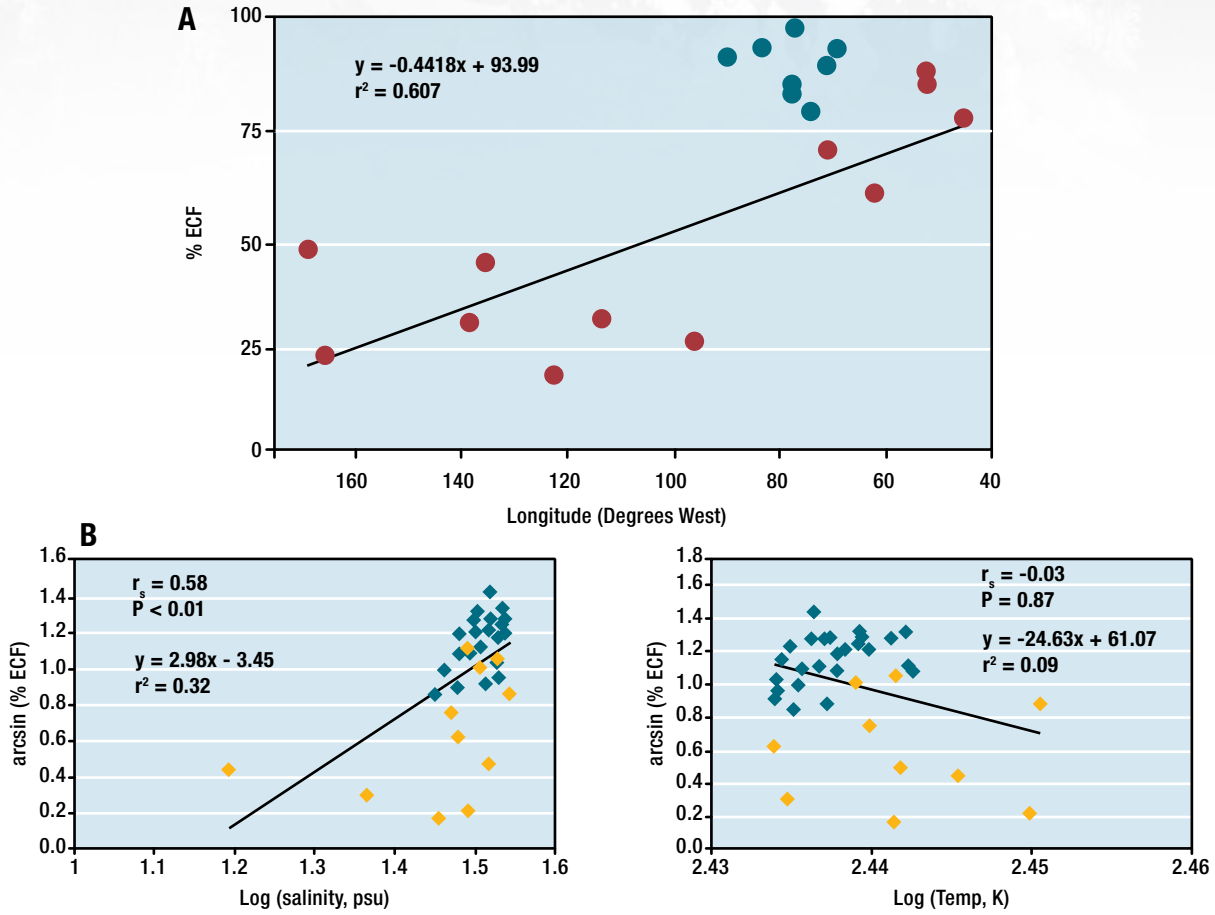

FIGURE 3.35

(A) Correlation between percent ECF PFOA and longitude. In both figures, red markers represent July 2005 West Greenland/ Canadian Archipelego/ Bering Strait cruise (#1–30), while blue markers represent September 2008 Baffin Bay/Lancaster Sound cruise. (B) Plots of arcsin (% ECF) versus log (salinity, psu) and log (water temperature, K) for the same sampling locations. The correlation coefficients (r) and p-values were obtained using Spearman rank order (Benskin et al. 2012a).

indicates very slow transportation by these ocean currents (Yamashita et al. 2008). In contrast, PFAS concentrations in the Labrador Sea did not decrease significantly with increasing depth which indicates that the water mass is well mixed in the vertical profile (Benskin et al. 2012b, Yamashita et al. 2008).

Yamashita et al. (2008) hypothesized that PFASs could be transported globally with the thermohaline circulation system, and the open-ocean water is acting as a final sink for PFOS and PFOA. In general, the concentration of PFOA is usually higher than of PFOS, which suggests higher emissions of PFOA. The environmental fate is influenced by their physicochemical properties which vary depending on their chain length and functional groups. The adsorption behavior of PFASs has been investigated in terms of the solid-water partition coefficient (K_d) (Ahrens et al. 2010, Higgins and Luthy 2006). The perfluorocarbon chain length and functional group were the dominating parameter influencing the partitioning of PFASs (Ahrens et al. 2010). Hence, the short-chain PFCAs (C < 7) were exclusively found in the dissolved phase, while long- chain PFCAs (C > 7), perfluoroalkyl sulfonates (PFSAs), ethylperfluorooctane sulfonamidoacetic acid (EtFOSAA), and perfluorooctane sulfonamide (PFOSA) appeared to bind more strongly to particles. In addition, the partitioning varied depending on the conditions (e.g., organic carbon content, pH value, metal ions). For example, an increasing sorption was found with increasing organic carbon content (Ahrens et al. 2010). As a consequence, the short chain PFCAs have a higher potential for aqueous long-range transport and PFSAs, EtFOSAA and PFOSA are rather distributed in biota or abiotic environments like sediment, which could act as a sink for PFASs. The physicochemical characteristics also have an influence on the mechanism of the

long-range transport in the aqueous environment (e.g., sea-spray, microlayer, surface water, deep ocean water).

Much of the total organofluorine (60–90%) in seawater has not been identified, which suggests the presence of other PFASs in addition to the known PFASs (Miyake et al. 2007). Overall, appropriate time series measurements are necessary to investigate seasonality and long-term changes. Furthermore, more studies about the partitioning behavior of PFASs is necessary, e.g., between solid-water and air-water phases (Ahrens et al. 2010) to get a better understanding of the relationship between sources, seawater concentration and the mechanism of long-range global transport.

3.2.3.2. Lake water

3.2.3.2.1. Current use pesticides

Chlorothalonil ranged from < 2–2,800 pg L^{-1} in 13 arctic and subarctic lakes in Canada sampled between 1999 and 2001, with a detection frequency of 31% (Muir et al. 2004). Dacthal was found in 13 Canadian subarctic and arctic lakes, where concentrations ranged from 10–110 pg L^{-1}. Chloropyrifos was detected in only one lake in the Canadian Archipelago at 1,600 pg L^{-1} and was < 17 pg L^{-1} in 12 other arctic and subarctic lakes (Muir et al. 2004).

Muir et al. (2007) determined α-endosulfan and endosulfan sulfate levels in lake water and snow melt tributary water from Lake Hazen in northern Ellesmere Island and Char Lake on Cornwallis Island in the Canadian Archipelago in 2005–2006. The results for α-endosulfan were comparable to those from Amituk Lake in the 1990s reported by Helm et al. (2002). Concentrations of α-endosulfan and endosulfan sulfate in the open lake waters of the Hazen and Char lakes were similar, in the sub-ng L^{-1} range. Endosulfan sulfate was found to be most detectable endosulfan related residue with concentrations about ten-fold higher than α-endosulfan. A tributary to Lake Hazen was found to have 30- and 5-fold higher concentrations for α-endosulfan and endosulfan sulfate, respectively, than the lake water itself. Thus major inputs to the lake are from snowmelt. Other CUPs identified in all the samples from lakes Hazen and Char were chloropyrifos, dacthal, trifluralin, endosulfan, endosulfan sulfate and PCNB.

3.2.3.2.2. Polyfluoroalkyl substances

Stock et al. (2007) determined PFASs in the water from Amituk, Char, Meretta and Resolute Bay lakes on Cornwallis Island. The PFASs concentrations in Char and Amituk Lakes were very similar to the means of total PFCAs and total PFSAs ranging from 0.3 ng L^{-1} to 10 ng L^{-1} (Table 3.10). In Amituk Lake the dominant perfluoroalkyl contaminant was PFOA, while PFDA was the dominant perfluoroalkyl contaminant in Char Lake. PFOS was the only perfluorosulfonate observed in both Amituk and Char Lakes (1.2 ng L^{-1} and 1.8 ng L^{-1}, respectively). Ratios of PFOA:PFNA and PFDA:PFUnA in Amituk and Char Lakes were generally consistent with ratios observed in arctic glacial ice caps (Young et al. 2007) and in precipitation from rural and remote sites in North America (Scott et al. 2006a) suggestive of a common atmospheric source.

The contamination profile for Resolute Lake was markedly different. PFOS was the dominant perfluoroalkyl contaminant and concentrations of PFHS, PFOS, perfluoroheptanoate (PFHpA), and PFOA were all significantly higher, up to 60-fold greater, than concentrations detected in the Amituk or Char Lakes. To investigate the source of contamination in Resolute Lake, the outflow from Meretta Lake was analyzed and found to contain similar concentrations and patterns of PFASs as Resolute Lake. Meretta Lake received wastewater discharge from 1949 until the early 1990s from the "North Base" of the Canadian Department of Transport Airport Base, located just south of the current Resolute Bay (NU) Airport. Stock et al. (2007) concluded that the pattern contamination observed in water samples from the Resolute and Meretta Lakes, with extremely high levels of PFHS and PFOS, in addition to PFHpA and PFOA, relative to background sites (e.g., Char Lake) was consistent with the use of aqueous fire fighting foams which have been detected following spills at airports (Moody et al. 2002) and in groundwater at Department of National Defence (DND) bases in Canada (Scott et al. 2007) and the US (Moody and Field 2000; Schultz et al. 2003). Further discussion of contamination in the Resolute and Meretta Lakes can be found in Chapter 4, section 4.1.2.1.3.

PFASs have also been measured in other remote arctic lakes (Table 3.9). Lakes North and Small, which are west of Resolute Bay, as well as Teardrop Lake which is near Meretta Lake, had very similar

TABLE 3.9. PFASs in arctic lake waters (ng L^{-1})[1]

Lake	PFHxS	PFOS	PFDS	PFOSA	PFHpA	PFOA	PFNA	PFDA	PFUnA	Ref[2]
Amituk (2003)	nd	1.2 (0.9–1.5)	nd	na	0.6 (nd–1.0)	4.1 (1.9–8.4)	0.3 (0.20.4)	1.1 (0.5–1.4)	2.5 (1.4–3.4)	1
Amituk (2008)	0.010	0.033		0.002	0.18	0.23	0.18	0.021	0.007	2
Char (2003)	nd	1.8 (1.1–2.3)	nd	na	0.3 (nd–0.5)	2.6 (1.8–2.4)	0.5 (nd–1.4)	4.2 (nd–7.3)	4.9 (4.1–5.9)	1
Char (2008)	0.16	0.17	na	0.00	0.16	0.23	0.09	0.01	0.00	2
Resolute (2003)	21 (19–24)	69 (49–90)	0.3 (nd–1.0)	na	31 (18–49)	14 (12–16)	2.0 (nd–6.1)	1.8 (nd–2.9)	2.9 (1.0–5.0)	1
Resolute (2008)	26	37		0.023	12	8.84	2.48	0.042	0.007	2
Meretta (2005)	16 (12–18)	56 (55–57)	11 (10–11)	ca	26 (22–29)	14 (13–15)	4.1 (3.8–4.4)	19 (16–24)	0.3 (0.2–0.5)	1
Meretta (2008)	28	36		0.05	12	9.6	2.6	0.073	0.019	2
North (2008)	0.016	0.046		0.002	0.15	0.21	0.18	0.025	0.009	2
Small (2008)	0.13	0.11		0.001	0.25	0.27	0.12	0.016	0.006	2
Teardrop (2008)	0.11	0.066		0.001	0.26	0.25	0.06	0.025	0.023	2
Lake A	Tba	0.025	na	na	0.104	0.149	0.119	0.015	na	3
Pingualuk	tba	0.045	na	na	0.030	0.065	0.030	0.025	0.030	4

[1] n.d.: non-detected; n.a.: non applicable

[2] References : 1. Stock et al. (2007); 2. Muir, D. Unpublished data. Environment Canada (2009); 3. Veillette et al. (2012); 4. Gantner et al. (2012)

concentrations of all PFASs as those of Char Lake. Lowest concentrations were found in Lake A, on northern Ellesmere Island (Veillette et al. 2012) and in Pingualuk, an isolated crater lake in northern Quebec (Gantner et al. 2012). However, PFAS concentrations in Lake A catchment snow were similar to spring-summer concentrations in accumulated snow from the Devon Ice Cap (8 degrees of latitude south of Lake A) sampled in spring 2006 (Young et al. 2007). Thus the supply of PFAS from snowmelt is likely relatively similar at Lake A as it is on the lakes of Cornwallis Island (Amituk, Char). Both Lake A and Pingaluk were sampled prior to the snowmelt freshet which would deliver snow bound PFAS. Also, a major difference between Lake A and Pingaluk compared with Char Lake and Amituk Lake is the greater extent of open water in the latter lakes during July and August and thus greater wind induced mixing compared with lakes that remain almost completely ice covered (Veillette et al. 2012).

3.2.4. Assessment

- Very low concentrations (low or sub-picogram per litre) of hydrophobic legacy POPs, such as PCBs and PBDEs, are present in seawater in the Arctic.
- However, there are only limited new data on concentrations of legacy POPs and almost no data for brominated flame retardants in seawater in the Canadian Arctic.
- Perfluorinated alkyl acids such as PFOS and PFOA are generally present at 5- to more than 10-fold higher concentrations than the PCBs and PBDEs, reflecting their higher solubility in water.
- The detection of perfluorinated compounds in all compartments of the arctic environment over the past 10 years has increased our appreciation for the importance of seawater transport of these chemicals and of other contaminants as well.
- Measured concentrations of PFCAs with ≥ 9 carbons in water sampled from remote locations are frequently below detection limits. However, these same homologues are often found to be important contributors to ΣPFCA levels in biota.
- As the long-term temporal trend measurements are the only way to forecast trends of chemicals in environmental compartments, continuous seawater and atmospheric measurements are required for new chemicals besides the legacy POPs.

3.3. Legacy and New POPs in Marine and Lake Sediments

Contributors: Derek Muir, Perihan Kurt-Karakus, Gary Stern and Marlene Evans

3.3.1. Introduction

Latitudinal and temporal variations of organochlorine contaminant deposition in sediment cores for eight lakes along a mid-continental transect from 49°N to 82°N and the Yukon were assessed in CACAR I (Jensen et al. 1997, Macdonald et al. 2000). In brief, subarctic lakes showed an onset of PCBs in the 1940s in reasonable agreement with historical usage patterns. In high arctic lakes, however, no significant PCB inputs were observed until the 1960s, lagging the initiation of production by approximately 20 years. This difference was attributed to the lag time in diffusion of PCBs released at mid-latitudes to the North. In the arctic lakes, HCB and ΣPCB levels also appeared to peak 5 to 10 years after the period of maximum production. Additional compounds such as toxaphene and chlorophenols were analyzed in some of the same cores studied in the 1990s (Stern and Evans 2003). In addition, results from sediment cores from other Arctic lakes such as Great Slave Lake, Coal Lake in the Yukon Territories, and a very rare laminated sediment core from Lake DV09 on Devon Island were reported. Over the period 2003–2010, relatively few studies have been conducted on dated sediment cores apart from those previously reported in the CACAR-II (Stern and Evans 2003) and associated special journal issues (Stern et al. 2005). Notable exceptions include results reported near a seabird colony at Cape Vera on Devon Island (Blais et al. 2005, Michelutti et al. 2009b), brominated flame retardants (Breivik et al. 2006) and PFASs (Stock et al. 2007) in sediments from high arctic lakes. New information has also been published on POPs in nearshore marine surface sediment samples.

Photo: Martin Fortier/ArcticNet

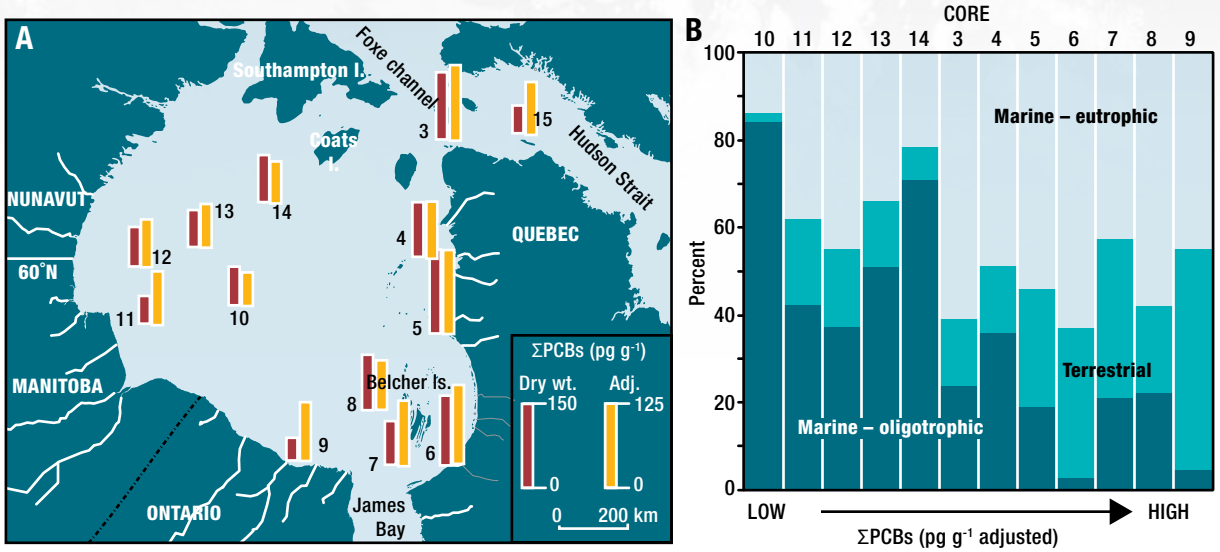

FIGURE 3.36

(A) ΣPCB concentrations in surface sediments of Hudson Bay (pg g^{-1} dw) (black bars) and after adjustment for partial dependence on sediment particle size and organic carbon content (white bars). (B) Variation in the proportions of organic matter of marine-eutrophic, terrestrial, and marine-oligotrophic origin, with increasing (adjusted) ΣPCB concentrations in the sediments.

3.3.1.1. Marine sediments

3.3.1.1.1. PCBs and OCPs

As part of studies to assess burial of PCBs on continental shalf sediments, Gustafsson et al. (2001) analyzed two cores from Baffin Bay; a northern location south of Thule Greenland (76° 10'N; 70° 51'W) and a site in outer Umanak Fjord (Schades; 71° 25'N; 54° 4'W). Total PCBs (sum of 14 congeners) in the 0–1cm horizon ranged from 595 pg g^{-1} dw at Thules to 39 pg g^{-1} dw at Schades. These concentrations are at the low end of the range reported in marine surface sediment samples collected in the Canadian Archipelago and eastern Hudson Bay in CACAR-II (Stern and Evans 2003). After normalizing for sediment organic carbon concentrations were similar at both locations. Gustafsson et al. (2001) also noted that for arctic marine sediments in general (De March et al. 1998) there was a significant correlation of PCBs and sediment organic carbon.

Kuzyk et al. (2010) determined ΣPCB concentrations (sum of 137 individual or coeluting congeners analyzed by GC-high resolution MS) and depositional fluxes in 13 dated marine sediment cores from Hudson Bay and investigated the importance of organic carbon (%OC) in the sequestration of PCBs. ΣPCB varied from 40 pg g^{-1} dw to 150 pg g^{-1} dw, with lowest concentrations occurring along the southwest coast (cores 9 and 11) and in the Hudson Strait (core 15), intermediate concentrations in central Hudson Bay (cores 10 and 14), and the highest concentrations in the eastern part of the Bay (cores 3, 5, and 6) (Figure 3.36A). ΣPCBs variance in surface sediment was related to sediment texture (percent fines) and percent OC and concentrations were adjusted for these parameters (see adjusted values in Figure 3.36A).

The origin of organic carbon was found to contribute to the spatial variation in ΣPCB in Hudson Bay. Terrestrial and marine sources of marine organic, and the relative contributions to the organic matter produced under eutrophic vs. oligotrophic conditions (determined using the carbon-nitrogen ratios and carbon isotope ratios ($\delta^{13}C$)) showed that the adjusted ΣPCB concentrations increase with increasing proportions of marine organic matter produced under eutrophic conditions (Figure 3.36B).

Kuzyk et al. (2005) measured PCBs in marine sediments in Saglek Bay, Labrador, which has been the site of a military radar station since the late 1950s. Collected from all four zones of Saglek Bay from water depths up to 165 m, PCB concentrations in 191 marine surface sediment samples were reported to be ranged between 0.24 ng g^{-1} dw to 62000 during the period 1997–1999. The concentrations decreased exponentially with distance from the source of contamination at the radar station Beach. Sediments from near the Beach and on the surrounding nearshore platform showed PCB concentrations in the order of 1,000–10,000 ng g^{-1}. Background PCB concentrations in surface sediments

in northern Labrador were reported to be closer to concentrations between 0.09 ng g^{-1} dw and 2.87 ng g^{-1} dw across the Canadian Arctic in the north of 73° latitude (Stern and Evans 2003).

Brown et al. (2009) examined the natural recovery of a local marine food web from a historic source of PCBs at Saglek Bay. Sediment samples were collected from the same area as Kuzyk et al. (2005) during two separate time periods; from 1998–2000 and from 2006–2007. This is discussed further in section 3.4.2.2.

Kelly et al. (2007) reported PCBs and a wide range of chlorinated pesticides in surface sediments (sampled with a Ponar grab sampler at 25–80 m depths) from along the eastern Hudson Bay coastline in close proximity to the village of Umiujaq. Concentrations of ΣPCBs, ΣDDTs, ΣHCHs, ΣCBz and Σcyclodienes (dieldrin, endosulfan, chlordanes) were 0.08 (0.01–0.57), 0.006 (0.01–0.04), 0.02 (0.005–0.05), 0.2 (0.05–0.6) and 0.01 (0.002–0.06) ng g^{-1} dw, respectively. The ΣPCB concentrations were in good agreement with those reported by Kuzyk et al. (2010) for nearshore eastern Hudson Bay sediments. Chlorobenzenes were the most prominent organochlorines with 1,2,4 TriCBz accounting for 81% of ΣCBz. The relatively high level of 1,2,4 TriCBz may reflect local contamination since it is a widely used industrial chemical used to make pigments and dyes (EuroChlor 2002).

3.3.1.1.2. PBDEs

Kelly et al. (2008a) reported PBDEs in bottom sediments collected between 1999 and 2003 from Hudson Bay. Average concentrations of ΣPBDEs and their range were 0.1 (0.01–1.6) ng g^{-1} dw, which was greater than for most legacy organochlorines (Kelly et al. 2007). BDE-209, the major BDE in arctic freshwater sediments (Breivik et al. 2006), was not determined so it is likely that total BDE concentrations were higher than reported. In a related study (Kelly et al. 2008b) analyzed the same sediments for OH-PBDEs and MeO-PBDEs, however, they were undetectable (<LOQ=0.1 ng g^{-1} dw). in sediment although they contributed substantially to the PBDEs present in biota (See Chapter 4, section 4.1.6.3).

3.3.1.1.3. PFASs

Kelly et al. (2009) also reported concentrations of perfluoroalkyl contaminants in the same set of sediment samples as in their previous studies (Kelly et al. 2008a, b). Concentrations of PFOS, perfluorooctansulfoamide (PFOSA), and C_7–C_{14} PFCAs ranged between 0.01 ng g^{-1} dw and 0.1 ng g^{-1} dw in sediments. PFOA, PFNA, PFDA, and PFUnA were commonly detected in sediments. Mean levels of PFOA (mean) (0.05 ng g^{-1} dw) and PFOS (< 0.04 ng g^{-1} dw) in sediments were lower than previous observations from more populated and urban locations (Higgins et al. 2005). PFSAs and PFCAs detected in sediment of three arctic lakes (Amituk, Char and Resolute) ranged from non-detected to 85 ng g^{-1}. The results of the study suggested the local perfluoroalkyl contamination of Resolute Lake, which is located downstream of an airport wastewater input (Stock et al. 2007). PFCAs and PFOSA comprised > 90% of ΣPFASs in sediments whereas detected levels of PFASs and PBDEs in the same set of sediments in two studies by authors Kelly et al. (2008b) and Kelly et al. (2009) were an order of magnitude higher than concentrations of organochlorine contaminants (range: 0.001–0.006 ng g^{-1} dw).

3.3.1.2. Lake sediments

3.3.1.2.1. Introduction

Lake sediments have been shown to be reliable archives for studying both current and historical accumulation of POPs (Czuczwa and Hites 1984, Eisenreich et al. 1989, Muir and Rose 2004). These studies involve the collection of cores from deep points in lakes followed by an analysis of extruded core slices. Dating of the slices is generally accomplished using ^{210}Pb, a naturally occurring radioactive element that is part of the uranium-238 radioactive decay series and with ^{137}Cs, a product of nuclear weapons testing which was elevated in the atmosphere in the 1950s and early 1960s (Blais et al. 1995, Oldfield and Appleby 1984). The ^{210}Pb has a half-life of 22.3 years, and therefore its usefulness as a geochronological tool is limited to the past 100–150 years. Low ^{210}Pb deposition at high latitudes as well as low sedimentation rates in most arctic lakes makes the application of radiometric dating challenging although the technique is nevertheless widely applied (Wolfe et al. 2004).

Sediment cores are subject to several kinds of artifacts that can make the interpretation of historical deposition difficult, including mixing from bioturbation and from the slumping of steep lake bottoms. Diffusion is an important consideration, particularly for chemicals with low sediment-water partition coefficients (Czuczwa and Hites 1984, Eisenreich et al. 1989, Muir and Rose 2004).

3.3.1.2.2. Legacy POPs in dated sediment cores

A rare and valuable type of core is one which has annual layers of sediment, with the colour or texture of layers differing, to form detectable laminations that can be counted. Such a core has not experienced

physical mixing (the laminations would have been obscured) and with such cores, the historical record is more intact. Stern et al. (2005) reported legacy POPs including PCBs, OCPs, and PCDD/Fs in laminated cores from Lake DV09 on Devon Island collected in May 1999. All cores were annually dated and the top 9 cm represented approximately 100 y of sedimentation. Dating of the sediment slices with ^{210}Pb coincided with counts of laminations and an average sedimentation rate of 295 g m^{-2} y^{-1} for two cores was reported. Total PCB flux peaked in the period of 1993–1997 with smaller maxima occurring in the core slices dated to 1971, during peak PCB production, and prior to the increased production in 1952. Maximum flux of ΣDDT occurred in the slice dated 1971, which corresponds to approximately 8 years after peak production. Total chlordane (ΣCHL) flux peaked in the core slice dated to 1971 and the maximum concentration of 0.2 ng g^{-1} dw was dated to 1988. The ΣHCH flux showed two maxima in the slices dated 1957 and 1971, corresponding approximately to the technical HCH production in the USA and China, respectively. Maximum concentration of the ΣHCH of 0.33 ng g^{-1} dw was detected in the slice dated to 1957. Maximum concentrations of lindane were 0.17 ng g^{-1} dw and the maximum flux was estimated at 12.9 ng m^{-2} y^{-1}. ΣPCDD/F concentrations in Lake DV09 core peaked in the 1970s with a maximum TEQ value of 0.07 ng g^{-1} dw detected in 1978.

Breivik et al. (2006) reported concentrations of legacy POPs in three high arctic lakes (AX-AJ, Romulus, Char) and one from northern Québec (B2) as part of a latitudinal transect of POPs deposition in sediments. Temporal resolution of the cores, while not as good as the laminated cores from Lake DV09, was improved over previous studies in the 1990s (Muir et al. 1996) due to the finer slicing of the cores (0.5 cm vs. 1 cm of most previous work) and with the selection of lakes with higher sedimentation rates. All lakes showed POPs appearing in sediment horizons dated to about 1940 (Figure 3.37). Low levels in some earlier horizons are probably best explained by diffusion (Eisenreich et al.

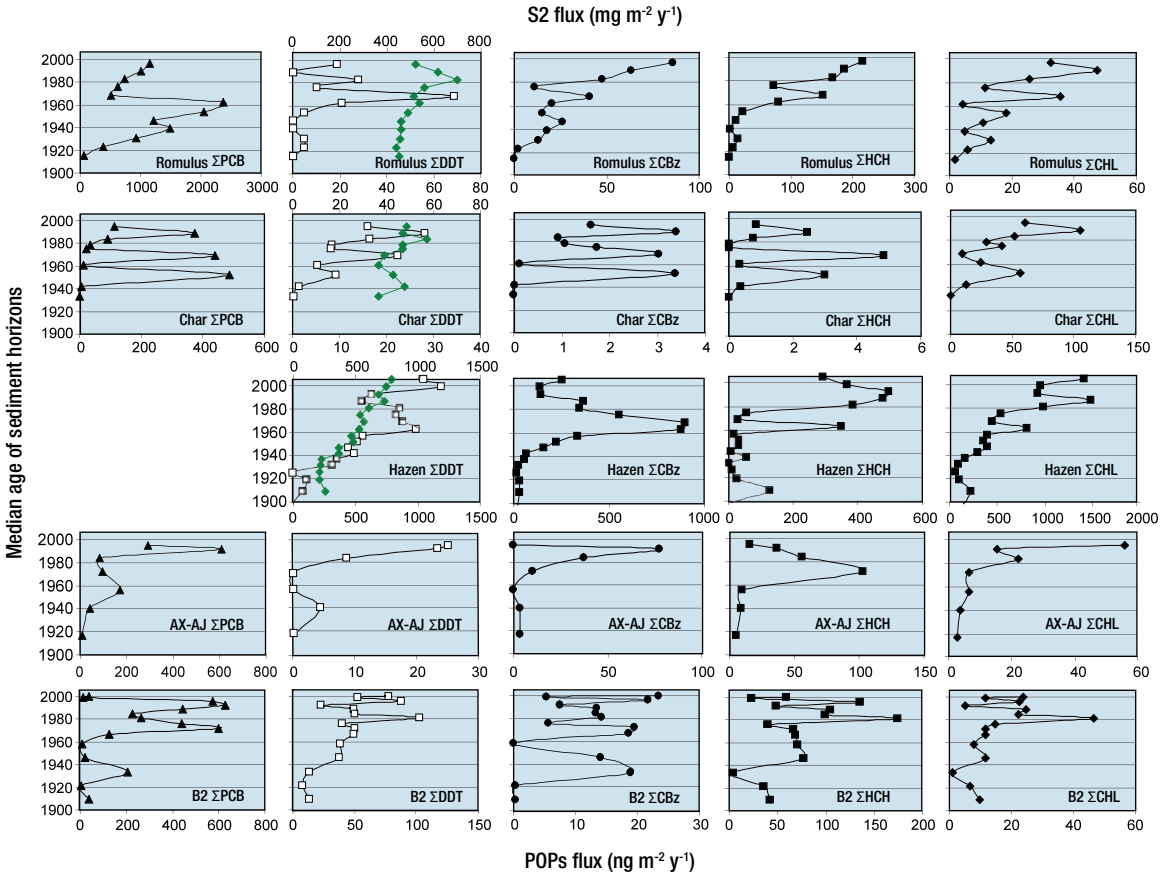

FIGURE 3.37

Historical flux profiles (ng m^{-2} y^{-1}) of ΣPCBs, ΣDDT, ΣCBz, ΣHCH, ΣCHL in sediments from lakes Romulus, Char, Hazen, AX-AJ, B2. All results except those for Lake Hazen are based on data in Breivik et al. (2006). Only chlorinated pesticides were determined in Lake Hazen (Muir et al. unpublished data). Also included are results for S2 algal carbon (upper horizontal scale; Green symbols) in Lakes Romulus, Char, and Hazen from Kirk et al. (2011).

1989) as well as smearing along sampler walls during the extrusion of sediment. Maximum fluxes of most POPs were achieved in the 1980s and 1990s in most lakes. This was particularly clear in B2 the most southerly lake. However, in several lakes (AX-AJ, Char, Hazen) ΣDDT and ΣCHL had maxima in surface slices.

The fluxes of POPs in Lake Hazen (Figure 3.37) were higher than in the other lakes, reflecting high sedimentation rates which averaged 1260 g m^{-2} y^{-1} in post-1960 horizons (Köck et al. 2012). Lake Hazen is the largest lake north of 74° latitude and is influenced by glacial runoff. Potential climate influences on the POPs profiles in Lake Hazen and other lakes are discussed in section 3.3.1.4.

3.3.1.2.3. Legacy POPs in Great Slave Lake sediment cores

A sediment core study was conducted in Great Slave Lake in 1994 with datable cores collected at four locations in the West Basin (Evans et al. 1996). POPs were measured in cores at two sites–at site 19 in 46 m deep waters offshore of Resolution Bay and Site 12 in 69 m deep waters offshore of Hay River. POPs concentrations were not reported for site 12 as the data were viewed as suspect, possibly due to contaminated glassware. In 2009, sediment cores were again collected at these sites and at a site in the East Arm to assess time trends.

Sedimentation rate for core 19B, collected in 1994, followed the same general time trends as that of the core collected in 2009 at the same site although sedimentation rates were higher for the 1994 core. Two cores were collected at this site in 1994 with core 19B, used for POPs analyses, showing a rate of 692 ng m^{-2} y^{-1} vs. 450 ng m^{-2} y^{-1} for core 19D. Both 19D (1994) and the 2009 core showed a gradual increase in total organic carbon in the sediments from the early 1960s to the early 1990s. For the 2009 core, concentrations of total organic carbon decreased through to the early 2000s before increasing again.

Chlordane flux in the 1994 core showed a strong increase from the early 1950s to the 1970s and then a declining trend thereafter; a weaker temporal pattern was apparent based on chlordane concentrations in the core. Similarly HCH flux increased from the 1950s to the early 1970s and the declined to the late 1980s with a small increase in 1990 due largely to the increase in sedimentation rate. Given that HCH concentrations have declined markedly in lake trout and burbot from the West Basin, it is expected that the sediment core from sites 12 and 19 would show a decline in HCH flux over this period.

DDT data were more variable than HCH data for unknown reasons. It is possible that some of the variation in DDT concentrations reflects periodic inputs from the Slave River from more agricultural areas further south. However, there was a broad pattern of increasing flux to circa. the 1970s and then an erratic decline in later years. With DDT concentrations declining in burbot and lake trout from the West Basin, it is anticipated that DDT fluxes also have declined at sites 12 and 19. The rates may differ at these two sites due to the differences in the locations. PCB flux showed a steady increase from the early 1950s into the early 1990s.

3.3.1.2.4. Biovector deposition of PCBs in sediments

Blais et al. (2005) and Michellutti et al. (2009b) measured POPs in sediment cores from ponds located near a large seabird colony at Cape Vera, Devon Island, in the Canadian Arctic (Figure 3.38). Surface sediment PCB concentrations were 5-fold greater in seabird-affected sites relative to a nearby control pond (Figure 3.39) and were correlated with independent indicators of seabird activity including, sedimentary nitrogen isotope ratios ($\delta^{15}N$) and lakewater chlorophyll a. Surface sediments from ponds near the seabird colony also contained 10 fold higher HCB and 60-fold higher DDT and its metabolites, than sediments from ponds outside the range of the seabird colony (Blais et al. 2005). PCB fluxes ranged from 290–2400 ng m^{-2} y^{-1} and are thus amongst the highest recorded in the High Arctic. Accumulation rates increased over time in the cores with the highest values recorded in the most recent sediments despite the wide spread ban of PCBs in the mid-1970s. Postulated mechanisms include: (1) enhanced PCB recruitment by sediments due to a seabird-derived nutrient driven increase in primary productivity, (2) delayed loading of PCBs from the catchment into the ponds, or (3) a biovector enhanced PCB delivery via guano and stomach oils containing biomagnified PCBs (Blais et al. 2005, Blais et al. 2007, Foster et al. 2010). Higher proportions of metabolites (e.g., DDE/DDT ratios) in proximity to the seabird colony provide evidence of contaminant delivery to sediments via guano and stomach oils deposited by the birds themselves. DDE/DDT ratios reached values as high as 0.9 in pond sediments near the seabird colony, similar to values measured directly in guano, suggesting that these contaminants were biologically processed rather than being deposited directly by atmospheric deposition (Blais et al. 2005, Blais et al. 2007).

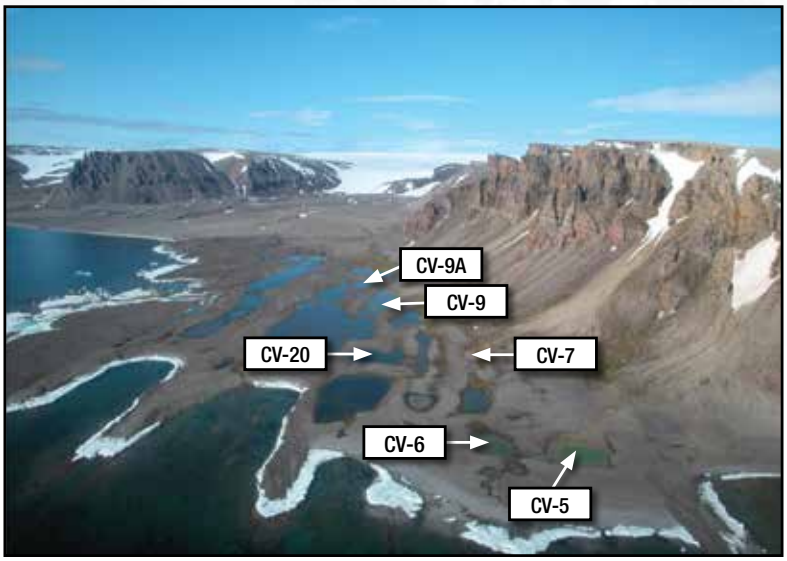

FIGURE 3.38

An aerial photograph of Cape Vera (Devon Island) showing the location of the study ponds near the seabird colony (Michelutti et al. 2009b).

Elevated contaminants from biovectors to lake sediments have also been observed in several other northern locations, from elevated PCBs and DDT in sediments of Lake Ellasjøen on Bear Island, Norway where large populations of kittiwakes, glaucous gulls, and little auks reside (Evenset et al. 2007b), to elevated PCBs in sediments that are related to densities of returning sockeye salmon in Alaska and northern British Columbia (Krümmel et al. 2005, Krümmel et al. 2003).

Lake trophic status is known to play a major role in the biogeochemical cycling of PCBs and other POPs (Dachs et al. 2000, Dachs et al. 2002). Higher organic production in the nutrient-enriched waters typically results in greater transfer of PCBs from the dissolved to the particulate organic matter (POM) phase and thus greater vertical flux to sediments; a situation that also favors increased movement of atmospheric PCBs into the pond (Dachs et al. 2000). This mechanism appears to be the best explanation for the pattern of PCBs and other POPs in the ponds at Cape Vera (Michelutti et al. 2009b).

3.3.1.3. New POPs in arctic lake sediment cores

The period 2003–2010 has seen increased measurements of new POPs in arctic lake sediments. Earlier work was reviewed in CACAR-II by Stern and

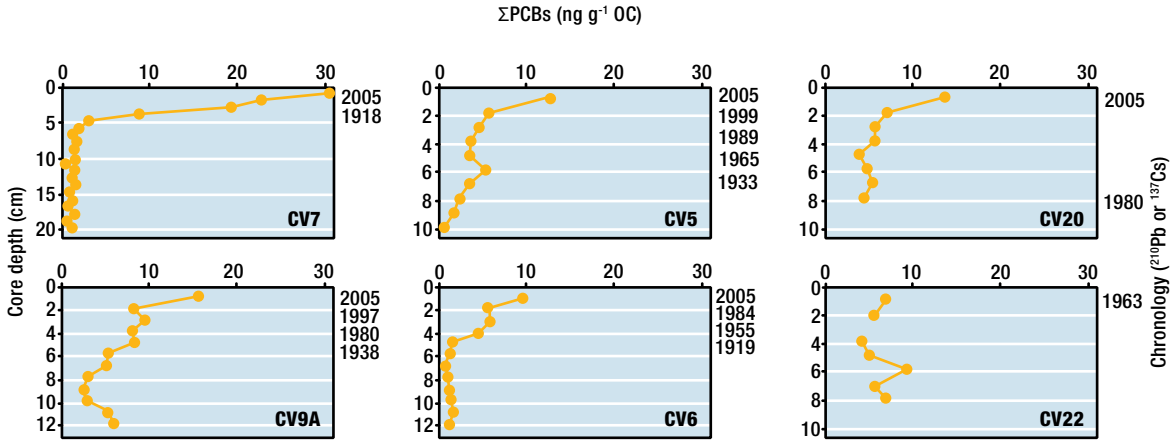

FIGURE 3.39

Sedimentary profiles showing ΣPCB concentrations (ng g^{-1} organic carbon) in cores in ponds near the Cape Vera seabird colony 1. Close proximity; CV-7 and CV-9A; intermediate proximity CV-5, CV-6 and CV-20; remote CV-22.

TABLE 3.10. Fluxes of BDE congeners and ΣPCB in arctic lake sediments (Breivik et al. 2006)

Location	Lake	Collection year	Lat/Long	Sedimentation rate[1]	FF[2]	Flux (ng m^{-2} y^{-1})				
				g m^{-2} y^{-1}		BDE-47	BDE-100	BDE-99	BDE-209	SPCB
Axel Heiberg Is	AX-AJ	1998	80°00'N, 87°00'W	110	1.0	<4	<4	1.7	8.3	292
Ellesmere Is	Romulus	2001	79°54'N, 85°06'W	820	2.6	<16	<16	<16	<3	1152
Cornwallis Is	Char	1997	74°40'N, 94°50'W	280	2.4	9.1	1.9	9.5	9.4	112
Northern Québec	B2-1	2000	57°45'N, 76°10'W	160	1.3	92	76	321	43	2242
Cornwallis Is	DV09	1999	75°34'N, 89°19'W	300	2.4	28.5	[3]	[3]	na[4]	370
West Greenland	Lake G	2000	67°03N, 51°13W	66.6	-4	1.34	na	na	na	220

[1] Sedimentation rates of the surface slice

[2] Sediment focusing factor

[3] Not reported

[4] Not analyzed

Evans (2003). Stern et al. (2005) reported new POPs endosulfan, SCCPs, and PBDEs in the laminated sediment core from Lake DV09 on Devon Island. The maximum concentration (0.04 ng g^{-1} dw) and flux (6.2 ng m^{-2} y^{-1}) of α-endosulfan were observed in the surface horizon and endosulfan was undetectable below horizons dated to 1988. The trend of increasing concentration of endosulfan in the 1990s observed by Stern et al. (2005) was in general agreement with those from mountain lake sediments (Usenko et al. 2007). Maximum SCCP flux occurred in surface sediment with a smaller peak in the core slice dated to 1957. The maximum concentration of ΣsPCAs was detected in a slice dated to 1997 with a concentration of 17.6 ng g^{-1} dw.

Sediment surface fluxes of BDE-209 ranged from < 3 to 43 ng m^{-2} y^{-1} in four arctic lakes (namely AX-AJ, B2, Romulus and Char), with the highest fluxes in the most southerly lake (see B2 of Table 3.10). Samples were collected in 1998, 2001 and 1997, respectively (Breivik et al. 2006). BDE-209 was generally detected only in the more recent horizons of the sediments, for which maximum flux occurred mainly post-1980 corresponding to the large scale production of PBDEs. However, historical profiles for BDE-209 do not follow estimated global historical production for BDE-209 and penta-BDE. Similar temporal resolutions of BDE-47 in Char Lake and Romulus Lake were also reported for sediments, and were approximately 1.3 ng m^{-2} y^{-1}, from Lake G in West Greenland (Malmquist et al. 2003).

ΣPBDE concentration in the Lake DV09 surface sediment was 0.25 ng g^{-1} dw. BDE-47 dominated, together with BDE-99 and BDE-100, accounted for over 80% of ΣPBDE. The maximum flux of the sum of BDE-47, BDE-99 and BDE-100 of 28.5 ng m^{-2} y^{-1} in a laminated sediment core from Devon Island in the Canadian Arctic (Stern et al. 2005) was similar to the flux estimated for Char Lake (ΣBDE47,99,100 = 20.5 ng m^{-2} y^{-1}) but higher than fluxes observed in Lake Romulus (< 16 ng m^{-2} y^{-1}) and AX-AJ (1.7 ng m^{-2} y^{-1}).

PFASs in sediment from Amituk, Char and Resolute Lakes were reported (Stock et al. 2007) while Veillette et al. (2012) reported PFAS in a core from Lake A on northern Ellesmere Island. Elevated levels of some PFASs measured in Resolute Lake sediment were consistent with the surface water samples. The ΣPFAS concentration in the top sediment slice in Resolute Lakes was approximately 15–20 times higher compared to concentrations detected in Char Lake (5 ng g^{-1} dw), and Amituk Lake (7 ng g^{-1} dw), and 200 times higher than those observed in Lake A surface sediments (0.08 ng g^{-1} dw; 0–0.5 cm depth).

PFAS profiles varied between the lakes. The major PFAS in Char Lake sediment was PFOA at concentrations up to 1.7 ng g^{-1} dw while in Amituk Lake, PFHpA was the dominant compound at concentrations of up to 3.9 ng g^{-1} dw and PFHxS was the major PFSA observed while perfluorobutane sulfonate (PFBS) and PFOS were also detected. In contrast, PFOS was the major PFAS in Lake A. The

surface sediment PFOS (0.066 ng g^{-1} dw) in Lake A was similar to that detected in the topmost slice of Amituk Lake sediments (0.062 ng g^{-1} dw), however, PFOS was only a minor component of the total PFAS in Amituk Lake. Resolute Lake sediments were dominated by PFOS with concentrations (range: 24–85 ng g^{-1} dw) that were 1–2 orders of magnitude greater than other measured PFASs. PFOA and PFHpA were the dominant PFCAs measured, with concentrations ranging from 2.3–7.5 ng g^{-1} dw and 0.95–6.8 ng g^{-1} dw in the first and second slices, respectively. PFNA was detected in levels up to 3.2 ng g^{-1} dw.

PFOA profiles in Char Lake sediment showed a predominance of the linear isomer, implying a mainly fluorotelomer alcohol source (De Silva et al. 2009). Char Lake sediment was dominated by the linear PFNA isomer (96–97%) whereas all four branched PFNA isomers (iso-, 1-, 3-, 4-) were detected and the iso-PFNA (2–3%) was the major branched isomer detected. In the Char sediment, the iso-isomer was the only branched isomer detected in the longer-chain PFCA profiles.

3.3.1.4. Climate warming and scavenging of POPs

An emerging hypothesis related to the pattern of PCBs in ponds at Cape Vera, is that recent climate change has exacerbated the fluxes of contaminants such as mercury, organohalogen pesticides and other industrial compounds into arctic and subarctic lake sediments (Outridge et al. 2007b, Outridge et al. 2005, Stern et al. 2005, Stern et al. 2009, Wang et al. 2010a), and may make them more available to lake food webs (Carrie et al. 2009). In these instances, the climate effect has been attributed to longer ice-free seasons, which allow for the greater production of algal-derived soluble and particulate organic matter (SOM and POM) in lake waters during spring and summer. SOM in turn coats the surfaces of finely suspended sediments (creating larger surface areas and porosities) which, together with POM, then scavenge particle reactive contaminants from lake surface waters. The effect is to act as a particle "concentrator" for organic compounds, which then sink to the bottom of the lake and thus accumulate at faster rates in the sediments.

Stern et al. (2005) found strong associations between diatom counts (as cells g^{-1} dw) in Lake DV09 sediment and increasing fluxes (µg m^{-2} y^{-1}) of PCBs, toxaphene, Σchlordane, and ΣHCH diatom counts over the period of 1960–1999. They did not observe any relationship for ΣDDT or PCDD/Fs and diatoms over the same period. It was postulated that the maximum, or increasing number of POPs observed for many of the major compound classes in Lake DV09 sediments may be influenced by climate variation and that the resulting increase in algal primary productivity (indicated by greater diatom abundance) could drive an increasing rate of scavenging of POPs from the water column.

Outridge and Stern (2009) examined the algal scavenging hypothesis in a core from Amituk Lake. Rather than diatom counts, they used the "S2" form of organic carbon (derived in this lake almost entirely from kerogen-like substances from algal cell walls (Outridge et al. 2007a)). They found a significant correlation of ΣHCH, dieldrin and ΣChlordane concentrations and S2 carbon but not for ΣPCBs or ΣDDT (Figure 3.40). It was concluded that the within-lake process of organic matter particle scavenging of POPs could be an important factor in producing the measured sedimentary profiles of certain POPs in Amituk Lake. Another factor that could influence the profiles would be anaerobic degradation (dechlorination) of chlorinated aliphatic POPs such as HCHs and cyclodiene pesticides as noted in the core from Lake DV09 (Stern et al. 2005).

The algal scavenging hypothesis can also be tested for POPs in 3 other high arctic lakes (Romulus, Char, Hazen) for which S2 algal carbon measurements have been reported by Kirk et al. (2011). The results in Figure 3.40 show that while S2 fluxes have increased during the 20th century, recent increases do not closely parallel the POPs profiles. Lake Hazen is an interesting case because it is the only lake influenced by glacial runoff. S2 levels have increased steadily in Lake Hazen similar to other lakes. Also, higher sedimentation rates were found in post-1960 horizons of the sediment core collected in 2005 compared to pre-1960 rates that could be due to increased glacial runoff and deposition of fine particles. Mobilization of POPs from the ice cap to the northwest of Lake Hazen may be occurring. Higher concentrations of CUPs were found in glacial fed streams compared to the open lake (see section 3.2.3.2). Bogdal et al. (2009) and Schmid et al. (2011) have reported that input of POPs into the high-alpine lakes has increased sharply since the late 1990s, Currently, input fluxes of organo-chlorines are similar to or even higher than those in the 1960s–1970s. This second peak supports the hypothesis that there is a relevant release of persistent organic chemicals from melting alpine glaciers.

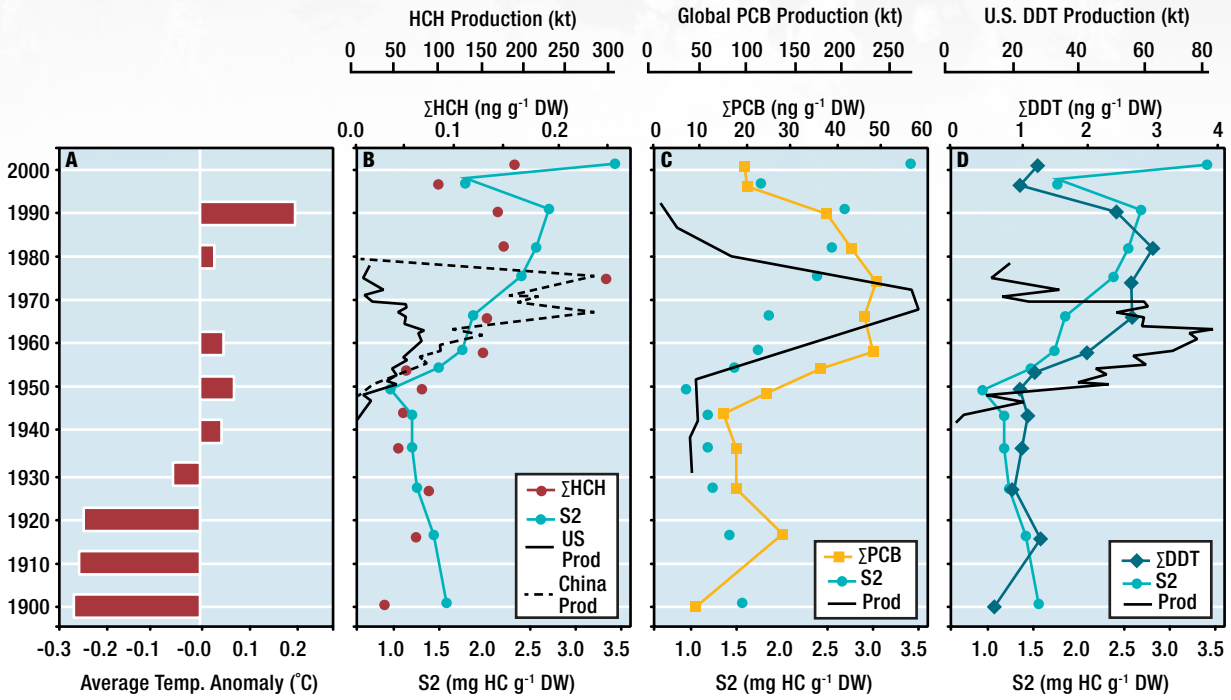

FIGURE 3.40

Average northern hemisphere temperature trends during the 20th Century (A), are compared with concentrations of POPs and algal-derived S2 carbon in a core from Amituk Lake: (B). ΣHCHs; (C). ΣPCBs; and (D). ΣDDT). Global production data for HCHs, PCBs and DDT are also shown (Stern et al. 2009).

3.3.2. Assessment

- Arctic lake sediments have been shown to be good archives of POPs including new POPs such as PBDEs and SCCPs.
- Use of sediment cores to assess POPs deposition, especially in the High Arctic, is challenging due to low concentrations and difficulties related to the dating of sediment cores.
- Higher organic production in nutrient-enriched waters may result in greater transfer of PCBs from the dissolved to the particulate organic matter (POM) phase and greater vertical flux to sediments.
- While algal carbon fluxes have increased during the 20th century, in many lakes recent increases do not closely parallel the POPs profiles.
- Results from other lakes not affected by seabird guano suggest that inputs of POPs may be influenced by climate warming, as shown by an increase in algal primary productivity, indicated by greater diatom abundance.
- Biovector transport and the deposition of PCBs and other POPs in arctic ponds was identified as an important route of input for sites near seabird colonies.
- Evidence exists that contaminants from anadromous salmon biovectors are transferred to aquatic food webs, though very few studies have been done in northern latitudes.

3.4. Local Sources of Contaminants in the Canadian Arctic

Contributors: Tanya Brown, Ken Reimer, and Monica Danon-Schaffer

3.4.1. Introduction

As discussed in Chapter 2 (section 2.3.7) local sources of contamination, in particular contaminated sites, have raised serious concerns because many, including DEW-line stations, mines, and other industrial sites, are located close to communities. When exchanging contaminants-related information with Northerners, the subject of local contaminants is consistently raised. It is being addressed through the Northern Contaminated Sites Management Program (INAC 2010), through the NCP's Community Based Monitoring and Research program and local projects supported by territorial contaminants committees (INAC 2012).

In this section of CACAR-III (2003–2011), two case studies present recent information regarding

local sources (a) from municipal waste sites and (b) a multi-year remediation project on terrestrial and marine ecosystem recovery in Saglek, Newfoundland and Labrador.

3.4.2. Local sources updated (post-2002)

3.4.2.1. PBDE contamination of soils by leachate in sites nearby dumpsites in Yellowknife, Cambridge Bay and Iqaluit

3.4.2.1.1. Background

A preliminary study was performed to investigate how polybrominated diphenyl ethers (PBDEs) are entering and transferred among landfill leachates, sediments and soils in the Canadian Arctic. Moreover, fate and transport of PBDEs and the spatial distribution of contamination were assessed by investigating the leachability of PBDEs from e-wastes. This is the first study in the Canadian North to investigate PBDE congener patterns in aqueous media (leachate, effluent and background water), and in soil. Soil, leachate, effluent and background aqueous samples were collected from northern Canadian dumpsites and nearby areas (Danon-Schaffer 2010). Sixteen soil samples were collected at depths of 0–20 cm below surface in the summers of 2004 and 2006 from various sites within Yellowknife (YELL), Cambridge Bay (CAMBY), and Iqaluit (IQ) (see map in Figure 3.41). Only samples with concentrations higher than in the procedural blanks are presented. Typical concentrations measured in procedural blanks are shown in Figure 3.41.

Ten leachate samples were collected from different locations in the Canadian North in 2006. Most sites had measurable BDE-209 concentrations and only three locations (Hall Beach, Cape Dorset and Whitehorse WEP) had measurable concentrations of BDE-47. Compared to all other leachate samples, Hall Beach (HB-01) showed higher-brominated congeners having elevated PBDE concentrations (Figure 3.42).

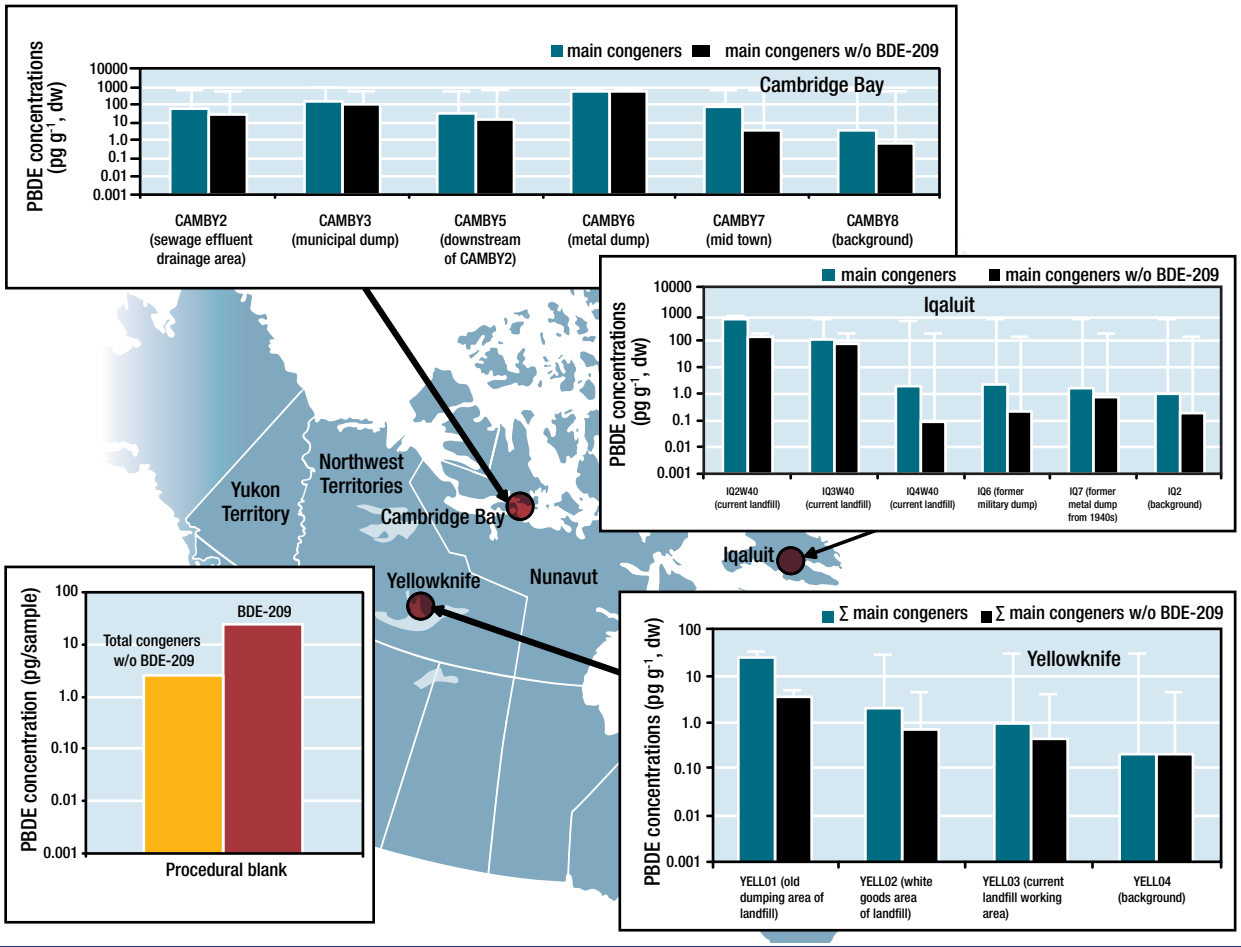

FIGURE 3.41

Sampling sites, locations and total PBDE concentrations in surface soil samples for Northern Canada (ng g^{-1} dw) (2006 data). Error bars indicate two standard deviations.

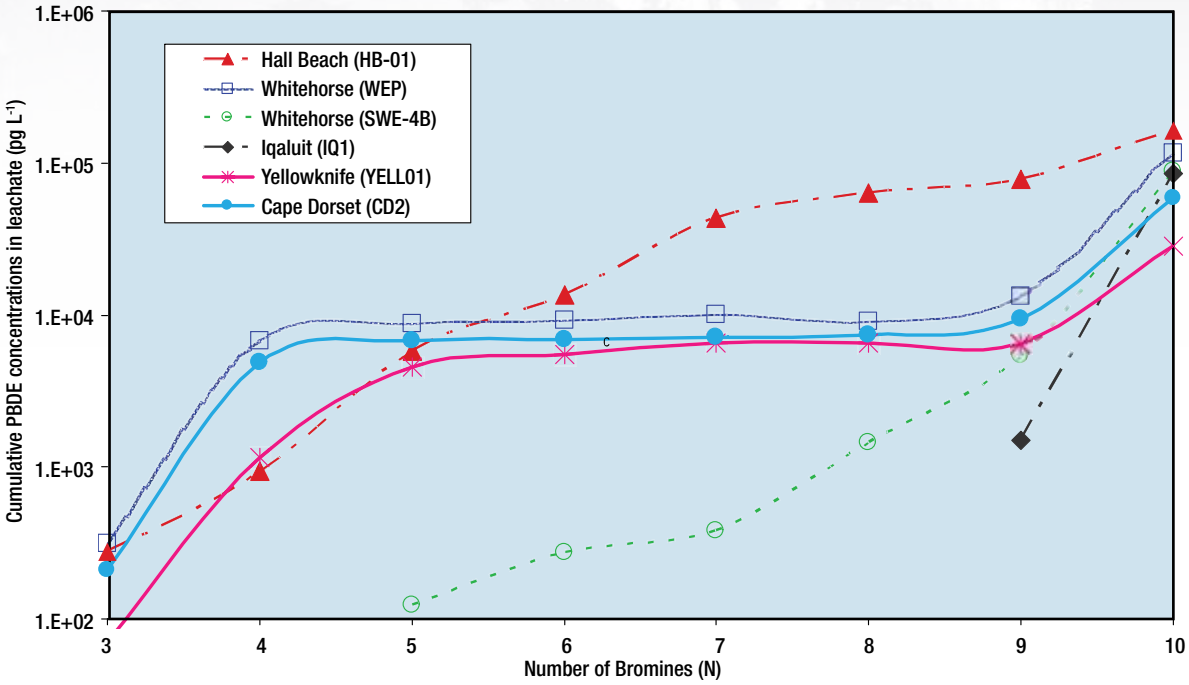

FIGURE 3.42

PBDE concentrations in blank-corrected leachates from Northern Canada, summer 2006. Ordinates give cumulative PBDE concentrations, i.e., sum of concentrations of all PBDE congeners having N or fewer attached bromines. The principal congeners discussed throughout this study, i.e., BDE-47 (N=4), -99 and -100 (N=5), -153 and -154 (N=6), -183 (N=7), -206 and -207 (N=9), and -209 (N=10), account for > 80% of the total PBDEs.

One reason may be due to the fact that the leachate was ponded in a low lying area. The Cape Dorset (CD-2) sample was also collected in a ponded area where the leachate could have been more concentrated. The Whitehorse (WEP) sample was collected from a depth of approximately 25 m. That location is known to have old leachate (i.e., 20 years or more), so that high PBDE concentrations are not surprising given the incorporation of PBDEs in products over time.

3.4.2.1.2. Distribution and congener patterns of PBDEs in leachate

The major PBDE congener measured in all of these leachate samples was BDE-209, ranging between 52% and 98% of the total BDEs, except for Inuvik (INUVIK2) and Tuktoyaktuk (TUK-2, TUK-3). The highest concentration of BDE-183, a major component of the Octa-BDE commercial product, was measured in HB-01 (28.4 ng L^{-1}). Large variations between the lowest and highest concentrations measured in these samples are likely due to a combination of factors, including the diversity of materials entering the dumpsites, different community characteristics, differences in rainfall and soil permeability and analytic errors, especially when the levels are low. For Cape Dorset (CD-2) and Whitehorse (SWE-4B), the presence of the commercial Deca-BDE product was more apparent, as BDE-207 and BDE-206 patterns are similar, and Deca-BDE is known to contain small amounts of these congeners in its formula. With the exception of HB-01, BDE-209 is the major contributor to the BDE concentrations found in these leachate samples.

3.4.2.1.3. Distribution and congener patterns of PBDEs in soil

The ΣPBDE concentrations of nine major congeners are shown in 3.41. The highest overall ΣPBDE concentrations measured in the soil samples from the major dumpsites were those from Iqaluit (1.1 ng g^{-1} to 766 ng g^{-1}, avg. 154) followed by Cambridge Bay (4.5 ng g^{-1} to 515 ng g^{-1}, avg. 132) and Yellowknife (0.89 ng g^{-1} to 24 ng g^{-1}, avg. 6.9). These levels were significantly higher than those measured in corresponding background sites: Cambridge Bay (CAMBY8) = 4.5 ng g^{-1}; Iqaluit (IQ2) = 1.1 ng g^{-1}; and Yellowknife (YELL04) = 0.9 ng g^{-1}. The large

difference in concentrations between the landfill and background soil samples suggests that PBDEs are being leached from the landfill. The congener pattern of the background samples was similar in all three instances, with the exception of BDE-47 in CAMBY8, which contained 2% of the total PBDE concentration, compared with 10% and 11%, respectively, for IQ2 and YELL04. The BDE-209 contribution for the background sites ranged between 74% and 88%, suggesting that other products were more prevalent and/or BDE-209 had degraded somewhat to the lower brominated congeners. It is important to note, however, that the major PBDE congener measured in most of the disposal site soil samples was BDE-209, ranging between 40% and 96% of the total PBDEs and at concentrations of up to 597 ng g^{-1}. Other major congeners detected in the soil samples of almost all sites were those of the Penta commercial mixture, i.e., BDE-47, -85, -99, -100, -153 and -154. An exception was the soil sample from a metal dump area in Cambridge Bay (CAMBY6) which exhibited a very high concentration of BDE-183, a major component of the Octa commercial mixture.

3.4.2.1.4. PBDE distributions in soil compared to commercial products

Total concentrations of major BDE congeners range from non-detected (nd) to 766 ng g^{-1} (dw). BDE-209 contributed more than 60% of the total PBDE concentrations for 8 of the 16 sites, suggesting widespread deca-BDE occurrence. The distributions of BDE congeners from locations in Iqaluit and Cambridge Bay appear to be similar to those of the commercial Penta-BDE formulation (DE-71, Great Lakes Chemical Corp.) as shown in Figure 3.43.

The congener profiles of the sample from the Cambridge Bay dumpsite (CAMBY 6) in Figure 3.44 have similarities with the profile of the octa-BDE commercial formulation (DE-79, Great Lakes Chemical Corp.). Evaluating the signature for the CAMBY3 dumpsite compared to the penta-BDE commercial product and the CAMBY6 dumpsite with the octa-BDE commercial product, one can observe the differences between these two nearby sites. CAMBY3 is the municipal dump, whereas CAMBY6 is the metal dump. The finding that these two sample sites differ substantially, with the apparent predomination of different commercial products, suggests local sources of PBDEs. To the best of our knowledge, this is the first time that potential commercial penta-BDE and octa-BDE have been reported in soil samples in the Canadian North.

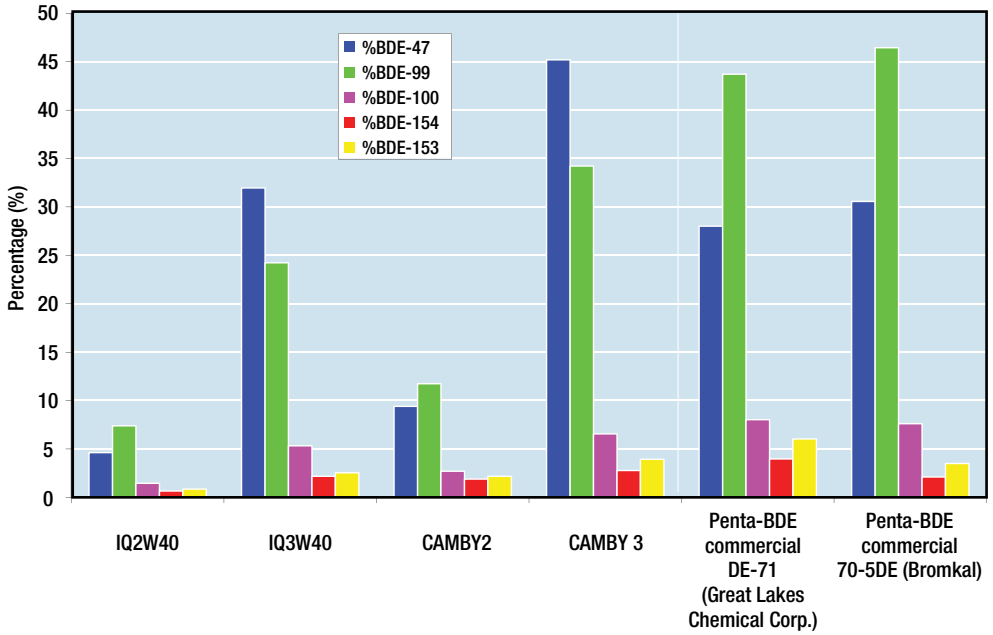

FIGURE 3.43

Penta-BDE (DE-71, 70-5DE) commercial product relative fractions of principal congeners (Rayne and Ikonomou 2002) compared to four soil samples from the Canadian Arctic. BDE congeners are included in the commercial formulation only where they were reported to be present.

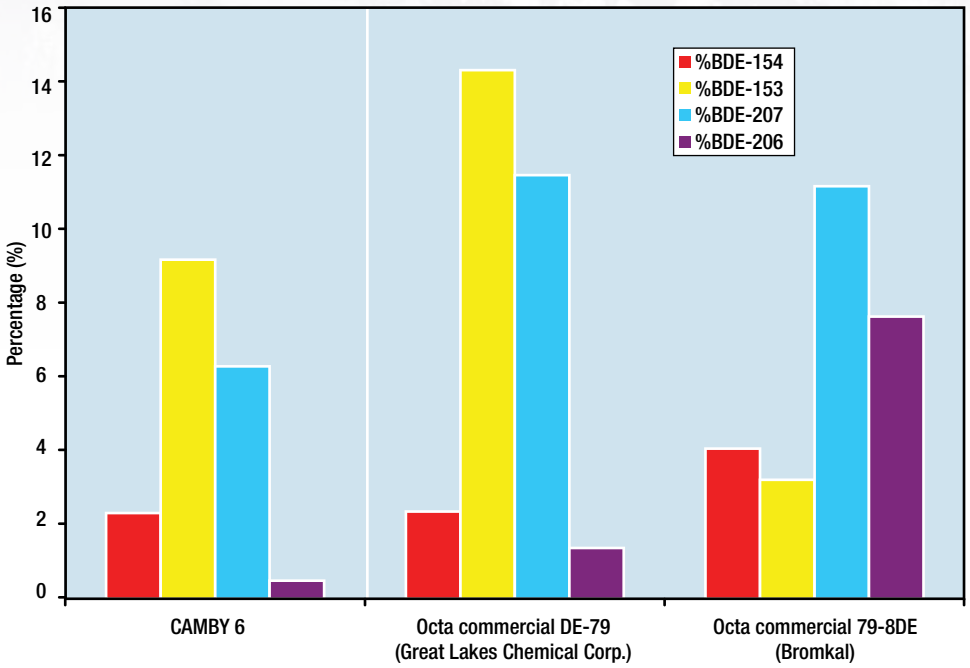

FIGURE 3.44

Octa-BDE (DE-79, 79-8DE) commercial product relative fractions of principal congeners (the source for congeners BDE-153 and BDE-154 (Rayne and Ikonomou 2002) and BDE-206 and BDE-207: (La Guardia et al. 2006) compared to soil samples collected in this work. BDE congeners are included in the commercial formulation only where they were reported to be present.

3.4.2.2. PCBs contamination in Saglek Bay, Nunatsiavut

3.4.2.2.1. Background and history

Saglek Bay is located on the northeast coast of Labrador at 58° 23'N, 62° 35'W, just south of the Torngat Mountains National Park and 225 km north of the nearest present day community of Nain. The mountainous and coastal region is ecologically characterized as alpine tundra. The region is supported by a rich community of terrestrial and marine wildlife and is an important traditional harvesting area for Labrador Inuit.

Outer Saglek Bay, is the site of a former radar and communications station that was built in the early 1950s as part of the Pole Vault line, a series of radar stations designed to provide early warning of airborne attack during the Cold War. The Saglek Pole Vault station (LAB-2) was abandoned in the early 1970s, and in the 1980s the Department of National Defence (DND) built a new radar station at the site as part of the North Warning System (NWS), which is operated by the North Warning System Office (NWSO). The site divides geographically into three areas: the Site Summit, Antenna Hill, and the Beach (Figure 3.45). During the sites operational period as a Pole Vault station, the Site Summit and Antenna Hill had large radar and communications installations. At the height of its operation Saglek was the largest site on the Pole Vault Line and supported in excess of 200 people. After the Pole Vault Line facility was closed, the Beach and the lower site were used in the 1970s and 1980s as a base for oil exploration activities. Most of the structures associated with the Pole Vault Line facility have been demolished, but some of the concrete foundations remain.

During the 1990s, extensive PCB soil contamination was found at the Site Summit, Antenna Hill and the Beach areas (ESG 1997). Studies were also conducted to determine the impact of contamination on the surrounding environment. Terrestrial studies on PCB contamination in the soil, plants, and lake sediments around the Saglek Bay station showed that redistribution of PCB contamination created a halo of influence 50 km in diameter around the source (Pier et al. 2003). Similarly, marine studies on sediment PCB levels displayed a 10 km radius of influence (Kuzyk et al. 2005). An ecological risk assessment indicated that both shorthorn sculpin and black guillemots were potentially at risk from contact with the PCB contaminated sediments during the assessment period of 1997–1999 (ESG 2002). Levels

of PCB exposures were so high that adverse health effects, including effects on the immune system, reproductive system and endocrine system, were measured in both indicator species. Elevated levels of PCBs were also found in terrestrial herbivores (ESG 1999). To help in the decision-making process for remediation of the site, a human health risk assessment (HHRA) was prepared regarding the consumption of local foods in the Saglek Bay Area in 2002 by the CHUQ-Public Health Research Unit at the Laval University Research Hospital. It provided supporting information to the Labrador Inuit Association about the potential health risks (Ayotte et al. 2002). The HHRA recommended avoiding the consumption of food items in the more contaminated zones at the site and adjacent marine environment.

These findings led to a multi-year soil remediation project. Soils containing PCBs in excess of the CEPA regulation of 50 µg g^{-1} (ppm) were excavated between 1997 and 1999. These contaminated soils, which amounted to approximately 20,000 m^3 were removed from the Beach, Site Summit and Antenna Hill, and stockpiled in a staging area. This material was screened and containerized over the summers of 2003 and 2004, and shipped off site for appropriate disposal. Soils remaining at the Site Summit and Antenna Hill areas, with PCB concentrations of less than 50 µg g^{-1} were secured in place with a 30-cm cap of clean fill. Soils with PCB concentrations between 5 and 50 µg g^{-1} were excavated from the Beach and secured at Antenna Hill because of the sensitivity of the marine environment. A terrestrial monitoring program has been put in place to monitor ecosystem recovery after the remediation. The risk management strategy implemented for the marine sediments was natural recovery with monitoring. This strategy, which was guided by a stakeholder group, was based on extensive studies which took place from 1999 to 2004 (ESG 2008). The long-term goal of this strategy is to achieve sufficient ecosystem recovery in order to protect human and ecological health.

The assessment and remediation of the entire site was also guided by the stakeholder group which continues to review and provide input on the outcomes of the monitoring programs. Results of terrestrial and marine ecosystem recovery are given in Chapter 5, section 5.2. Only the results for PCBs in surface sediments of Saglek Bay are presented here.

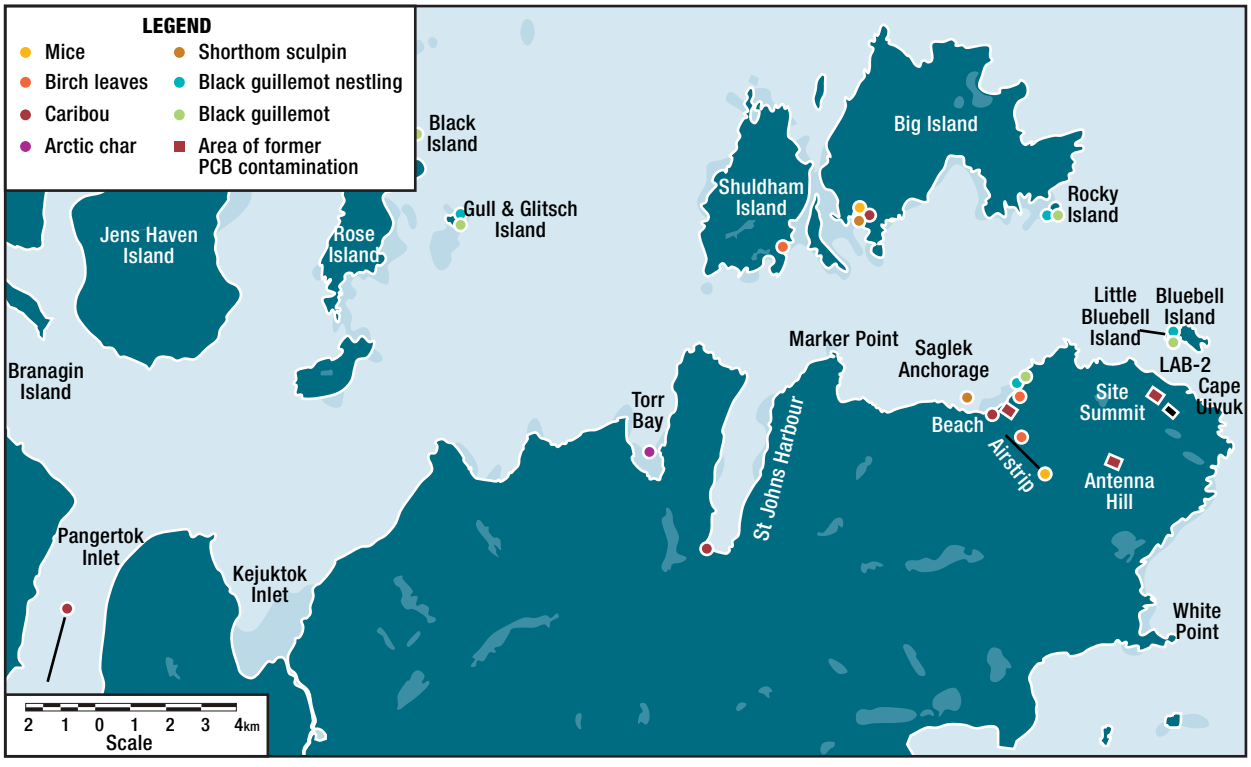

FIGURE 3.45

Map of Saglek Bay (Nunatsiavut) showing the locations of mice, birch leaves, caribou, arctic char, shorthorn sculpin and black guillemot collections and the area of former PCB contamination.

3.4.2.2.2. PCB concentrations in surface sediment

In 2006, PCB concentrations were measured in surface sediments to determine whether the extent of PCB contamination in the marine environment had decreased since the removal of the chronic terrestrial PCB source. Surface sediment samples were collected from four zones in Saglek Bay, up to a depth of 165 m (Figure 3. 46). PCB concentrations ranged from 1–800 ng g^{-1} dw and decreased with increasing distance from the former source of contamination at the Beach (Brown et al. 2009). The spatial pattern of the 2006 PCB concentrations in sediment was consistent with results from initial marine investigations conducted in 1998–1999 (ESG 2002, Kuzyk et al. 2005), with the highest concentrations being reported north and west of the former source. Temporal trends show that the extent and average concentrations of PCBs decreased in surface sediments throughout Saglek Bay (Figure 3.47).

The 2006 nearshore (zone 1) sediment concentrations were an order of magnitude lower than the 1998–1999 sediment concentrations, with average values falling from 1,120 ng g^{-1} dw in 1998–1999 to 100 ng g^{-1} dw in 2006. Sediment concentrations from zones 1B, 1C, and 3 also decreased significantly from 1998–1999 concentrations.

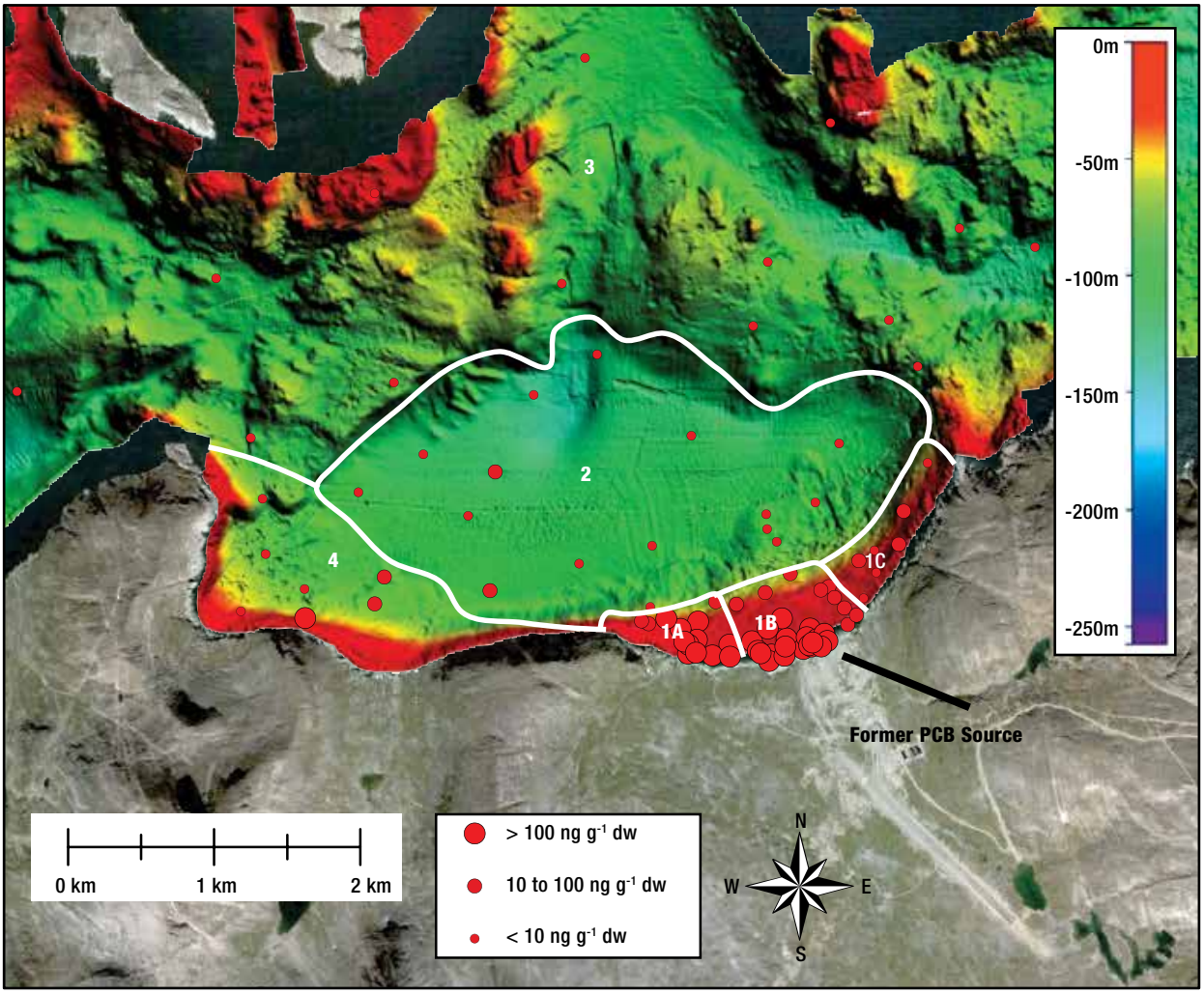

FIGURE 3.46

General bathymetry and the four bathymetric zones in the Saglek-Anchorage area (modified from Brown et al. 2009).

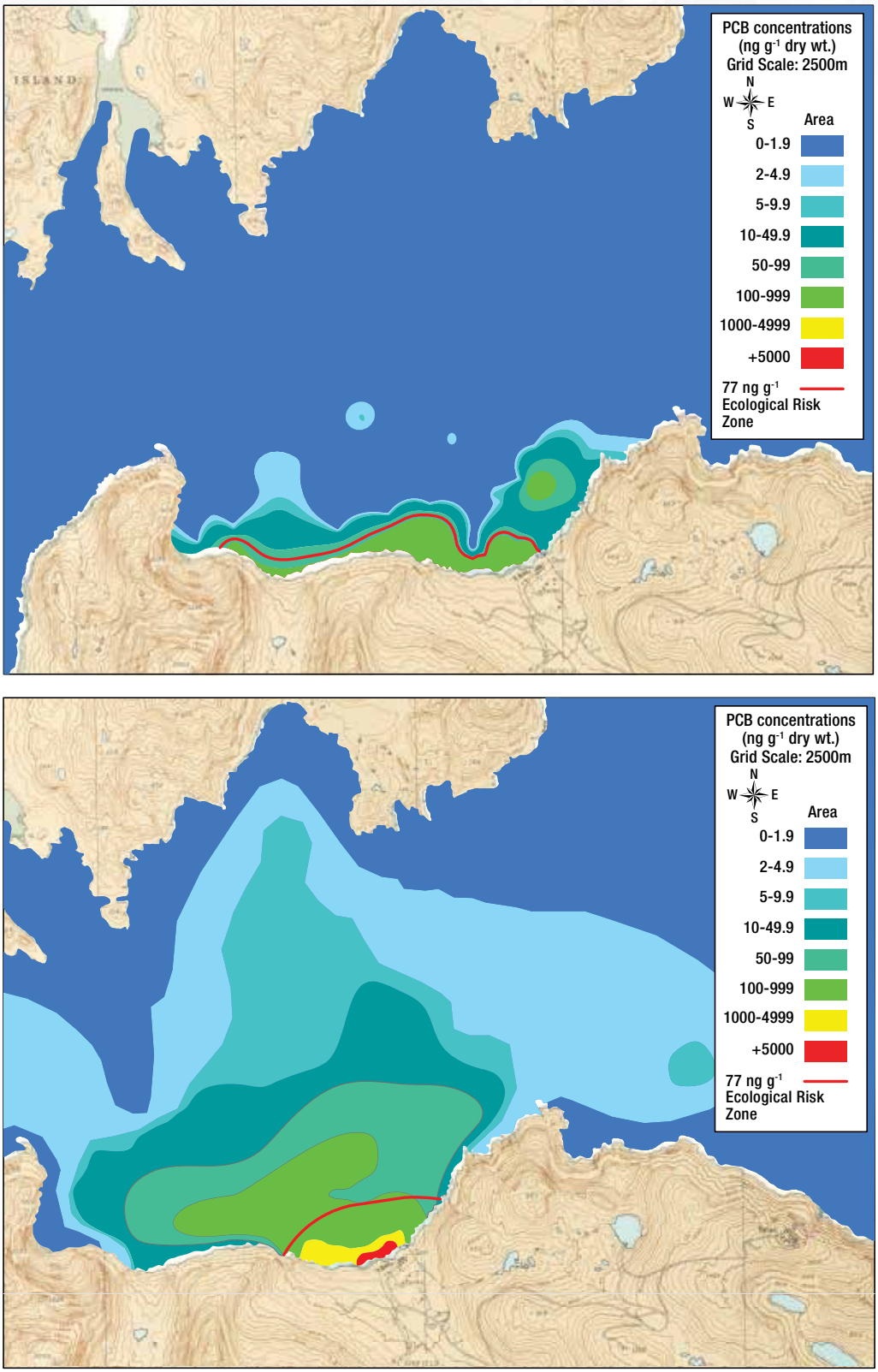

FIGURE 3.47

PCB contamination in marine surface sediments of Saglek Bay: (top) 2006 PCB concentrations in surface sediments; (bottom) 1998 PCB concentrations in surface sediments (Brown et al. 2009).

There also appeared to be a trend to lower PCB concentrations immediately west (zone 1A) and further west (zone 4) of the Beach area but the changes were not statistically significant (Brown et al. 2009). The decrease in PCB levels in the nearshore area indicated that sediment PCB contamination was decreasing quickly and approaching the site-specific threshold of 77 ng g^{-1} established for probable adverse effects in black guillemot nestlings (Brown et al. 2013). Sediment PCB concentrations in 2006 confirmed previous qualitative predictions that decreases in PCB contamination in the shallow area near the former contaminated Beach would occur relatively rapidly (in less than 10 years). It was also confirmed that fine-grained to coarse-grained sand would be transported from areas of highest PCB concentrations near the contaminated Beach primarily towards the west, somewhat to the north, and to a much lesser extent to the east (Solomon 2000). Sediment PCB concentrations in 2006 also suggested that the finer sediments were being transported toward the western end of the shallow Saglek Bay area and were deposited under the influence of oceanic transport processes. In addition, the contaminated sediments that were being deposited to the north, in the deep muddy basin, appeared to be simultaneously diluted and buried with "clean" sediment, resulting in an overall decrease to the surface sediment PCB levels in this area.

From 2008 to 2011, a marine monitoring program was executed to evaluate temporal trends of the level and extent of PCB contamination in the marine sediments in three zones (1A, 1B, and 4) of the Saglek-Anchorage area (Figure 3.46). These three zones were chosen for monitoring because previous investigations (Brown et al. 2009, ESG 2008) reported the highest concentrations in the nearshore area north and west of the former source. Surface sediment measurements indicate temporal decreases in both the spatial coverage and concentration of PCBs in the nearshore area of Saglek Bay (Figure 3.48). The results also suggest that sediments continue to be transported toward the western end of the shallow Saglek-Anchorage area and are simultaneously diluted and deposited in the deeper areas. The decrease in PCB concentrations in zone 1 from 2009 to 2010 may have been due to increased storm activity over that period. Overall, the decrease of PCB contamination in zones 1A, 1B and 4 indicates that sediment PCB concentrations in the nearshore area are decreasing quickly and that since 2010, have remained below the site-specific threshold established for probable effects in black guillemot nestlings (77 ng g-1). The marine monitoring program has confirmed that average sediment PCB concentrations are below levels which could impact the health of most fish and bird species for the area and that the site is recovering from the PCB contamination. As average PCB levels in the sediments continue to decrease over time, monitoring of these matrices is no longer necessary.

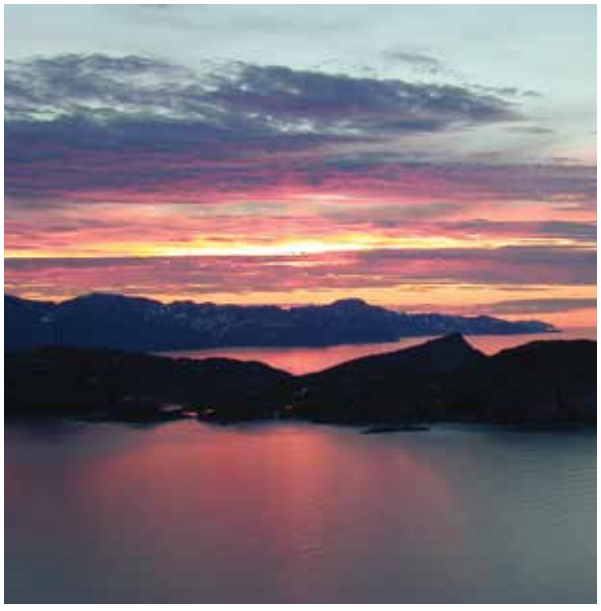

Photo: Jason Stow

3.4.3. Assessment

- New POPs including PBDEs, PFOS and SCCPs have been shown to be sources of local contamination in or near communities in the Canadian Arctic.
- Previous (and ongoing) contamination from DEW-line sites are of serious concern at a local level and they may contribute to global sources of POPs as the soil burdens and residues in contaminated sites are released through permafrost melting or from greater climate warming.
- Dumpsites in Iqaluit, Cambridge Bay and Yellowknife showed significantly higher ΣPBDE concentrations compared to corresponding background sites in these locations, suggesting that PBDEs leach from the landfill.
- Continued studies at Saglek Bay have shown that sediment PCB concentrations in the nearshore area are decreasing quickly.
- The continued study of PCBs at Saglek Bay has improved the knowledge of the fate of sediment associated contaminants in nearshore arctic marine environments and particularly on their transport to offshore depositional areas.

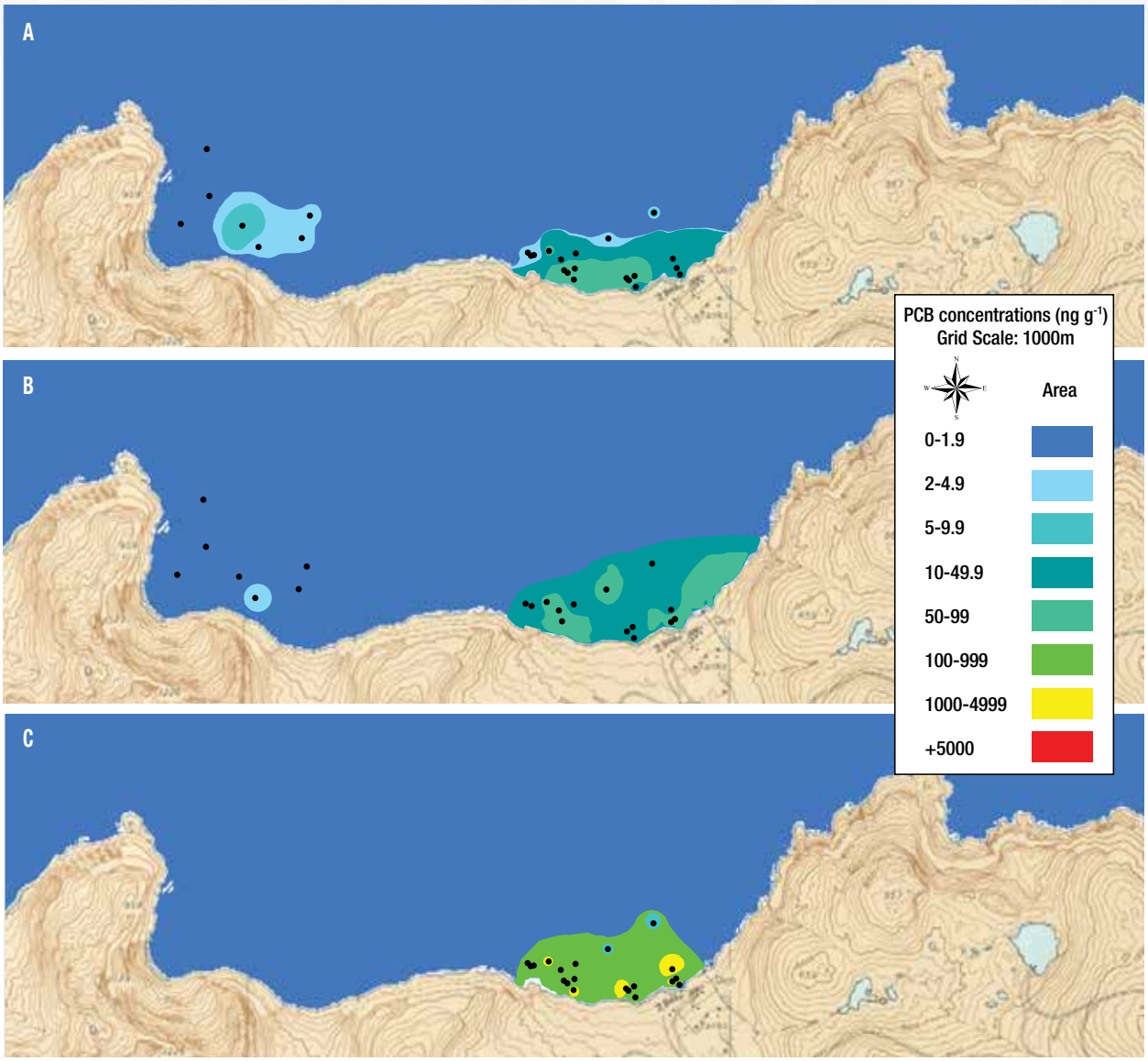

FIGURE 3.48

PCB contamination in marine surface sediments of Saglek: (A) 2011 PCB concentrations in surface sediments; (B) 2010 concentrations in surface sediments; (C) 2009 PCB concentrations in surface sediments.

3.5. Atmospheric Transport/ Deposition and Climate Change

Contributors: Jiamin Ma and Hayley Hung

3.5.1. Introduction

The atmosphere is one of the most efficient pathways of POP transport to the Arctic. Changes in POPs in arctic environments through atmospheric transport and deposition are determined by the interaction of primary and secondary emissions in source regions, wind field, precipitation rates, degradation and transformation, and partitioning. Climate change may affect primary emissions of POPs to air by changing their rate of mobilization from materials or stockpiles, or by altering use patterns, and secondary emissions through re-volatilization from secondary sources. The strength of these two sorts of emissions from low-mid latitudes, where both primary and secondary emissions take place, to the far north where secondary re-emission from reservoirs accumulated from the past is also a major emission type, determines the magnitude of POPs delivered to the Arctic via atmospheric transport. Climate warming occurring in low and mid latitudes may enhance POPs emission

and increase degradation. Higher vapour pressure alters partitioning between bulk phases (air vs. surface media such as soil, water and vegetation) and between the gaseous and particle-bound phases in air. As a result, stronger emissions from primary and secondary sources and a shift towards higher gaseous fractions in air may take place. All of these factors make POPs more available for long-range transport to the Arctic under favorable atmospheric conditions. Climate change may either increase or decrease precipitation which will enhance or reduce washout of POPs in air during their journey to the Arctic (UNEP/AMAP 2011; Kallenborn et al. 2012).

3.5.2. Climate indices and atmospheric circulation patterns

Atmospheric transport of POPs is strongly linked with wind flows and atmospheric circulation associated with inter-annual time-scale climate variation, or atmospheric circulations, notably the North Atlantic Oscillation (NAO), the El Niño-Southern Oscillation (ENSO), and the Arctic Oscillation (AO) in the Northern Hemisphere (Becker et al. 2008, Ma et al. 2004, Macdonald et al. 2005, MacLeod et al. 2005). The Arctic Oscillation has been demonstrated to be the most important atmospheric circulation pattern causing changes in winds, temperature, and sea-ice over the Arctic (Macdonald et al. 2005). Recent findings revealed that the arctic atmospheric Dipole Anomaly (DA) pattern, a local, second–leading mode of sea–level pressure anomaly in the Arctic, produced a strong meridional wind that drove more sea-ice out of the Arctic Ocean from the western to the eastern Arctic into the northern Atlantic during the summers of 1995, 1999, 2002, 2005, and 2007, corresponding to observed lower sea-ice extents (Wang et al. 2009). Anomalous changes in these atmospheric circulation modes alter the intensity and position of major meridional or longitudinal wind streams in the Northern Hemispheric atmosphere, thus enhancing meridional or pole-ward atmospheric transport depending on the phase of these climate variations. These large-scale atmospheric circulation patterns occur mostly during the wintertime. Therefore, atmospheric transport of POPs associated with the climate variations is strongest in this season. For legacy POPs, however, lower temperature during the wintertime may retard their re-emission from the secondary sources. This will lower their atmospheric level, so that the atmospheric transport of the legacy POPs become less significant during the cold season. Current knowledge revealed a positive correlation between POPs level in the arctic atmosphere and a positive mode of the NAO and AO (Becker et al. 2008, Ma et al. 2004). A recent modeling study for the numerical assessment of the cold trapping effect and LRAT of POPs to the Arctic simulated relatively lower atmospheric concentrations of lindane in 1998. This corresponds to stronger than normal atmospheric westerly flow across the Northern Hemisphere associated with the strong El Niño (positive phase of ENSO) event, that weakened the meridional air mass exchange between the Arctic and mid-low latitudes (Zhang et al. 2010). In contrast, the highest mean air concentration occurred in the spring of 1999 as the strong La Niña (the negative phase of ENSO) event took place and intensified the meridional atmospheric exchange.

In a composite analysis, the indices of the NAO, AO and ENSO from 1950 to 2001 were examined and selected for those years when the positive indices of NAO and AO and negative index of ENSO exceeded their respective standard deviation over this period, predicting the occurrence of NAO, AO and La Niña events. The annual meteorological data in the years when NAO, AO and La Niña events took place were averaged to obtain composite means. Figure 3.49 and Figure 3.50 display the vertical profiles of the composite anomalies of zonally-averaged annual air temperature (T, K) and meridional wind (v, m s^{-1}) over the course of the event years (indices > one standard deviation), as departures from their long-term means in the period of 1950–2001, respectively. As shown in the figures, negative temperature anomalies dominate low and mid-latitudes during the La Niña events (Figure 3.49 top panel), suggesting cooling in the Northern Hemisphere (Diaz et al. 2001, Ma et al. 2004). The air temperature anomalies during the positive phase of NAO and AO exhibit similar patterns, showing warmer conditions from mid to high latitudes (mid and bottom panel of Figure 3.49). Strong warming in the Arctic is also associated with the positive NAO. The similar pattern in the cross section of meridional wind anomalies is also evident in the positive phase of NAO and AO (mid and bottom panel of Figure 3.50). Stronger than normal southerly winds (v > 0) dominate relatively higher latitudes extending from 45°N to the Arctic. This wind pattern is particularly favorable

for the poleward LRAT from Eurasia where the major emission sources of POPs lie mostly north of 40°N (Breivik et al. 2007). However, for those POPs with emission sources south of 40°N, stronger northerly winds ($v < 0$) associated with the positive phase of NAO and AO would retard their poleward LRAT, especially for the AO (bottom panel, Figure 3.49). The La Niña events are also characterized by stronger southerly winds in the region extending from 45°N to 60°N which are, however, weaker than those during the positive phase of NAO and AO.

In addition to inter-annual changes, some of these climate variations (e.g., NAO and AO) also exhibit inter-decadal variation that has been linked to global warming (Hoerling et al. 2001). The association between POPs level in the atmosphere and these climate variations may likely contain a signature of the effect of decadal or longer time-scale climate change on their long-range atmospheric transport (Gao et al. 2010). The correlation of negative and positive phases of the AO to HCH concentrations was investigated in a recently published study (Becker et al. 2008). The Dynamic Harmonic Regression (DHR) model fit was applied on the respective datasets available for both stations Alert (NU) and Ny Ålesund (Svalbard/Norway) (Becker et al. 2008). A correlation to AO fluctuations was found in the α-HCH time-series at the Ny Ålesund monitoring site, but not at Alert.

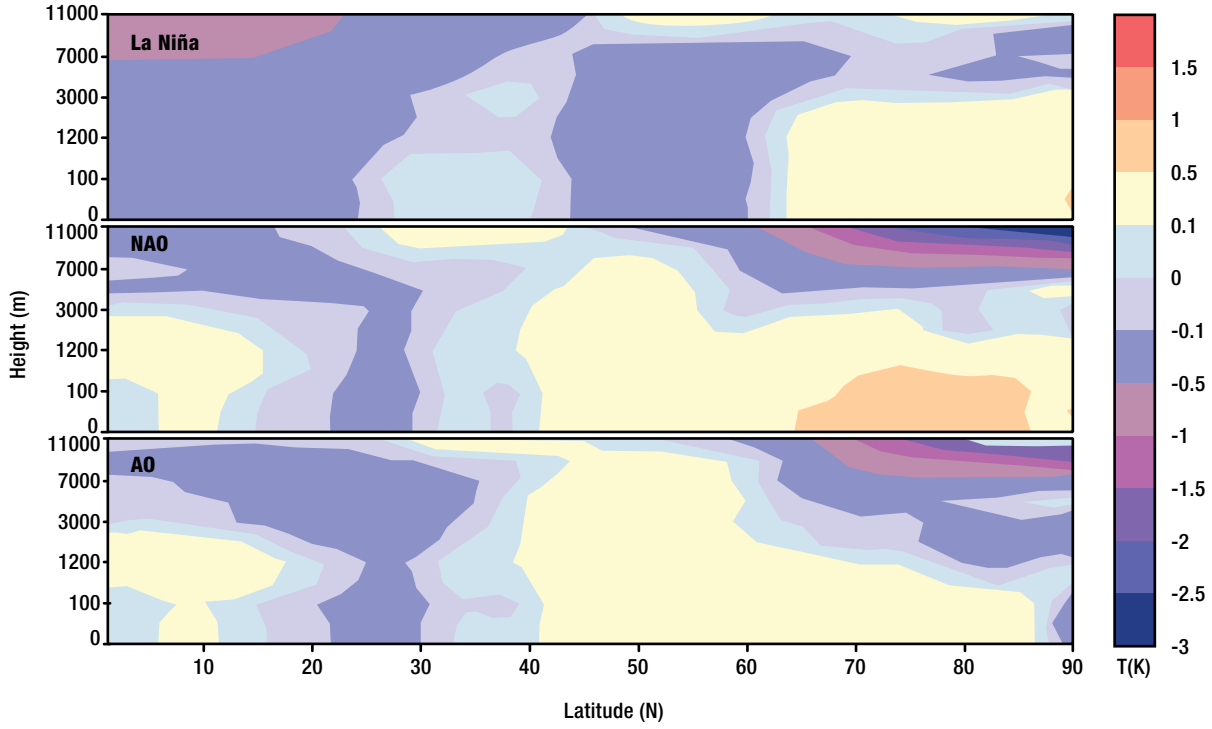

FIGURE 3.49

Vertical profile of composite anomalies of zonally-averaged annual air temperatures (T) averaged for those years when yearly indices of NAO, AO, and La Niña exceed their respective standard deviation from 1950–2001. The composite anomalies were obtained by considering the annual zonal-mean air temperatures for these years, summed to obtain composite mean temperatures which were then subtracted from mean temperature averaged over 1950 to 2001.

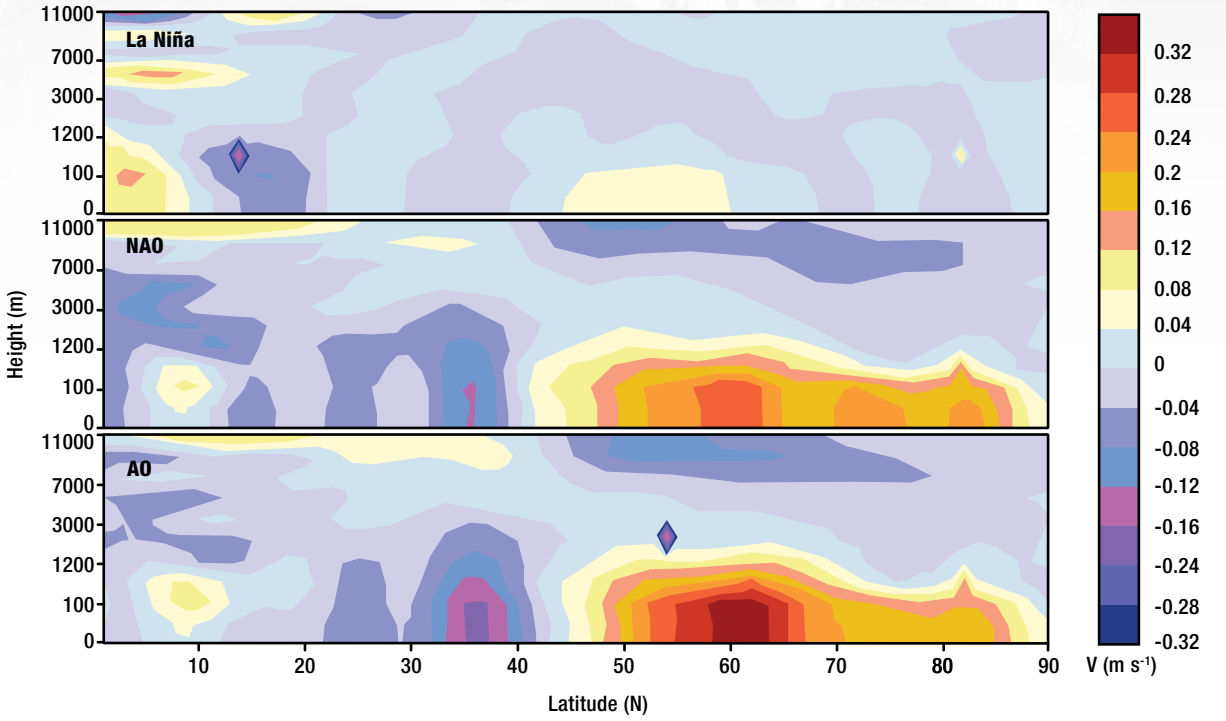

FIGURE 3.50

Vertical profile of composite anomalies of zonally-averaged annual meridional winds (m s^{-1}) averaged for those years when yearly indices of NAO, AO, and La Niña exceed their respective standard deviation from 1950–2001. Annual zonal-meridional winds for these years were summed to obtain composite meridional winds, which were then subtracted from mean meridional winds averaged over 1950 to 2001 to obtain composite anomalies.

The differences in intra-annual patterns indicate that much larger concentration variations between the summer and winter months are occurring during the years when AO is in a decadal scale negative phase, as during the 2000s. During positive AO years in the 1990s, the concentration difference between summer and winter is much less pronounced.

3.5.3. Influence of climate on atmospheric transport and deposition of POPs

Compared with inter-annual climate variability, there are more uncertainties and unknowns for the association between pole-ward atmospheric transport and deposition of POPs and climate change, when we refer to changes in air temperature and precipitation on decadal or longer time-scales. These uncertainties and unknowns are primarily due to (1) sparse air measurement data of POPs that are not long enough to illustrate signals of climate change in monitored temporal trends of air concentrations. (2) In the context of decadal or longer time-scale climate change, changes in magnitude and direction of global winds as a consequence of climate change are more difficult to assess because such changes are not readily measurable. (3) There are very limited measurements of POPs in multi-compartment environments (ocean, soil, ice and snow, permafrost) in the Arctic, making it difficult to precisely assess the exchange of POPs between these compartments and the spatial distribution of POPs across the Arctic. On the other hand, profound warming recorded during past several decades in the Arctic revealed that average annual temperatures in the Arctic have increased by approximately double the increase in average global temperatures (UCS 2011), especially in the 2000s during which arctic warming accelerated. This warming trend has led to stronger ice and snow melt and thawing permafrost, providing more open waters in Arctic Ocean where POPs accumulated in the past. The signature effect of this dramatic warming is likely contained in the relative short time series of measured POPs atmospheric concentrations. In this sense, POPs monitoring programs in the Arctic provide valuable data to fingerprint the impact of arctic warming (Arctic

amplification) on the environmental fate of POPs. Figure 3.51 shows the weekly time series of detrended (removal of an underlying upward or downward trend to present a normalized baseline view) γ-HCH from 1993–2007 at Ny Ålesund and Alert. The linear trends of weekly moving averaged mean air temperature and sea-ice concentration anomalies, normalized by their respective standard deviations and averaged over the Arctic, are also plotted. As seen from the figure, the detrended γ-HCH atmospheric concentrations at both monitoring sites underwent an increasing trend, corresponding nicely to an increasing trend of arctic mean air temperature and a decreasing trend of sea-ice concentration, especially since the late 1990s. This suggests the likelihood of the influence of arctic warming and ice melt on the atmospheric cycling of POPs and that the interdecadal warming and ice retreat trend in the Arctic is reflected in the residual (detrended) time series of γ-HCH. A detrended time series of other POPs (OCPs, PCBs, HCB) in air measured at the European Arctic site (Ny Ålesund) shows a similar increasing trend but such a trend was not significant in the residue time series of many other observed atmospheric POPs concentrations at the Alert (NU) site. Nevertheless, a similar increase was still observable in the detrended weekly *cis*-chlordane concentrations at Alert as compared to that at Ny Ålesund (Figure 3.52). Both series show an increasing trend from 2000 to 2007, corresponding again to a trend in arctic warming and declining sea-ice extents as shown in Figure 3.52.

It is recognized that factors other than climate change can lead to non-linearity on observed air concentrations (Roberts 2012). Given that there are only a limited number of arctic sites where air concentration measurements of POPs are available with relatively short time series (< 20 years) compared to climate change that spans decades, it is currently not possible to quantify the impact of any individual environmental factor (including climate change factors) which influence POP air concentrations in the Arctic.

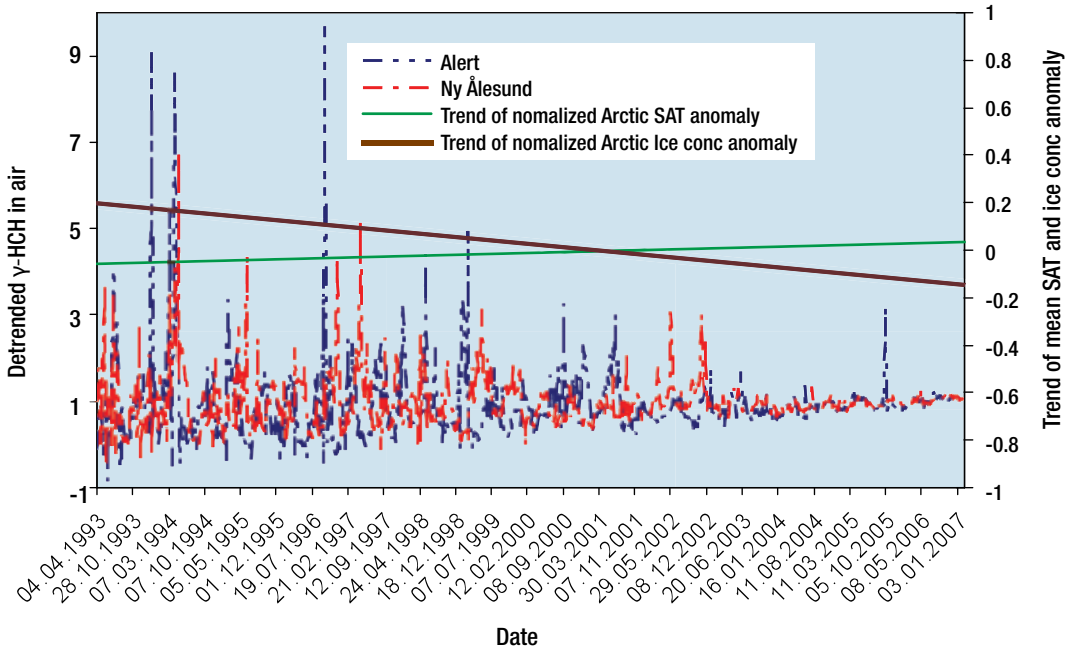

FIGURE 3.51

Detrended (residual) and normalized (by the standard deviation) time series of weekly sampled air concentration of γ-HCH at Alert (NU) (dashed blue line) and Ny Ålesund (Svalbard/Norway) (dashed red line) from 1993 through 2007. The linear trend of the normalized mean surface air temperature (SAT) anomaly (solid brown line) and the normalized mean ice concentration (solid green line) over the Arctic are also presented (Ma et al. 2011).

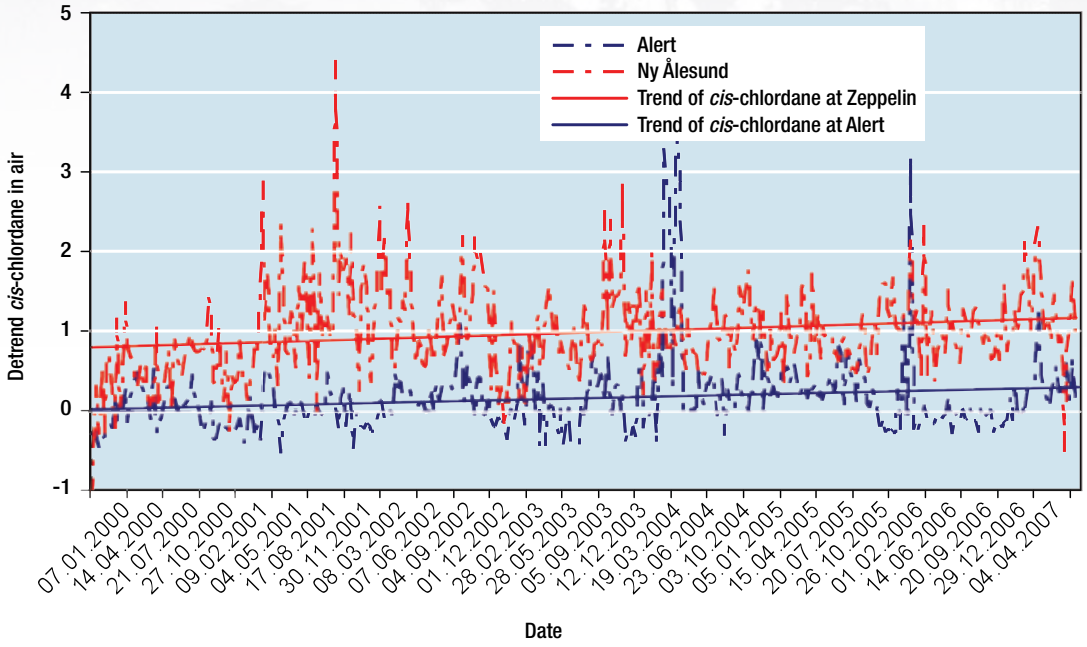

FIGURE 3.52

Detrended (residual) and normalized (by the standard deviation) time series of the weekly sampled air concentrations of *cis*-chlordane at Alert (NU) (dashed blue line) and Ny Ålesund (Svalbard/Norway) (dashed red line) from 1993 through 2007. The overall trends of *cis*-chlordane (solid lines) at these two sites are also shown in the figure.

3.5.4. Perturbation modeling to evaluate trends in atmospheric POPs

The mechanisms of arctic warming are complex, not well understood and not predicted consistently by global climate models. Previous studies have attributed arctic warming to various feedback mechanisms within the arctic climate system and the increase of air pollutants (ACIA 2005). There are also different predictions as to the magnitude of the arctic warming in the 21st century. Under the IPCC (Intergovernmental Panel on Climate Change) A1 and B2 emission scenarios (IPCC 2011) and the projected decline of sea-ice extent in the range of 1.4–3.9% per decade in winter and 4.8–22.2% per decade in summer, a global climate model has predicted an increase in the mean surface temperature of the Arctic ranging from 4–14 °C by the end of the 21st century, equivalently 0.04–0.14 °C y^{-1}. To examine the response of POPs in multi-compartments, through air-surface exchange and to projected increase in air temperature and precipitation (Ma and Cao 2010) under arctic warming, a perturbation model was applied to numerically evaluate the fluctuations of POPs in arctic environments induced by selected arctic warming scenarios. This perturbation model was developed based on a two-box model in air and surface media (soil, water, snow and ice). In the model, the concentration of POPs in air and surface compartments (soil, water, snow) is the sum of a mean concentration and a perturbed concentration due to climate change

$$c = \bar{c} + c' \qquad \text{Eq. 19}$$

where $\bar{c}$ is the mean or time averaging concentration of POPs and c' is the deviation from the mean, induced by climate change (Ma and Cao 2010). This modeling study projects the increase of perturbed air temperature by arctic warming from 2 °C/100 y to 10 °C/100 y by end of the 21st century into the model, respectively. The model does not account for the effect of the change in winds on POPs environmental fate but only deals with POPs in a closed two-compartment system in which wind speed is taken as a constant. Its focus on the summer season (June to August), during which arctic atmosphere is seldom affected by outside influences and thus leading to weak long-range atmospheric transport, generates the lowest input of POPs to the Arctic from their sources in lower and mid-latitudes under summer atmospheric circulations (Zhang et al. 2008). In the summertime and September, arctic ice and snow melting are also strongest. Figure 3.53 presents modeled perturbations of PCB-52 and

PCB-153 in air in the closed air-water system over a period of 70 years. Compared with the mean air concentration of PCB-52 at 1 pg m^{-3} and PCB-153 at 0.4 pg m^{-3} derived from measured data over the period of 1993 through 2007 at Alert (NU), modeled maximum perturbations of PCB-52 and 153 are approximately 0.08 and 0.012 pg m^{-3} in the warming scenario of 10°C/100 y. The results suggest that this warming scenario could result in 8% and 3% increases in PCB-52 and PCB-153, respectively, through air-water exchange or re-volatilization from arctic waters in summer conditions. The perturbation of the more hydrophobic PCB-153 incurred by arctic warming exhibits much slower declining rate throughout the 70 year period as compared with PCB-52.

A recent study has revealed that arctic warming may push the zonal jet stream, a narrow, strong air current across the Northern Hemisphere, farther south. However, this mostly occurs in the wintertime and it is yet unclear if this change in the jet stream associated with arctic warming would increase or decrease pole-ward atmospheric transport of POPs. In general, the direct effect of inter-decadal or longer time scale climate change and arctic warming on large-scale wind fields is not clear yet. Although the link between climate change induced winds and atmospheric transport is difficult to assess precisely, it is expected that climate change could substantially affect the long-range transport potential (LRTP) (Beyer et al. 2000) or arctic contamination potential (ACP) (Meyer and Wania 2007, Wania 2003, 2006) of POPs.

LRTP is a main criterion for evaluating the ability of POPs to be transported on the hemispheric and global scale. Persistence of chemicals in environmental media such as water or soil leads to the potential for these substances to undergo multi-hop transport. The LRTP (characteristic travel distance) of POPs is determined not only by winds but also by residence time in air and surface compartments, and the ability to undergo re-volatilization and partitioning from

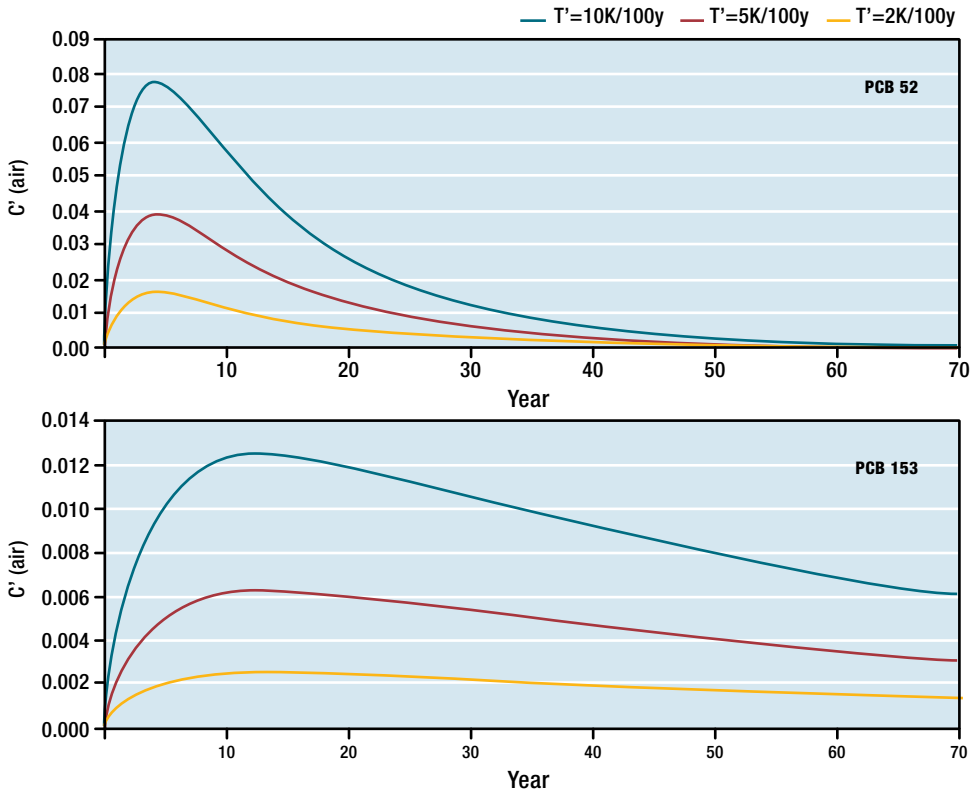

FIGURE 3.53

Modeled perturbations of air concentrations of PCB-52 and -153 under different arctic warming scenarios at 10K/100 y, 5K/100 y, and 2K/100 y (perturbed air temperature) for a 70 year period in the closed air-water system. Mean summer air temperature over the arctic is 276 K and mean air concentrations of PCB-52 and PCB-153 are 1 pg m^{-3} and 0.4 pg m^{-3}, respectively.

surface media to the atmosphere. These metrics for LRTP are all influenced by air temperature and precipitation (Beyer et al. 2000) and hence climate change. Likewise, as a numerical indicator of an organic chemical's potential to be transported to polar latitudes and to accumulate in the arctic ecosystem, the ACP is also calculated based on chemical-physical properties (e.g., log K_{OW} and log K_{OA}) of POPs depending on air temperatures and precipitation. It can be deduced that a warming atmosphere would increase the LRTP and ACP of POPs because warming generally favours the vapour phase and, therefore, atmospheric transport.

Exchange and partitioning of POPs between different environmental media and different phases are other key factors influencing atmospheric transport and deposition. Arctic warming likely increases volatilization of POPs from their reservoirs in water, snow, ice, and land where they have accumulated in the past. Consequently, this will result in an increase in air concentration of POPs. Although many POPs measured in the arctic atmosphere have been undergoing a declining trend, arctic warming likely slows down the removal of POPs from the arctic atmosphere. There is a likelihood of a "climate driven residence time" that significantly increases the atmospheric half-life of POPs in the Arctic. Using weekly sample γ-HCH air concentrations at Alert (NU), estimated apparent half-life ($t_{1/2}$ = *ln 2/slope*) of the chemical from 1993–1999 is 3.46 year whereas the apparent half-life extends to 9.52 year from 2000–2007 when arctic warming and ice retreat sped up. Slower declining of POPs air concentrations under warming conditions can also be illustrated by examining the time trend of perturbed and mean air concentrations. Figure 3.54 shows such time trends for $\bar{c}$ and c' of HCB for a 70 year period generated under the perturbed temperature conditions of T'=5 K/100 y with the mean air temperature $\overline{T}$=276.2 K. While perturbed concentration c' declines slowly after reaching its maximum, the mean air concentration $\bar{c}$ decreases more rapidly to zero in about 40 years, despite the latters' one order of magnitude higher initial concentration. After the mean concentration becomes zero, the predicted air concentrations $c = \bar{c} + c'$ would be determined solely by perturbed air concentration c' induced by arctic warming.

3.5.5. Evidence for enhanced atmospheric transport of POPs

Eckhardt et al. (2007) have attributed high air concentrations of PCBs measured at Ny Ålesund in July 2004 and spring 2006 to boreal forest fires in Yukon and Alaska, and agricultural fires in Eastern Europe, respectively. Several high air concentration episodes of *cis*-chlordane, *p,p'*- and *o,p'*-DDE were also observed at Alert and Ny Ålesund in 2004 during the forest fire events

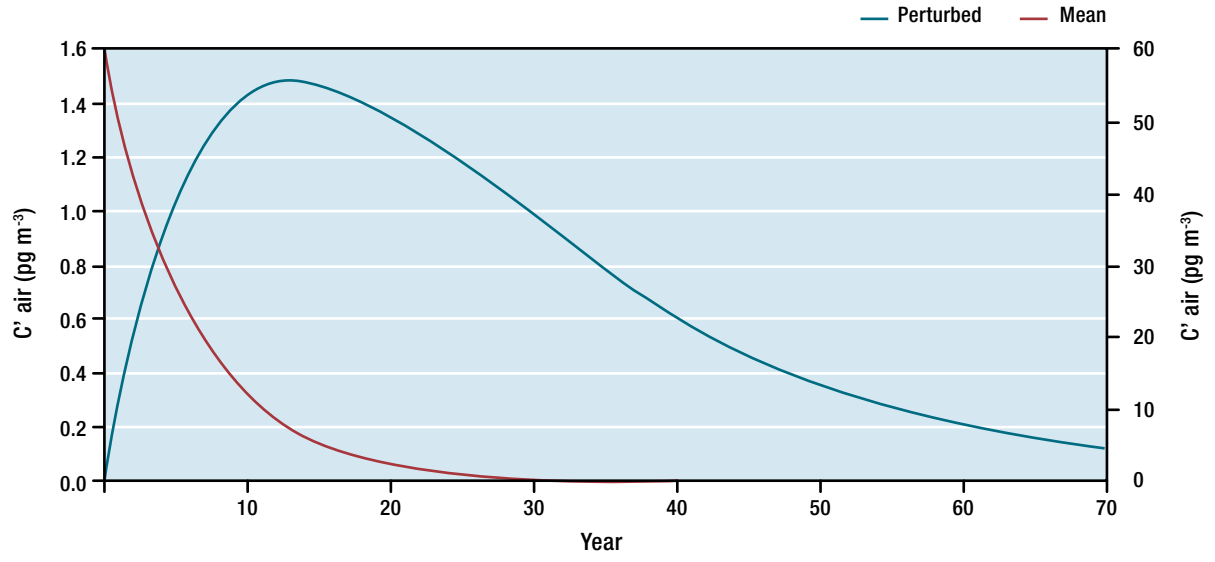

FIGURE 3.54

Mean (C) (scaled on right y-axis) and modeled concentration perturbation (C') (scaled on left y-axis) of HCB air concentration under same mean degradation rate constant computed using same mean air temperature of 273.2 K in the Arctic. Perturbed air temperature is taken as 0.05 K y^{-1} (5 K/100 y).

(Hung et al. 2010). Sofowote et al. (2011) examined PAHs air concentrations measured at a subarctic site in Yukon, Canada and traced higher concentrations in August 2008 to strong wildfires that burned in California during the fall of 2008. In addition to direct emissions of some compounds during biomass burning (e.g., PAHs). It is believed that biomass burning can enhance the volatilization of previously deposited organic chemicals, such as PCBs, from soil (Eckhardt et al. 2007; Genualdi et al. 2009). Increasing frequency of extreme climate events with global warming poses another challenge to understanding the relationship between climate and POPs environmental fate in the Arctic. For instance, forest fires are projected to increase with climate warming, releasing more contaminants into air and terrestrial surfaces.

3.5.6. Enhanced ocean-atmosphere exchange

Oceans and rivers provide another important pathway for input and output of POPs into the arctic ecosystem. Oceanic transport of POPs is associated primarily with ocean currents, exchange with the atmosphere via gas exchange and deposition, and riverine inputs. In the context of climate change, concern is for increase in wet deposition, as discussed in section 3.5.2. Oceanic transport applies essentially to water soluble chemicals. β-HCH is a typical example for such transport.

Differing from α-HCH loading to the Arctic Ocean through atmospheric transport and deposition, β-HCH enters the western Arctic through ocean currents passing through the Bering Strait (Li et al. 2002). Although the presence of neutral and ionic PFASs at Alert (NU) supports their atmospheric long-range transport, fluorinated contaminants such as PFOA and PFCAs are likely to be delivered to the Arctic mainly by oceanic pathway due to their low volatility. The high level of these fluorinated chemicals with strong water solubility in the arctic marine environment and wildlife has been attributed to their transport through ocean currents directly from their emission sources.

An atmospheric transport model for POPs, the Canadian Model for Environmental Transport of Organochlorine Pesticides (CanMETOP) (Ma et al. 2003), was used to simulate water-air exchange of α-HCH over the Arctic Ocean in two designated modeling scenarios. The first model scenario uses annual mean ice concentrations averaged from 1969 through 2003 and the second scenario accounts for daily ice concentrations in 2007, during which arctic sea-ice experienced the strongest retreat over the last several decades.

Figure 3.55 shows the CanMETOP modeled difference of α-HCH air-water exchange fluxes (ng m^{-2}) across the Arctic Ocean from two modeling scenarios for 2007 (fluxes from the second scenario

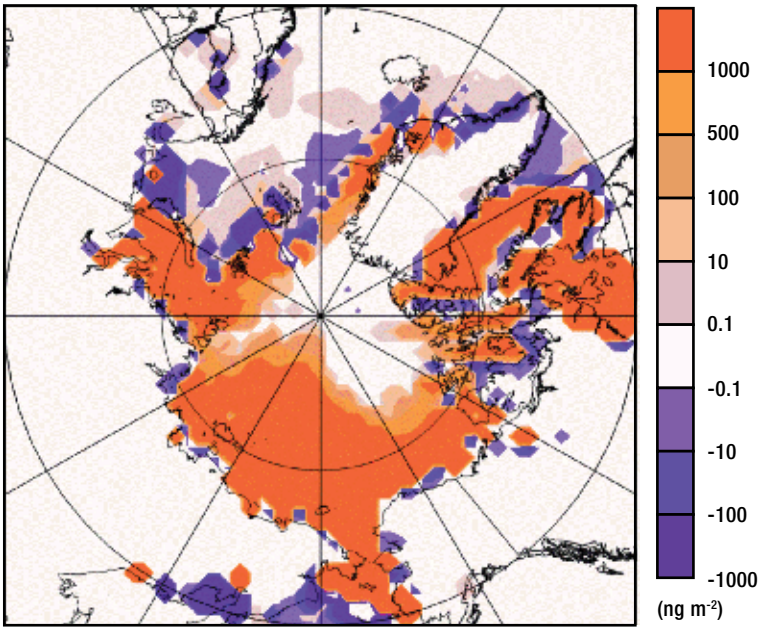

FIGURE 3.55

CanMETOP modeled difference of α-HCH air-water exchange fluxes (ng m^{-2}) across the Arctic Ocean from two modeling scenarios for 2007. The results were calculated by considering the fluxes using summer meteorology and ice concentrations averaged over 1969–2003 minus the fluxes using daily summer meteorology and ice concentrations in 2007.

minus those from the first model scenario). This can be also be termed as air-water exchange flux anomalies in 2007 against the fluxes under mean ice concentrations. Positive values indicate evaporation from ocean waters and negative values indicate deposition. It is known that a sink to source reversal of α-HCH in the Arctic Ocean occurred in the early 1990s and since then the re-volatilization of the compound from water to air has been observed in many places of the Arctic Ocean (Bidleman et al. 1995; Wania et al. 1999; Jantunen et al. 2008; Wong et al. 2011). Higher air temperatures favor aqueous phase to gas phase partitioning of α-HCH. This leads to stronger re-volatilization of the compound from water to air. Higher upward fluxes, showing evaporation from seawater to air, can be found from the East Siberia Sea to the Canadian Archipelago. The lowest water concentration of HCHs in the eastern Arctic Ocean suggests that this part of the Arctic Ocean is not a major source of α-HCH in the atmosphere.

Figure 3.56 shows the January–July 2007 accumulated thawing degree-days anomaly (left panel) and the July 2007 sea-ice concentration anomaly (right panel) (GWS 2010). These anomalies resulted from the influx of warm Pacific water from the Bering Sea. The route of heat flux of the Pacific Ocean entering the Arctic Ocean has also been identified as a potential pathway of α- and β-HCH from East Asian sources to the Arctic through both air and ocean (Ding et al. 2007, Li et al. 2002), and to the Chukchi Sea. The modeled α-HCH air-water flux anomalies in 2007 correspond well to the sea-ice concentration and accumulated thawing degree-days anomalies for the same year. The spatial pattern of the exchange fluxes also correspond to measured water and surface air temperatures across the Arctic Ocean. This suggests that the input heat flux from the Pacific Ocean to the Arctic Ocean through the Bering Strait, warmer temperature, and sea-ice retreat interact to contribute to the transfer of the chemical from ocean waters to air, and is observed in the region extending from East Siberia Sea to Beaufort Sea, as shown in Figure 3.56.

3.5.7. Ice cap, precipitation, snow

One of the most dynamic changes to the globe in recent decades has been the rapid decline of arctic sea-ice. Climate warming in the Arctic will reduce ice and snow cover. The decline of sea-ice is in turn amplifying warming in the Arctic, which has major implications for temperature patterns over adjacent, permafrost-dominated land areas and for weather patterns across the Northern Hemisphere. Reduced ice extents will provide more open water in the Arctic Ocean, exposing a greater area of the ocean to the heat of the sun and driving more warming for the entire planet. Wind and water currents are being affected, causing unstable climatic conditions and extreme weather. This will in turn affect atmospheric and oceanic transport of POPs (sections 3.5.1 and 3.5.2). The increased area of open waters also enhance the release of POPs as elaborated in section 3.5.2 (Figure 3.56), remobilizing them into the atmosphere for redistribution. In the case of chemicals which are predicted to undergo net gas-phase deposition to the Arctic Ocean, the arctic warming and loss of ice cover will likely lead to

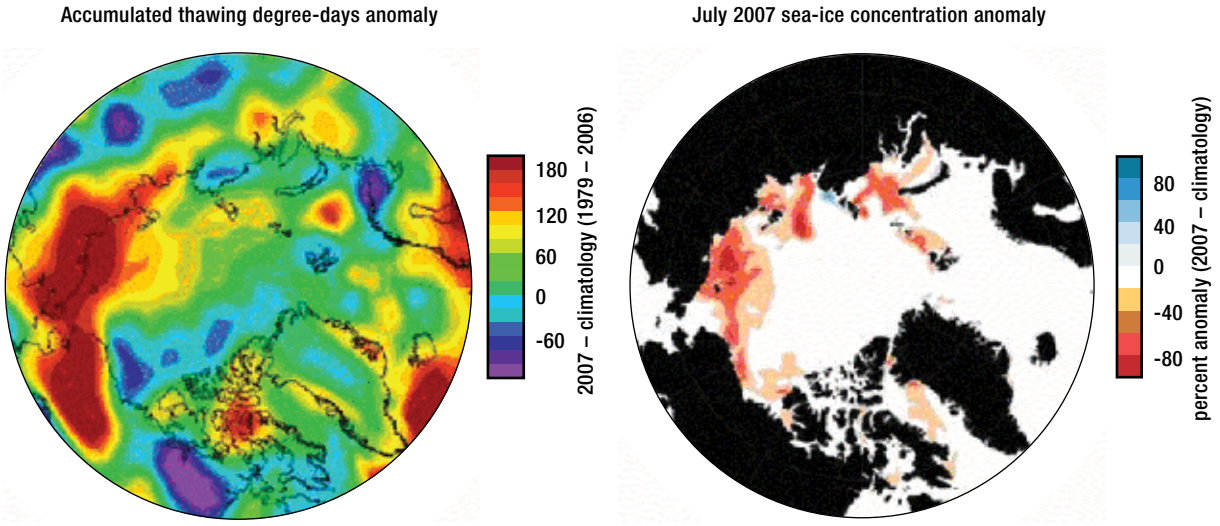

FIGURE 3.56

Accumulated degree-days anomaly over January–July 2007 (left panel) and sea-ice concentration anomaly in July 2007 (right panel).

a reversal from deposition to volatilization. Melting ice can also impact the nutrients in the water column, affecting primary productivity. Biological processes in the water column affect the gas exchange of POPs through sorption of settling particles. Plankton blooms can deplete dissolved phase PCBs, especially the more hydrophobic ones, and alter gas exchange fluxes (Dachs et al. 1999, Gioia et al. 2008). With higher temperatures, more wintertime polynyas will be present leading to an increase in sea fog, which scavenges and deposits POPs in areas known to be important for biota (Macdonald et al. 2005).

Due to its potential for chemical scavenging and exchange with the lower atmosphere, snow notably influences the transport dynamics of POPs in the Northern Hemisphere. A change in the extent of snow cover brought about by a changing climate may affect the global fate of POPs (Macdonald et al. 2003, Stocker et al. 2007). Falling snow is highly efficient at scavenging both vapour and particle-bound POPs from the atmosphere. Vapour scavenging is a function of the air temperature as well as the specific surface area (SSA) of the snow. It is predicted to be most pronounced for snow possessing high SSA (e.g., 1 m^2 g^{-1}) and at cold temperatures (< -10 °C), resulting in scavenging ratios for semi-volatile chemicals being generally higher than rain by over an order of magnitude (Lei and Wania 2004). The seasonal snowpack, therefore, serves as a repository for chemicals transported to higher altitudes-latitudes with observed concentrations reported for a number of different POPs in both mountain and arctic snow (Blais et al. 1998, Herbert et al. 2006).

The snowpack is a highly dynamic compartment with regards to chemical exchange with the lower atmosphere. Substantial re-emission of POPs is observed during snow ageing and compaction following fresh snowfall (Herbert et al. 2005a), thereby amplifying atmospheric levels of POPs.

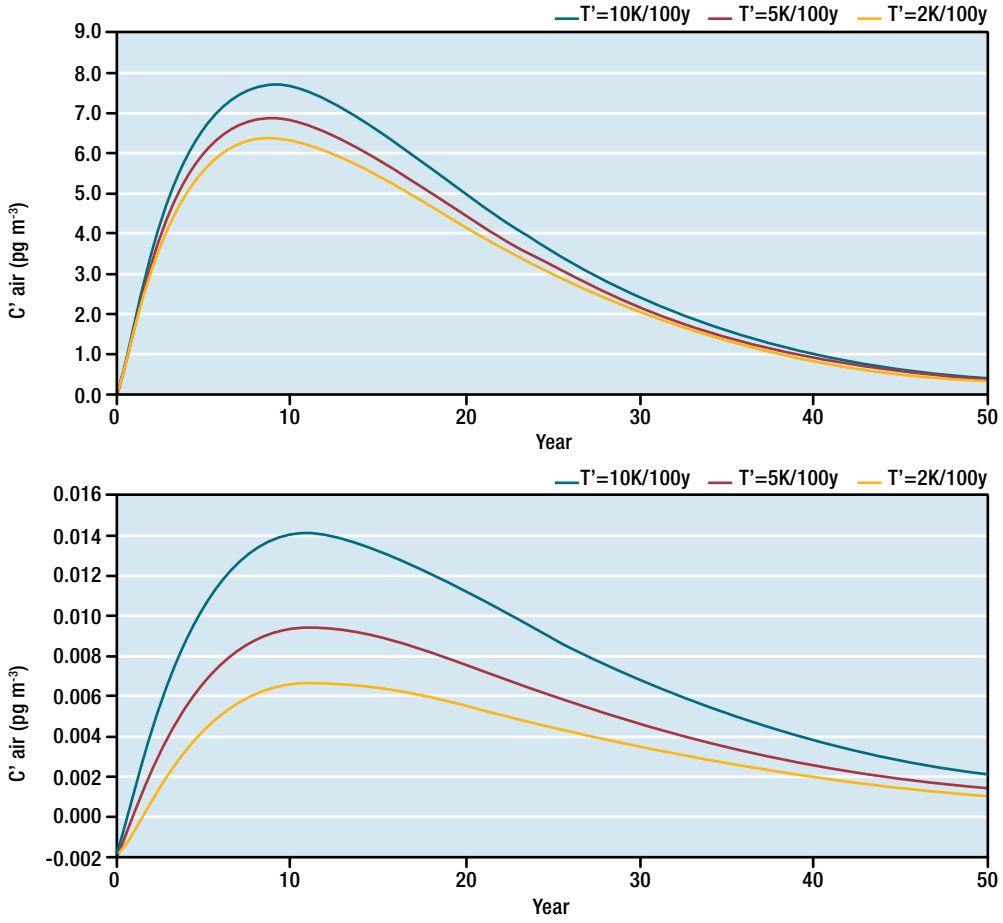

FIGURE 3.57

Modeled perturbation of air concentrations (pg m^{-3}) of α-HCH (upper panel) and PCB-28 (bottom panel) under different arctic warming scenarios at 10 K/100 y, 5 K/100 y, and 2K/100 y for a 50 year period in the closed air-snow system. Mean temperature is taken as 273.19K, air and snow concentrations for α-HCH are 32 pg m^{-3} and 5 ng m^{-3}, and for PCB-28 1.5 pg m^{-3} and 0.06 ng m^{-3}, respectively. The decline of perturbed concentrations after the maximum is due to degradation of the mean concentrations in air and snow subject to mean temperature.

Furthermore, fresh snowfall and diffusive vapour exchange are processes which will add or remove chemicals to the standing snowpack. Figure 3.57 presents perturbed air concentrations of α-HCH and PCB-52, derived from the perturbation model (Ma and Cao 2010), for a period of 50 years under three arctic warming scenarios at perturbed air temperatures of 10 K, 5 K and 2 K/100 y in the closed air-snow system. Model inputs of mean concentrations in air, snow and surface air temperature are given in the figure captions. With mean air temperature of 0.04 °C from May–September in the Arctic, these warming scenarios result in a marked increase in modeled air concentration perturbations for both toxic chemicals due to their release from snowpack. Compared with mean air concentration of α-HCH at 32 pg m^{-3} used in the perturbation modeling, the perturbed air concentration is as high as 8 pg m^{-3}, only a factor of 4 lower than the mean estimated with the arctic warming scenario 10 K/100 y, suggesting a strong release from contaminated arctic snowpack (with mean concentration in snow at 5 ng L^{-1}) (Hansen et al. 2008b, Meyer and Wania 2007). In other words, α-HCH concentration in the atmosphere could increase up to 20–25% due to air-snow exchange under selected arctic warming scenarios. In the case of PCB-52, the arctic warming scenario at 0.1 K y^{-1} (10 K/100 y) leads to a maximum concentration perturbation of 0.014 pg m^{-3}, which is a factor of two greater than that derived from the warming scenario at 0.02 K y^{-1}.

A warmer atmosphere will lead to increased evaporation and hence to increased precipitation. Changes in precipitation associated with arctic climate change may cause wetter conditions in some places and drier conditions in others across the Arctic. For the Canadian Arctic, annual precipitation rates collected from the NECP/NCAR reanalysis exhibit an increasing trend from 1970 to 2010 (Figure 3.58). Climate models have predicted about a 20% increase in annual total precipitation over the Arctic as a whole by the end of 21st century, with most of the increase coming as rain (ACIA 2004). In the Canadian Arctic, NCEP data that were re-analyzed shows a 10% increase in the mean annual precipitation rate in the 2000s (2000–2010) as compared with that from 1948–1999. This will increase loadings of chemicals to the Canadian Arctic directly through washout and indirectly through river runoff, but, on the other hand, decrease the POPs level in the atmosphere. After examining the sensitivity of POPs to changes in precipitation in the Arctic, Meyer and Wania (2007) found that a 10% change in rain could result in about 5% change in HCHs deposition. Figure 3.59 displays the perturbation model (Ma and Cao 2010) simulated γ-HCH perturbations in air in the arctic environment with an annual mean surface air temperature of 260.7 K and a mean annual precipitation of 250 mm y^{-1} for the Canadian Arctic. Changes in perturbed concentrations in the closed air-water system are forced by the interaction of the mean air temperature and precipitation, degraded mean concentrations subject to the mean air temperature, the arctic warming scenario of 5 K/100 y, and

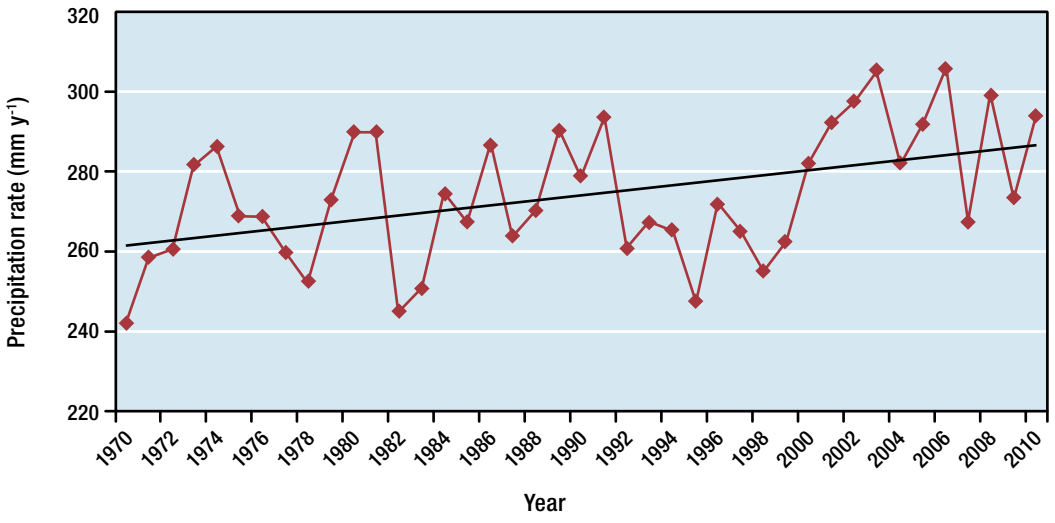

FIGURE 3.58

Annual mean precipitation rate (mm y^{-1}) averaged over the Canadian Arctic using NCEP/NCAR reanalysis data, retrieved from http://www.esrl.noaa.gov/psd/cgi-bin/data/timeseries/timeseries1.pl.

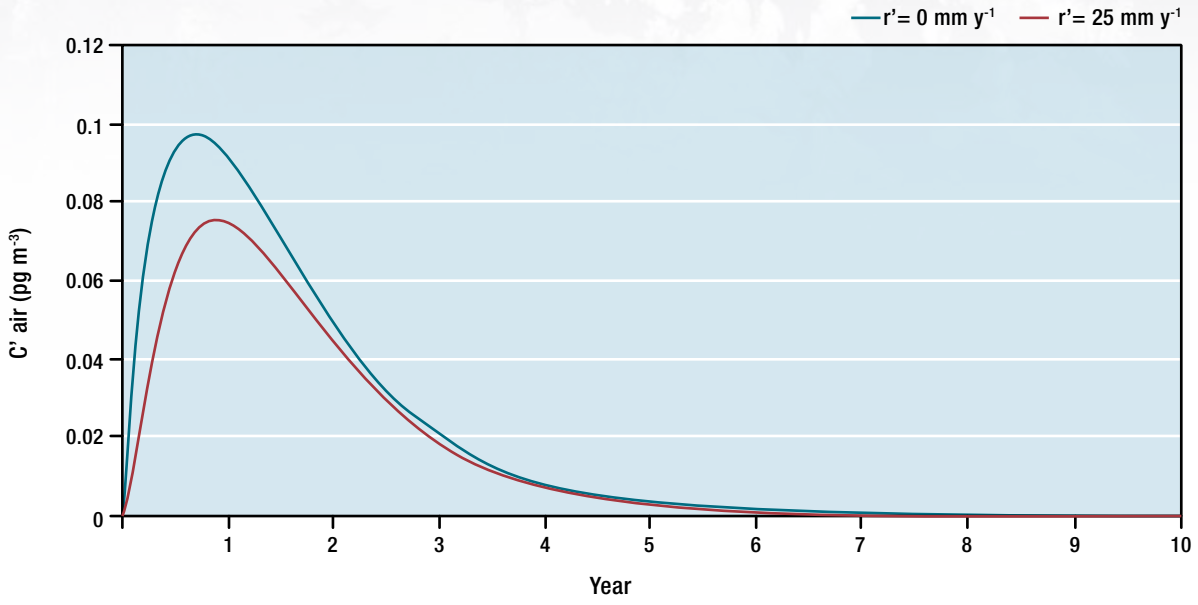

FIGURE 3.59

Modeled perturbation of γ-HCH in air for a 10 year period in a closed air-water system in the Arctic. Annual mean air temperature and precipitation are 260.7 K and 250 mm y^{-1}, respectively. Perturbed air temperature due to arctic warming is 5 K/100 y and perturbed precipitations are 0 (blue line) and 25 mm y^{-1} (red line). Mean concentrations in air and water are 12 pg m^{-3} and 2 ng L^{-1}, respectively. The decline of perturbed concentrations after the maximum is due to degradation of the mean air concentration in air and water, subject to mean temperature.

an increased precipitation of 10% (precipitation perturbation of 25 mm y^{-1}). Compared with the model scenario with zero precipitation perturbation, the increase of 10% precipitation yields a maximum 23% decrease in perturbed air concentration for a 10 year period.

3.5.8. Assessment

- There is evidence from atmospheric monitoring that biomass burning enhanced transport of compounds (e.g., PAHs) and also of previously deposited POPs volatilized by burning.
- A warmer and wetter Arctic, predicted by climate models will likely lead to changes in the geographic pattern of POPs deposition as arctic climate change causes wetter conditions in some places and drier conditions in other places.
- Reduced ice extents will provide more open water in the Arctic Ocean and is another major factor which will likely influence the dynamics of POPs in the Arctic.
- Modeling suggests that greater open water as well as warmer waters are interacting to contribute to the transfer α–HCH from ocean waters to air.
- Biological processes in the water column that are stimulated by greater sunlight and warming, such as algal blooms, may affect the gas exchange of POPs through sorption to settling particles.
- Pertubation modeling has been used to assess the impact of warming trends. The model assumes that the POPs air concentration is the sum of a mean concentration and perturbed concentration due to climate change.
- The detrended data for γ-HCH atmospheric concentrations suggests that it underwent an increasing trend, corresponding nicely to an increasing trend of arctic mean air temperature and a decreasing trend of sea-ice concentration, especially since the late 1990s.
- Factors other than climate change can lead to non-linearity in observed air concentrations and thus the perturbation modeling approach needs further confirmation.

3.6. Biovector Transport of Contaminants

Contributors: Karen Foster and Jules Blais

3.6.1. Introduction

Biological vectors (biovectors) for contaminants have only received scant attention; however there is mounting evidence that biovectors can play an important role in contaminant transport, fate, and accumulation, particularly in northern environments remote from local point sources. Biovector transport has been defined as a focusing of contaminants, often marine-derived, into a particular location or receptor site via mass migration of congruous animals, a process which follows three crucial stages: (1) collection and concentration (e.g., via bioaccumulation, bioconcentration and/or biomagnifications) of the contaminant by an organism such as a seabird or anadromous salmon from a broadly diluted medium such as the ocean; (2) transport of the contaminant in the body of the migratory animals to a receptor site (e.g., seabirds returning to their coastal nesting site, or anadromous salmon returning to their natal spawning lake or stream); and (3) deposition, release or transfer of the contaminant to the receptor site where it is incorporated into local environmental media and food webs (Figure 3.60).

Thus, in principle, any organism that accumulates contaminants and relocates or focuses them into a particular region constitutes a biovector. Congruous animals, such as seabirds or anadromous fish, have been found to be particularly effective biovectors and are highlighted here.

From left to right in Figure 3.60, contaminant emissions are released into the environment from industrial, municipal and agricultural regions where they begin to circulate globally via the abiotic processes of distillation and grasshopping. Some of these contaminants are loaded into the ocean by processes such as atmospheric deposition or runoff where they become diluted and widely distributed in the upper ocean through exchange, wet and dry deposition, advection and mixing. Partitioning into the bottom of the food chain followed by biomagnification up the food chain constitute the collection phase of contaminants (e.g., PCB, DDT, toxaphene, methyl mercury) into animals (e.g., fish, birds) that forage at sea. Migratory animals then transport and focus these contaminants, sometimes over long distances, to locations where they congregate in large numbers (e.g., spawning rivers, hatcheries, seabird nesting sites). Once there, they deposit some or all of their contaminant burden in their excreta, feathers or carcasses (Blais et al. 2007).

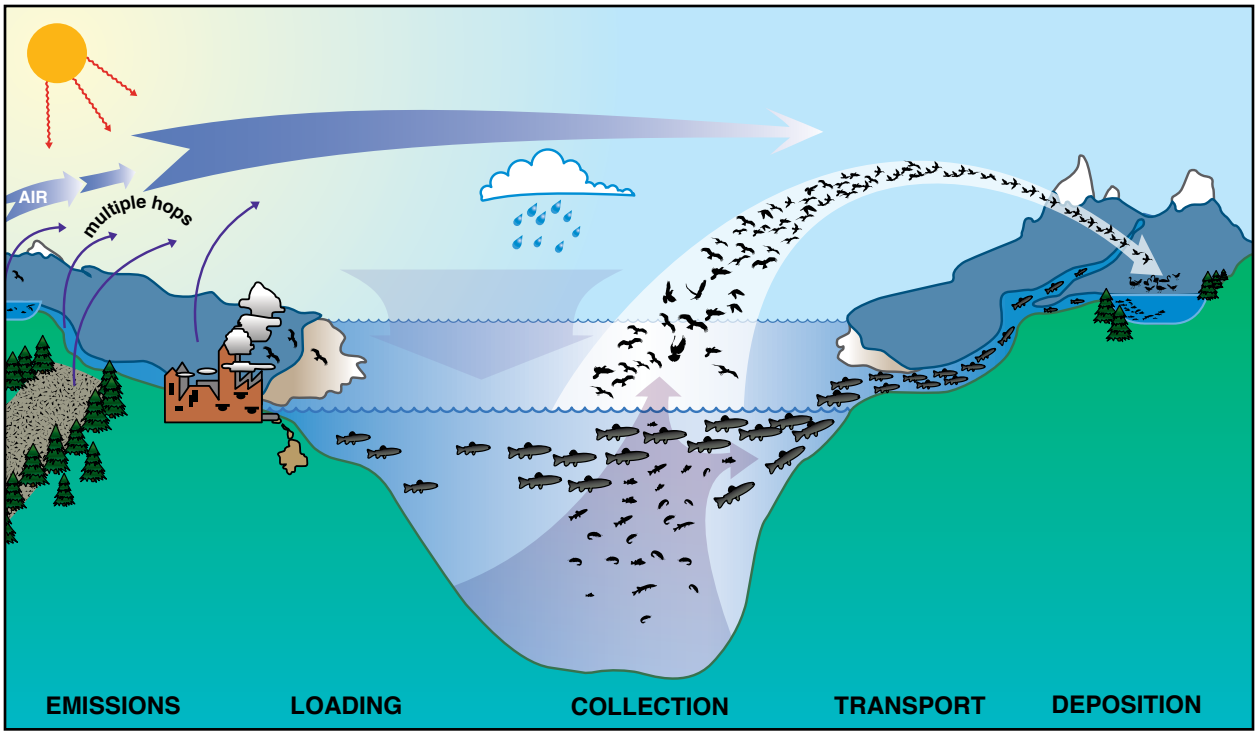

FIGURE 3.60

The critical stages to biovector transport (based on Blais et al. 2007).

3.6.2. Seabird biovectors

Seabirds are thought to accumulate contaminants from the prey items collected across their broad marine foraging range. They transport, and deposit these contaminants at their coastal nesting sites in seabird media such as excreta, feathers and carcasses (Blais et al. 2007). In this way, seabirds efficiently focus marine-derived contaminants, which may have already undergone bioaccumulation and biomagnification at previous rungs in the food chain, into coastal receptor sites near their colonies. To put the process of seabird biological vectors of contaminants into a global context, seabirds consume 70 million tonne y^{-1} of marine-derived food (Brooke 2004b). This food has an associated amount of contaminants —a portion of which is transferred to the landscape at the nesting sites in seabird media. Indeed, seabird colonies have been shown to elevate local environmental concentrations of contaminants in the West Indies and the Antarctic (Klekowski et al. 1999, Roosens et al. 2007). However, seabirds are a contaminant vector to which remote arctic ecosystems are particularly sensitive given the extensive coastline in the Arctic and the large number of seabirds that nest there. In the Canadian Arctic there are an estimated 10 million breeding pairs of seabirds (Mallory and Fontaine 2004). Local food webs are particularly vulnerable as seabirds also provide much needed marine-derived nutrients to the impoverished arctic coastline, they support a range of biota from lush, green "ornithogenic vegetation", to insects, terrestrial birds and mammals like arctic fox, lemmings and ermine,. Thus, seabird biovectors may be particularly relevant to contaminant fate, accumulation, and terrestrial food web exposure in arctic coastal regions.

Lake Ellasjøen, on Bjørnøya (Bear Island) in the Norwegian Arctic, is host to a number of colonies of different seabird species, including little auk, black-legged kittiwake and glaucous gulls (*Alle alle, Rissa tridactyla* and *Larus hyperboreus*, respectively), and was found to have sediment concentrations of ΣPCBs and *p,p'*-DDE that were 13 and 14 times higher, respectively, than that of Øyangen, a comparable nearby lake with no seabirds (Evenset et al. 2004). Similar trends were seen for a number of other organochlorine contaminants including some chlordanes and hexachlorocyclohexanes. Using a mass balance approach based on measured concentrations in abiotic sources of contaminants (e.g., in rain and snow), as well as in seabird guano, and using environmental variables (e.g., average annual precipitation rates, water retention times in the lakes, etc.), it was determined that approximately 80% of the total influx of PCBs to Lake Ellasjøen was seabird-derived (Evenset et al. 2007a). Patterns of PCB congeners in water and organisms from Lake Ellasjøen were also more similar to those patterns in seabird guano, than were seen in Lake Øyangen. Down-core sediment profiles from both lakes were used to assess the historical delivery of metals as well as PCB, DDT and PBDE contaminants to both lakes (Evenset et al. 2007b).

In the Canadian High Arctic, a large colony of northern fulmars (*Fulmarus glacialis*) nesting at Cape Vera on Devon Island has been shown to elevate concentrations of metals and organochlorine contaminants in the sediments of nearby freshwater ponds in a consistent fashion with increasing fulmar inputs. A survey of surface sediment concentrations from eleven ponds, found that with increasing seabird inputs, which was inferred from the stable isotope ratio $\delta^{15}N$ in sediments, concentrations of hexachlorobenzene, total mercury and ΣDDT increased in ponds receiving the most seabird inputs having concentrations 10-, 25- and 60-fold higher, respectively, than those with the least (Blais et al. 2005). Total mercury concentrations in ponds receiving the most seabird inputs approached or exceeded Canadian environmental quality guidelines for protecting wildlife. The study also noted higher DDE/DDT ratios in sediments from the ponds receiving the most seabird inputs, indicating that DDT in these ornithogenic sediments was more "biologically processed", which is consistent with the contaminant having passed through marine food webs. Using sectioned and radiometrically dated sediment cores, each discrete layer of the core representing conditions present at that time, profiles of $\delta^{15}N$, chlorophyll a, chironomid head capsule counts, cadmium, and ΣPCB concentrations indicated that PCB delivery to the sediment has accelerated and that the northern fulmar colony at Cape Vera has increased within the last 50 years (Michelutti et al. 2009a, Michelutti et al. 2009b). A number of seabird-derived elements were also identified at Cape Vera, having elevated concentrations in seabird guano, low concentrations in background sediments, and exponentially decreasing concentrations in pond sediments with increasing distance from the fulmar colony (Brimble et al. 2009b). The fulmar colony was also shown to have a distinctive impact on water chemistry, nutrient concentrations, and diatom assemblages in the ponds at Cape Vera (Brimble et al. 2009a, Keatley et al. 2009).

The elevated contaminant concentrations in environmental media near seabird colonies have been associated with elevated contaminant levels in members of local food webs. In the Norwegian Arctic, concentrations of ΣPCBs and ΣDDTs in zooplankton, chironomid larvae and tadpole shrimps and arctic char from Lake Ellasjøen, which hosts a number of seabird colonies, were consistently higher than those from Lake Øyangen, which does not receive seabirds (Evenset et al. 2004). Resident arctic char concentrations were particularly high in Ellasjøen, on average 2,389 ± 1,528 ng g^{-1} ww as compared with 27.5 ± 37.7 ng g^{-1} ww in Øyangen, and with lipid weight concentrations comparable to those in the blubber of polar bears from Svalbard (Evenset et al. 2007a). Similarly, concentrations of chlorobornanes, PBDEs, polybrominated biphenyls, and PCNs were measured at significantly higher concentrations in biota from Lake Ellasjøen than in Lake Øyangen (Evenset et al. 2005). Gewurtz et al. (2009) used food web modeling to investigate the reasons for the exceptionally high concentrations of contaminants in resident arctic char from Lake Ellasjøen and concluded that contaminant inputs from seabird guano as well as differences in food web structures between Lakes Ellasjøen and Øyangen accounted for the observed differences in arctic char concentrations.

In the Canadian Arctic, members of the local terrestrial food web adjacent to, and remote from, the fulmar colony at Cape Vera were surveyed for total mercury, $\delta^{15}N$, PCBs and organochlorine pesticides (Choy et al. 2010a, Choy et al. 2010b). Collectively, the samples represented primary producers (including jewel and worm lichens), herbivores (collared lemmings), insectivores (snow buntings) and upper trophic level predators (ermine). Significant trends in total mercury concentrations in samples collected along a gradient of seabird influence were not observed, nor was an enrichment of total mercury in the local food web detected (Choy et al. 2010a). However, evidence suggesting that seabird-derived organohalogen contaminants were transferred to some members of the terrestrial food web was found (Choy et al. 2010b). Snow buntings collected from Cape Vera were found to have elevated concentrations of ΣPCB and ΣDDT in their whole body homogenate that exceeded guidelines for protecting wildlife, and also exceeded concentrations measured in buntings from other arctic locations. Additionally, PCB congeners typical of fulmar guano were found to be proportionally enriched in both jewel and worm lichens collected close to the fulmar colony.

Most studies of seabird biovectors to date have assumed that seabirds primarily transfer OHC to their coastal nesting sites in their guano. The unique physiology of particular seabird species, such as the production of stomach oils by seabird species from the order *Procellariiformes*, has not been considered. *Procellariiformes*, commonly called petrels or tubenoses, produce stomach oils from their prey items and use these oils for defensive purposes (i.e., to spit at intruders), as well as to feed their young and themselves (Warham 1977). Stomach oils are an energy-rich, readily transportable food source that enables petrels to exploit distant food sources and return to their nest with food for themselves and their nest-bound young (Warham 1990, 1996). Recently, stomach oils were shown to contain concentrations of organochlorine contaminants that were elevated over that of dietary prey items from which the oils were produced (Foster et al. 2010). Additionally, using mass and energy balance calculations, it was shown that chicks fed stomach oils receive a higher contaminant exposure than chicks that do not. The implications of these findings to biomonitoring and diet analysis research were suggested and discussed. However, it is probable that stomach oils also contribute to elevated contaminant levels in environmental media and food webs near colonies of petrels. Petrels are a widely distributed seabird order comprising over 100 species (Warham 1990, 1996). They are also present in large numbers; globally there are approximately four million northern fulmars alone (Brooke 2004a), and petrels consume approximately 34% (or 24 million t y^{-1}) of the total food consumed by seabirds globally (Brooke 2004b). Thus, petrels and their unique physiological adaptation of stomach oil production, are likely to be highly relevant to further studies of seabird biological vectors.

3.6.3. Anadromous salmon as contaminant biovectors

For some spawning lakes and streams of Alaska and northern British Columbia, anadromous fish have been shown to be the dominant source of persistent organic pollutants (Ewald et al. 1998, Gregory-Eaves et al. 2007, Krümmel et al. 2005, Krümmel et al. 2003, Krümmel et al. 2009). The nature of this transfer depends on the migratory behavior and life-cycle of the fish biovector in question. Only a few studies exist for the movement of POPs via fish biovectors in northern environments, though the

Photo: Linda Kimpe

potential for this process is considerable in light of the large anadromous spawning populations in northern Canadian territories as well as in Alaska, Asia, and Scandinavia.

Most of the research conducted on anadromous fish biovectors has been on sockeye salmon (*Oncorhynchus nerka*), which spawn in gravel beds associated with lakes and their tributary streams. The hatching juveniles will spend 1 to 3 years in freshwater before migrating to the ocean (Burgner 1991). The maturing salmon will then spend 1 to 4 years in the ocean where they acquire > 95% of their biomass from a carnivorous diet that consists of plankton, squid, and once they are older, other fish (Burgner 1991). Upon returning to their nursery streams and lakes, the sockeye salmon stop feeding and start consuming their stored fat, which dramatically concentrates contaminants like PCBs and chlorinated pesticides in their tissues (Ewald et al. 1998). After spawning, they die, releasing a large quantity of nutrients to the nursery lakes, which are typically unproductive and oligotrophic at northern latitudes (Moore et al. 2007, Naiman et al. 2002).

The release of contaminants from salmon carcasses to their natal lakes and streams has also been investigated, but few studies exist for northern latitudes. Ewald et al. (1998) presented early evidence of contaminant delivery by anadromous sockeye salmon in Copper River (AK) and showed that resident grayling had higher PCBs and organochlorine pesticide concentrations in a lake receiving anadromous salmon compared to a lake receiving no salmon. Similarly, Christensen et al. (2005) found that salmon-eating grizzly bears in British Columbia had elevated contaminant concentrations and different contaminant signatures than those consuming a higher proportion of vegetation. Grizzlies with salmon in their diets were determined to obtain 70% of all organochlorine pesticides, 85% of lower brominated PBDEs and 90% of PCBs from salmon (Christensen et al. 2005). In a study of eight Alaskan lakes, Krümmel et al. (2003) showed that PCBs in lake sediments correlated strongly with sockeye salmon density and Gregory-Eaves et al. (2007), provided evidence of sockeye salmon derived contaminant focusing on food webs from natal spawning lakes. Interestingly, PCB concentrations in radiometrically dated sediment cores from lakes receiving salmon did not exhibit PCB declines after the mid 1990s, as seen in other North American lakes (Krümmel et al. 2005, 2009). This may either suggest that curtailing PCB emissions affects the atmospheric pathway more

rapidly than the pathway involving the upper Pacific Ocean and marine salmon, or it may provide evidence that contaminant delivery to sediments is more efficient with the production of autochthonous organic matter which is stimulated by nutrient additions from the salmon biovector. A study by Stern et al. (2005) also observed maximum concentrations of PCBs, endosulfan and other POPs at or near the sediment surface in a remote lake in the Canadian High Arctic. These authors hypothesized that a recent increase in algal productivity due to climate change would have caused an increase in the scavenging of contaminants from the water column.

Evidence exists that contaminants from anadromous salmon biovectors are transferred to aquatic food webs, though very few studies have been done in northern latitudes. Gregory-Eaves et al. (2007) found that PCBs and DDT in resident rainbow trout (*Onchorhynchus mykiss*) correlated positively and significantly with the density of sockeye salmon spawners in seven lakes from Alaska and northern British Columbia. They also found $\delta^{15}N$ and $\delta^{13}C$ of food web components (periphyton, zooplankton, and rainbow trout) in spawning lakes were correlated positively and significantly to salmon spawner densities, demonstrating a connection between salmon-derived nutrient and contaminant pathways in Pacific salmon nursery lakes. Chlorinated fatty acids are also transferred from migrating sockeye salmon to resident grayling in Alaska (Mu et al. 2004).

Taken together, these examples demonstrate that contaminant biotransport by migratory species can have a dramatic effect on contaminant distributions in northern and arctic receptor sites. While the biovector transport of contaminants is not a process restricted to northern and arctic regions, the simultaneous transport of nutrients by the biovector makes this process of particular relevance in ecologically important areas such as productive salmon nursery lakes and streams where the salmon provide a valuable food source to wildlife, and in coastal arctic regions where seabird colonies fertilize the landscape and form ecological "oases" for other plants and animals. Contaminant transfer from biovector to receptor sites and food webs is particularly efficient, owing to its directionality and ability to focus contaminants originating from a broadly diluted oceanic medium into a specific receptor site, as well as its direct mode of entry into the receptor food web, often consumed at an elevated trophic level (Blais et al. 2007). It is anticipated that other important examples exist of biotransported contaminants from arctic migratory birds, whales, terrestrial mammals, and fish. An improved understanding of how biotransported nutrients mediate contaminant cycling in these environments could prove beneficial.

3.6.4. Assessment

- Biovector transport and deposition of PCBs and other POPs in arctic ponds was identified as an important route of input, at least for sites near seabird colonies.
- Evidence exists that contaminants from anadromous salmon biovectors are transferred to aquatic food webs, though very few studies have been done in northern latitudes.
- Combined with other studies, e.g., on Bjørnøya (Bear Island) in the Norwegian Arctic, these results suggest that this route could be important in more locations across the Canadian Arctic and deserves further investigation.

Photo: Martin Fortier/ArcticNet

3.7. Conclusions, Knowledge Gaps and Recommendations

3.7.1. POPs in the arctic atmosphere

3.7.1.1. Conclusions

- Many legacy POPs, including OC pesticides and PCBs, are declining in the arctic atmosphere, although in some cases the rates of decline have slowed or levels have increased slightly due to climate-change perturbations of the arctic system, particularly changes associated with sea-ice cover and the cryosphere in general.
- While temporal trend studies of legacy POPs are now very strong datasets, spatial and temporal atmospheric trends of emerging chemicals of concern for the Arctic are more limited or lacking.
- There are also limited measurements of these contaminants in environmental matrices, that are in contact with the atmosphere, i.e., snow-wet precipitation, water, ice caps, soils.
- In addition to the parent compounds, there is little knowledge about the occurrence of, and the risk associated with their transformation products, including their atmospheric reaction and degradation products generated during transport and deposition.
- The time required for the target chemical to reach the Arctic is influenced by the locations of the source, the chemical's transport pathways and its physical chemical properties. A non-declining atmospheric trend may not necessarily indicate ineffectiveness of control. Proper interpretation of temporal trends requires an understanding of these influencing factors which can be estimated using appropriate transport models.
- On the other hand, atmospheric and water monitoring data can be used to validate and improve model parameters used to elucidate contaminant transport to the Arctic.
- There is atmospheric monitoring evidence of enhanced transport of compounds during biomass burning (e.g., PAHs) and also of previously deposited POPs volatilized by the burning.
- Although extensive studies have been devoted to atmospheric transport and deposition of POPs to the Arctic, current knowledge of the dynamics and their transport at higher atmospheric elevation and their subsequent accumulation in arctic environments is still poor.
- Given the stronger winds at the higher atmospheric level that favor atmospheric transport and large cloud covers over the Arctic, wet deposition of POPs likely plays a more important role in POPs accumulation in arctic surface compartments, particularly since the POPs level in arctic air have exhibited a declining trend.
- This suggests that a lower atmospheric concentration of POPs measured near the ground surface may not necessarily suggest low risk for POPs accumulation. Further investigations in this aspect are needed.
- There are limited measurements and a lack of time trends of atmospheric POPs in the western and eastern Canadian Arctic. Short-term measurements have been conducted at the satellite stations of Tagish and Little Fox Lake in the Yukon and Kinngait on Baffin Island. However, with limited measurements, it is difficult to assess intercontinental transport, i.e., trans-Pacific transport to the western Arctic and trans-Atlantic transport to the eastern Arctic, as well as long-range transport from southerly sources to the lower Canadian Arctic.
- A wide range of new, potentially persistent and bioaccumulative chemicals, have been detected in the arctic atmosphere over the past 10 years.
- Screening for "new" flame retardant related chemicals in air samples taken at Alert (NU) has shown the presence of a range of brominated and chlorinated chemicals. BTBPE, EHTeBB and TBPH were generally detected with concentrations similar to those of the dominant BDE congeners.
- The presence of neutral and ionic PFASs and the cyclic methyl siloxanes at Alert (NU) supports their atmospheric long-range transport.
- The cyclic methyl siloxanes levels in air at the five monitoring sites in the Arctic are in the ng m^{-3} range, i.e., 1–2 orders of magnitude higher than atmospheric concentrations of polychlorinated biphenyls (PCBs) and hexachlorocyclohexanes (HCHs), which are regulated internationally under the Stockholm Convention.

3.7.1.2. Recommendations

- Monitoring programs need to consider including a broader range of chemicals, including both parents and transformation products, which may have POP-like properties to assess their potential for long-range transport as well as to assess changes by developing time trends in different media. Chemicals with potential for arctic contamination can first be identified using fate and transport models.

- Coordinated multimedia measurements within the same vicinity would allow for the assessment of fluxes and understanding partitioning processes among different environmental media. It would provide information on the relative importance of primary and secondary sources in a changing Arctic, which is essential for model validation and parameterization. Given the availability of atmospheric time trends and ancillary data, e.g., temperature and other meteorological data, at arctic air monitoring stations, such as Alert (NU), it is recommended to conduct multimedia measurements at these sites.
- The use of passive air samplers and FTS would allow for an increased spatial coverage of measurements. Intercontinental and long-range transport can then be assessed by coupling measurement data and time trends with transport models and back-trajectory analysis.
- Given the importance and versatility of passive sampling methods, better calibration and development of passive air samplers for particle-phase compounds is needed.
- Low air concentrations in the Arctic may result in detectability issues. This problem can be resolved by combining passive air samplers with the flowthrough sampler (FTS), which has shown comparable results at a much lower cost and maintenance than high volume air sampling at Alert (NU). As the FTS does not require electricity supply, it is suitable for use at remote arctic locations.
- Sources of emerging chemicals, such as stain-repellent-related perfluorinated compounds, PBDEs and other flame retardants, as well as siloxanes and perfluorinated alcohols are more wide-spread than many legacy POPs. Use of SIP disk-based passive air samplers and the FTS enables the assessment of levels at remote communities which may be exposed to these chemicals locally, e.g., from nearby landfills.
- The occurrence of many new chemicals in air at the remote arctic station of Alert (NU) highlights the urgency for further investigations to determine their temporal trends and to determine if they are present in arctic biota.
- In addition, the presence of degradation products of these various chemicals needs to be investigated given the importance of the perfluoroalkyl acid degradation products from volatile precursors.
- In the case of the cyclic siloxanes, the silanols, formed by degradation and which may be more rapidly scavenged from the atmosphere, should be examined.

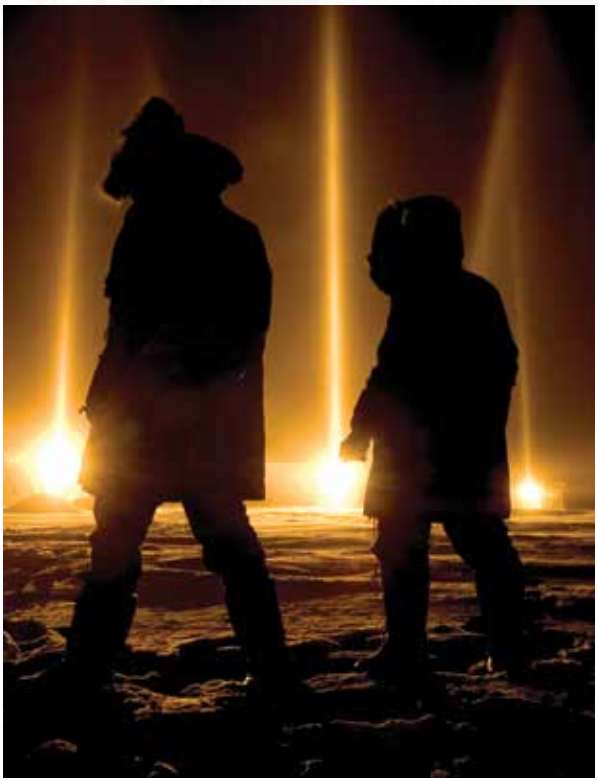

Photo: Alex Urosevic

3.7.2. POPs in seawater and freshwater

3.7.2.1. Conclusions

- Very low concentrations (low or sub-picogram per litre) of hydrophobic legacy POPs such as PCBs, OCPs and PBDEs are present in seawater in the Canadian Arctic.
- Perfluorinated alkyl acids such as PFOS and PFOA are generally present at 5- to more than 10-fold higher concentrations than the PCBs and PBDEs, reflecting their higher solubility in water.
- The detection of perfluorinated compounds in all compartments of the arctic environment over the past 10 years has increased our appreciation for the importance of seawater transport of these chemicals and of other contaminants as well.
- There are only limited new data on the concentrations of legacy POPs and almost no data for brominated flame retardants in seawater in the Canadian Arctic.
- New results for CUPs indicate that chlorothalonil, chlorpyrifos and dacthal are present in seawater frequently at higher concentrations than endosulfan. Lower concentrations were found under sea ice suggesting there may be a seasonal effect.
- Measured concentrations of PFCAs with ≥ 9 carbons in water sampled from remote locations are frequently below detection limits. However, these

same homologues are often found to be important contributors to ΣPFCA levels in biota. The lack of data in remote surface waters hinders the ability to assess the plausibility of emission estimates (direct and indirect) and source-receptor relationships (e.g., relative importance of different sources and pathways).

- As the long term temporal trends measurements are the only way to forecast trends of chemicals in environmental compartments, continuous seawater and atmospheric measurements are required for new chemicals besides legacy POPs.
- Useful insights into dominant sources and transport pathways of PFCAs and PFOS could be gained through robust assessments of the levels and patterns (e.g., linear:branched isomer ratios in abiotic samples) between remote lake and marine environments in reasonably close proximity.

3.7.2.2. Recommendations

- High-quality data on the inventories and concentrations of above mentioned chemicals in Arctic Ocean seawater are urgently required to validate models, to interpret trends in marine biota and to understand spatial variation.
- Linkages between air-water monitoring results and emission estimates should be improved in order to determine transport pathways and identification of the major source regions of both legacy and new chemicals.
- Time-series data for POPs and new contaminants in seawater are crucial for understanding the fate and trends of contaminants and would be particularly useful for the less bioaccumulative chemicals such as current use pesticides and perfluorinated compounds.
- There is a need to clarify the relative importance of atmospheric and oceanic inputs as well as the relative importance of direct and precursor emissions to different remote ecosystems.
- Given the challenges of obtaining POPs data by large volume water sampling due to ship board contamination and infrequent cruises, consideration needs to be given to deploying passive water samplers.

3.7.3. POPs in lake sediments and biovector transport

3.7.3.1. Conclusions

- Arctic lake sediments have been shown to be good archives of POPs including new POPs such as PBDEs and SCCPs.
- Low concentrations and difficulties related to the dating of sediment cores, especially in the High Arctic, make it challenging to use sediment cores to assess POPs deposition.
- Biovector transport and deposition of PCBs and other POPs in arctic lakes and ponds was identified as an important route of input, at least for sites near seabird colonies and in some salmon nursery lakes.
- Higher organic production in the nutrient-enriched waters typically results in greater transfer of PCBs from the dissolved to the particulate organic matter (POM) phase and greater vertical flux to sediments.
- Results from other lakes not influenced by seabird guano inputs also suggest that inputs of POPs may be influenced by climate warming with the resulting increase in algal primary productivity (indicated by greater diatom abundance.
- Evidence exists that contaminants from anadromous salmon biovectors are transferred to aquatic food webs, though very few studies have been done in northern latitudes.
- Combined with other studies e.g., on Bjørnøya (Bear Island) in the Norwegian Arctic, these results suggest that this route could be important in more locations across the Canadian Arctic and deserves further investigation.

3.7.3.2. Recommendations

- Further research is needed to assess the influence of climate change on the profiles of POPs in arctic lake sediments.
- Further research in fish would be useful for understanding the relative importance of this pathway to deliver contaminants to arctic lakes inhabited by anadromous arctic char, whitefish, or salmon.

3.7.4. Local sources of POPs in the Canadian Arctic

3.7.4.1. Conclusions

- New POPs including PBDEs, PFOS and SCCPs have been shown to be sources of local contamination in or near communities in the Canadian Arctic.
- Previous (and ongoing) contamination from DEW-line sites are of serious concern at a local level and they may contribute to global sources of POPs as the soil burdens and residues in contaminated sites are released through permafrost melting or greater warming.

- Dumpsites in Iqaluit, Cambridge Bay and Yellowknife showed significantly higher ∑PBDE concentrations compared to corresponding background sites in these locations, suggesting that PBDEs leach from the landfill.

3.7.4.2. Recommendations

- Better knowledge of local contamination sources is needed for the interpretation of spatial and temporal trends, particularly of new POPs which are in consumer products and therefore found in homes and dumpsites in all arctic communities.

3.7.5. Process studies in the abiotic environment

3.7.5.1. Conclusions

- Measurements of POPs in snow have increased since the last CACAR was published, particularly for new contaminants.
- The discovery of current use pesticides, perfluorinated alkyl acids and brominated flame retardants (e.g., deca-BDE) in ice caps across the Canadian Archipelago at relatively high concentrations compared to levels observed for "legacy" POPs in previous arctic snow studies, demonstrates the importance of atmosphere as a source of these chemicals.
- The accumulation of some of these chemicals, particularly PFOS and the penta-BDE show some evidence of a decline from the mid-1990s to mid-2000s. This is not apparent for the perfluorocarboxylic acids and deca-BDE, reflecting their ongoing global use, and long-range atmospheric transport.
- The ice cap studies also point to the importance of particle-bound organic contaminants entering the Arctic via long-range atmospheric transport. This route has been well documented for metals but ignored until recently for organics.
- Increasing trends of equivalent black carbon (EBC) at Alert (NU) between 1998 and 2002 has been reported. The increase in EBC may also enhance input of heavier PCB and PBDE congeners.
- The processing of POPs and other organic contaminants in the sea-ice system of the Beaufort Sea and Amundsen Gulf region is complex, but sea-ice, particularly first-year ice, shows an "enrichment" in hydrophobic POPs such as HCHs in the ice-brine, with expulsion of ice-brine during the winter resulting in elevated concentrations of these chemicals in the beneath-ice environment. This process is likely to be exacerbated in a warmer Arctic which will be dominated by fresh and first-year sea-ice with higher levels of brine relative to multi-year ice.
- Measurements in sea-ice snowpack demonstrate that low volatility chemicals such as PFOS and the PFCAs do not decline in the snowpack due to evaporative loss during late winter unlike more volatile POPs. Spring melt of the ice-rafted snowpack will therefore provide an additional source of these chemicals to surface marine waters.
- This may account for the elevated levels of PFCAs observed in the polar mixed layer of the western Beaufort Sea and Amundsen Gulf which are comparable to, or higher than, levels observed in North Atlantic surface water.

3.7.5.2. Recommendations

- High levels of deca-BDE in arctic snow not only suggest considerable potential for long-range transport via particles, but also show the urgent need for more research on other particle bound organic chemicals that may be entering the arctic environment.
- The fate of deca-BDEs in the environment is of additional importance because deca-BDEs have been found to break down to lower brominated (and already regulated) BDEs.
- The perennial snowpacks of the Canadian Archipelago ice caps provide a useful environmental record of contaminant accumulation and could serve to support the long-term air monitoring programme required to understand contaminant trends and as an initial screening process for the occurrence of new chemicals entering the Arctic through atmospheric sources.
- Quantification of contaminant fluxes and subsequent loading between key environmental compartments most affected by a warmer climate is required. Diminishing sea-ice cover and ice-quality (age) as well as ablating glaciers and ice caps are influencing contaminant transfer fluxes, resulting, in some cases, in the remobilization of "old stocks" or in amplifying contaminant concentrations, such as in the brine-environment of first-year sea-ice. The consequences with regards to localized biota exposure are not fully understood.

3.7.6. Mass balance modeling of contaminants and links to climate change

3.7.6.1. Conclusions

- Proper interpretation of temporal trends requires an understanding of the factors influencing trends and these can be estimated using appropriate transport models.
- Important factors that could influence climate-change perturbations of the arctic system, are changes associated with sea-ice cover and the cryosphere in general.
- It is currently not possible to quantify the impact of any individual environmental factor (including climate change factors) which influence POP air concentrations in the Arctic.
- There has been a tremendous expansion of modeling of ocean transport of contaminants, particularly of PFOA and PFOS to the Arctic in the last 5 years. Results are in reasonable agreement with currently available data suggesting that available emission estimates for these two compounds are plausible.
- Modeling results suggest that redistribution of these contaminants from lower latitudes to the Arctic Ocean is ongoing and the total mass (and average concentration) of PFOA and PFOS in the marine environment is expected to increase for the next 10–20 years.
- The Distant Residence Time concept provides valuable information for guiding global modeling efforts and for presenting findings in a relatively simple and understandable manner.
- A warmer and wetter Arctic, predicted by climate models will likely lead to changes in the geographic pattern of POPs deposition as arctic climate change causes wetter conditions in some places and drier conditions in others.
- Reduced ice extents that will provide more open water of the Arctic Ocean is another major factor likely to influence the dynamics of POPs in the Arctic.
- Modeling suggests that greater open water and warmer waters are interacting to contribute to transfer α–HCH from ocean waters to air.
- Biological processes in the water column that are stimulated by greater sunlight and warming, such as algal blooms, may affect the gas exchange of POPs through sorption to settling particles.
- Pertubation modeling has been used to assess the impact of warming trends. The model assumes that the POPs air concentration is the sum of a mean concentration and perturbed concentration due to climate change.
- The detrended data for γ-HCH atmospheric concentrations suggests that it underwent an increasing trend, corresponding nicely to an increasing trend of mean arctic air temperature and a decreasing trend of sea-ice concentration, especially since the late 1990s.

3.7.6.2. Recommendations

- Much further work is needed to assess whether climate change, particularly warming trends, is affecting POPs transport to the Arctic.
- Climate change and accelerated melting of glaciers and sea ice may enhance the release of POPs that were deposited and accumulated in ice and ocean during earlier times of higher emissions. The release of POPs from the cryosphere and the ocean should be measured.
- To understand how climate change and variations affect the input and behavior of POPs in the Arctic, measurements must be continued to provide temporal trends spanning over similar time-scales as climate change observations, i.e. over decades.
- The perturbation modeling approach needs further confirmation because factors other than climate change can lead to non-linearity on observed air concentrations. Continued air monitoring of POPs will improve the contaminant time series and is critical for further evaluation of this approach.
- Where different models exist, there should be active model comparison programs to identify strengths and weaknesses with a view to improving predictive capabilities.
- Efforts should be made to devise internationally acceptable methods, using models, of identifying source-receptor relationships between geographic regions.
- More data are required on the quantities of chemicals used and emitted in source regions.

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CHAPTER 4

Occurrence and Trends in the Biological Environment

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Photo: Lisa Loseto

CHAPTER 4

Occurrence and Trends in the Biological Environment

Coordinating authors: Derek Muir, Perihan Kurt-Karakus and Jason Stow

4.1. Levels and Spatial Trends of POPs in Biota

Contributors: Jules Blais, Birgit Braune, Craig Butt, Emily Choy, Amila De Silva, Marlene Evans, Perihan Kurt-Karakus, Barry Kelly, Nic Larter, Robert Letcher, Melissa McKinney, Adam Morris, Derek Muir, Gary Stern, Gregg Tomy

4.1.1. Introduction

This chapter focusses on spatial and temporal trends and the biomagnification of POPs in biota in the Canadian Arctic. It builds upon previous assessments of POPs in arctic biota conducted by the Northern Contaminants Program (NCP) in the 1990s and early 2000s (Fisk et al. 2003, Jensen et al. 1997) and review articles related to those assessments (Braune et al. 1999, Muir et al. 1999, Braune et al. 2005, Gamberg et al. 2005, Evans et al. 2005). The goals and context of the assessment of POPs in biota are discussed in more detail in Chapter 1 (sections 1.1 and 1.2) and are also outlined annually in the Northern Contaminants Program call for proposals (INAC 2004, 2012). While legacy POPs remain important a major focus in this assessment is on "new POPs", which are defined as any chemical not in the original "dirty dozen" listing under the Stockholm Convention of 2004 (section 1.2.2) judged to have similar properties in terms of environmental persistence and bioaccumulation potential.

Photo: Paul Nicklen/National Geographic Society

Table 1.3, in Chapter 1, includes a list of "new" chemicals that have been analyzed under the NCP since 2003. Assessment of most of these new chemicals was not previously possible due to a lack of measurements. However, results from analyses in the Canadian Arctic to approximately 2008 were included in reviews conducted as part of the AMAP POPs assessment in 2009 (Butt et al. 2010, de Wit et al. 2010, Hoferkamp et al. 2010). The Annex Tables of this chapter provide more details on the concentrations of individual compounds as well as the major groups of POPs in key species.

Individual contributors to this chapter have chosen the format with which to present their results. Most data regarding levels and spatial trends are presented as arithmetic means (± standard deviations). Concentrations are reported on the basis of wet weight (ww) or lipid weight (lw) that has been adjusted for fraction lipid. The spatial trends of POPs in biota discussed here are often qualitative because they are based on the evaluations of means and ranges of concentrations from different studies. In the case of the sums of groups of compounds, such as PCBs and chlordanes (CHLs), some laboratories have included more congeners or components than others in the ΣPCB and ΣCHL results. Rigorous comparisons between locations also require information on age, sex, blubber thickness, nutritional status, collection season, and reproductive status of the animals, all of which have an important influence on contaminant concentrations. This information is available for many locations, but is used here only qualitatively in spatial trends analysis. Temporal trends have generally been assessed using log transformed lipid weight concentrations (further discussion in section 4.2.1). Analytical methodology and quality assurance for most of the studies discussed here are addressed in Chapter 6, which describes the results of the NCP Interlaboratory Quality Assurance program. Systematic names of species are provided in the Glossary. They have generally been omitted for commonly monitored species but included for vegetation, invertebrates and less frequently monitored animals.

4.1.2. Freshwater biota

4.1.2.1. Introduction

Measurements of POPs in fish and freshwater food webs in the Canadian Arctic have been conducted since the 1970s. Early studies were summarized and reviewed by Lockhart et al. (1992). With the start of the NCP in 1991, a substantial amount of data on POPs in fish and food web organisms were generated during NCP Phase I and Phase II studies. Reviews by Braune et al. (1999) and Evans et. al. (2005) summarize the state of knowledge on POPs in fish and freshwater food webs to late 2002. The major "new chemicals" analyzed in Arctic and subarctic fresh-water biota during the period 2003–2010 were the PBDEs and PFASs. Also on the list of analytes were other brominated flame retardants such as HBCDD, PBEB, BTBPE and DBDPE. In addition, endosulfan measurements were improved with the introduction of analysis using GC-electron capture negative ion MS (GC-ECNI MS) as well as the addition of endosulfan sulfate to the analytical list.

The priority under the NCP "Blueprint" for monitoring from 2004 to 2011 (INAC 2004, 2012) was to build on previous studies of burbot from Fort Good Hope, of lake trout and burbot from Great Slave Lake, Lake Laberge and Kusawa Lake, as well as of landlocked arctic char in the High Arctic. A study of POPs in anadromous arctic char was added as of 2004, and other studies on POPs in fish in the Canadian Arctic were also included. The sampling locations for these studies are shown in Figure 4.1. In this section concentrations of POPs in major species of freshwater and anadromous fish, including new chemicals not reported in previous assessments, are discussed and spatial trends are assessed. Temporal trends in these species are discussed in section 4.2.2.

4.1.2.1.1. Anadromous arctic char

Char are members of the Salmonidae family with a more northerly distribution than lake trout. They are widespread throughout much of the Arctic (Scott and Crossman 1998). Arctic char is found primarily in the eastern Arctic and Dolly Varden (*S. malma*) is found primarily in the western Arctic with their range extending as far east as the vicinity of the Mackenzie River outflow. Sea-run char are important components of the diet of northern coastal communities (Johansen et al. 2004, Van Oostdam et al. 2003). More importantly, char form the basis of a number of commercial fisheries. Arctic char have highly complex life histories that vary within and between lakes (Gantner et al. 2010a, Gantner et al. 2010b, Swanson and Kidd 2010, Swanson et al. 2010). Some char live in lakes with no connection to the sea and are called landlocked. Others live in lakes, which retain some connection with the sea but do not migrate to the sea; these char are called resident char. A third type of char (sea-run or anadromous) migrates to the sea where they feed voraciously for a few weeks before migrating back inland; these migrations may occur every two years.

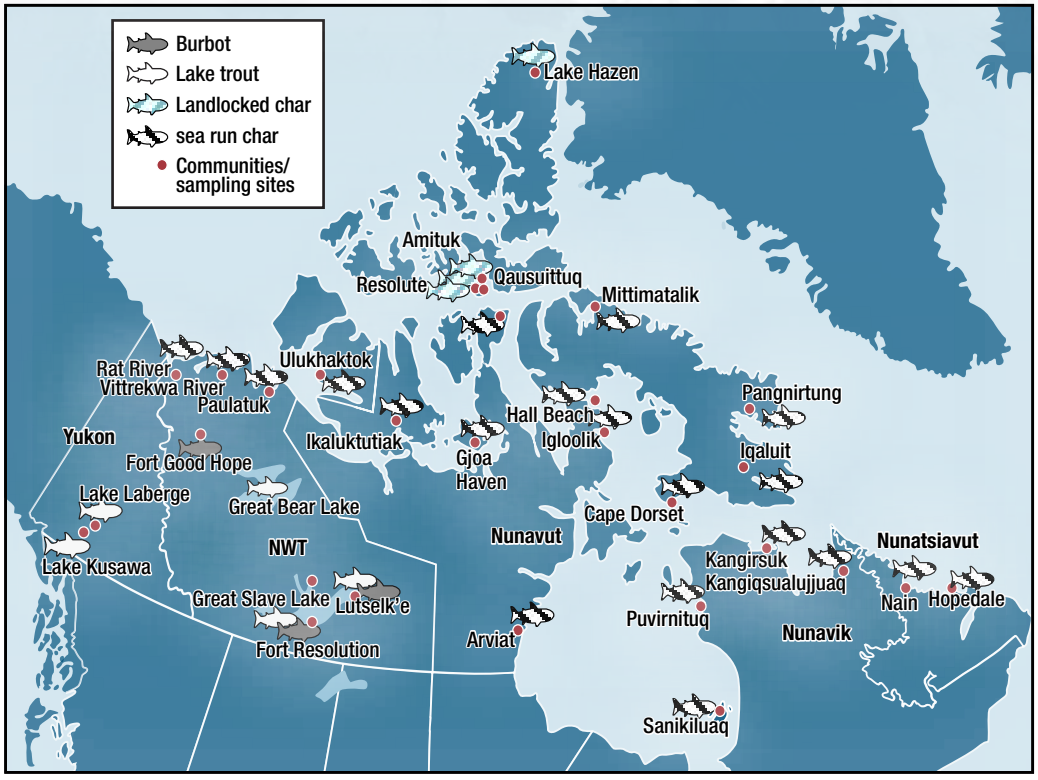

FIGURE 4.1

Sampling locations for fish collected between 2003 and 2011 for POPs analysis.

4.1.2.1.1.1. POPs in anadromous arctic char

Only limited measurements of POPs in sea-run populations were conducted prior to or under previous NCP programs (Evans et al. 2005, Fisk et al. 2003, Lockhart et al. 2005, Muir et al. 1990). These studies determined that concentrations of POPs were very low in sea-run char and thus an excellent food choice for those who wished to reap the nutritional benefits of consuming traditional country food while minimizing their contaminant intake.

From 2004 to 2009, sea-run char were analyzed for POPs and other influencing variables from the domestic harvest of 20 communities (Figure 4.1). Spatial trend data for the 20 sites sampled over the period 2004–2009 are summarized by location to show general patterns (Figure 4.2). Mean fork length was 575.5 ± 92.3 mm and age 9.9 ± 3.9 yr (all years). In general, the smallest and youngest fish were caught in the Northwest Territories and in Labrador. While there can be many reasons for this, including the selection at the community level as to which fish to submit for analyses, the size of the local fish population may also be affected by intense fishing, resulting in a reduction in average fish size. The char population is small in the Rat River, Vittrekwa River, Paulatuk, and Iqaluit because of fishing pressures with quotas established on catches. At Nain, char also experience significant fishing pressures. As contaminant levels tend to increase with fish age and size, higher contaminant levels would be expected for less exploited char populations, all other factors being equal.

Mean lipid content of the fillet averaged 8.9 ± 2.2% with the very high content at Ulukhaktok (34.7 ± 7.9%) due to the fact that fat-rich belly fillet rather than dorsal fillet were provided for analyses. Since the majority of the POPs that were analyzed in this study are lipophilic, Ulukhaktok would naturally tend to have higher concentrations of such contaminants (expressed on a fresh or wet weight basis) than other locations simply because of the high fat content of the tissues analyzed.

ΣHCH, ΣCBz, ΣCHL, ΣDDT, ΣPCB and toxaphene occurred in low ng g^{-1} ww concentrations (Figure 4.3; Annex Table A4-1) in sea-run char at all locations averaging 2.0 ± 1.3 ng g^{-1}, 2.8± 1.3 ng g^{-1}, 4.4 ± 2.3 ng g^{-1}, 2.0 ± 1.4 ng g^{-1}, 11.3 ± 4.1 ng g^{-1} and 15.1 ± 8.3 ng g^{-1} respectively (excluding Ulukhaktok data). ΣPCB (and possibly ΣDDT) concentrations at Nain, while low, were not as low as

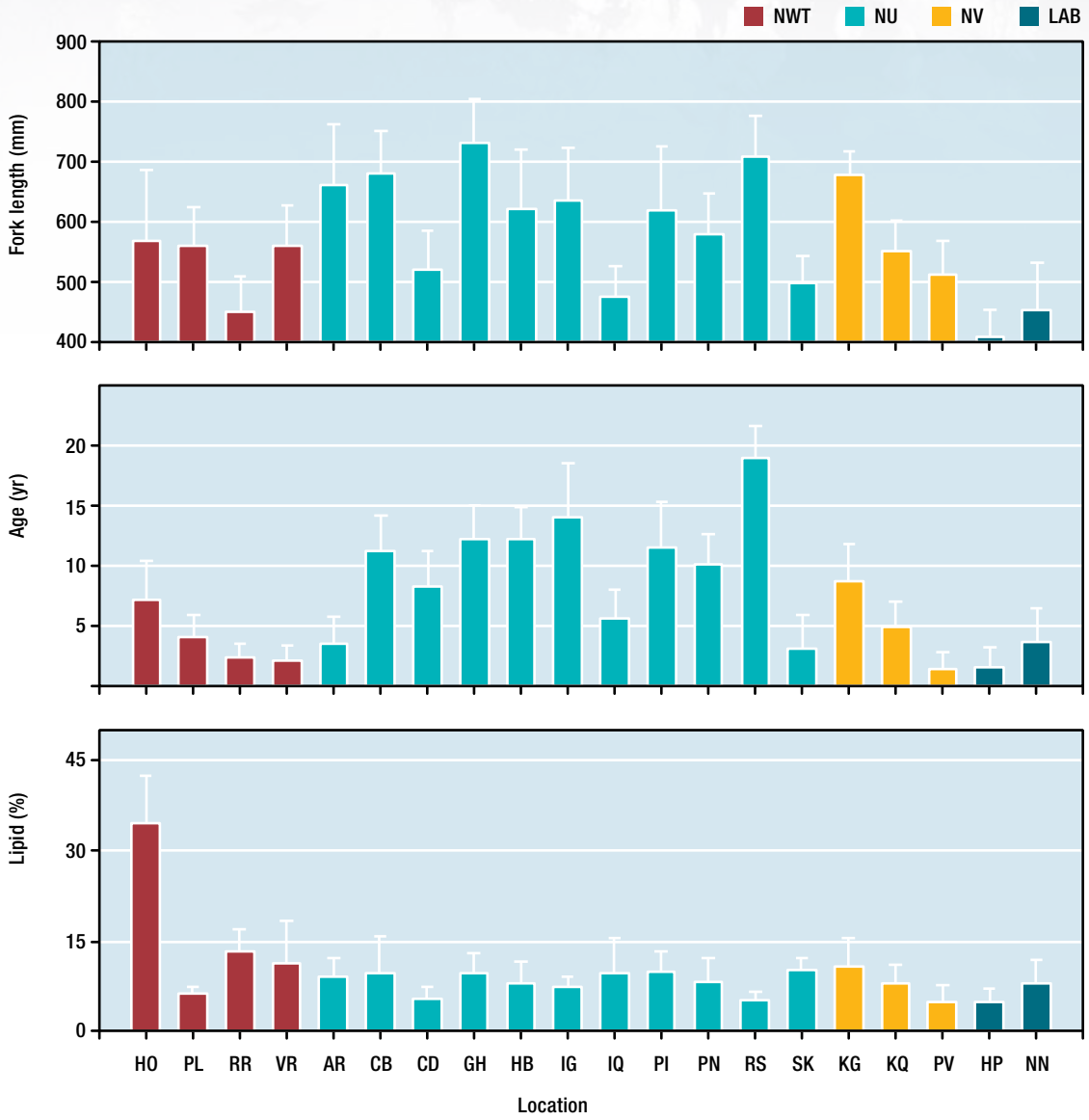

FIGURE 4.2

Mean (and standard deviation) fork length, age and percent lipid of sea-run char sampled in 20 locations over the period 2004–2009. Ulukhaktok/Holman (HO), Paulatuk (PL), Rat River (RR), Vittrekwa River (VR), Arviat (AR), Cambridge Bay (CB), Cape Dorset (CD), Gjoa Haven (GH), Hall Beach (HB), Igloolik (IG), Iqaluit (IQ), Pond Inlet (PI), Pangnirtung (PN), Resolute (RS), Sanikiluaq (SK), Kangirsuk (KG), Kangiqsualujjuaq (KQ), Puvirnituq (PV), Hopedale (HP), Nain (NN). Lipid analyses for Ulukhaktok considered belly fillet while the other 19 communities are based on dorsal (skin-on) fillet.

may have been expected for the small and young fish measured at this site. Toxaphene was the most prominent legacy POP in char with concentrations generally 5 to 10 times higher than for ΣDDT, ΣCHL, and ΣHCH. Concentrations of all four major groups of chlorinated pesticides showed a similar spatial trend, with char from Gjoa Haven having higher concentrations than most other locations. ΣPCB concentrations were typically higher than the chlorinated pesticides, except for toxaphene, and had a more uniform spatial pattern of concentrations. This spatial variation was influenced by the lipid content, which was positively correlated with concentrations of the six major groups of POPs.

4.1.2.1.1.2. New POPs in anadromous char

Over the period 2004–2009, PBDEs were also analyzed in skin-on muscle of sea-run char from the domestic harvest of six communities per year from the western Rat and Vittrekwa Rivers in the western Arctic, east along the coastal Arctic to Baffin Island, as far north as Creswell Bay near Resolute, and as

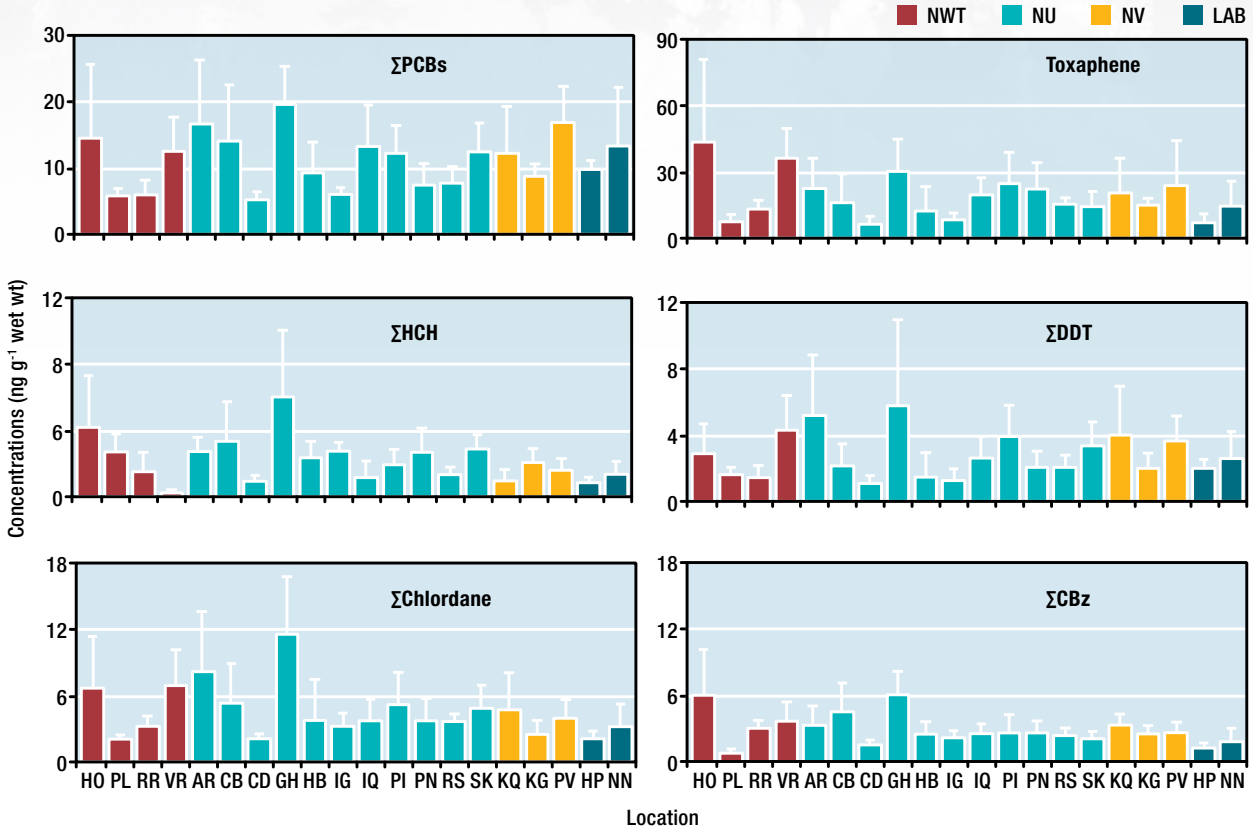

FIGURE 4.3

Mean (and standard deviation) concentrations of major legacy POPs (ng g^{-1} ww) in sea-run char sampled in 20 locations over the period 2004–2009. Ulukhaktok/Holman (HO), Paulatuk (PL), Rat River (RR), Vittrekwa River (VR), Arviat (AR), Cambridge Bay (CB), Cape Dorset (CD), Gjoa Haven (GH), Hall Beach (HB), Igloolik (IG), Iqaluit (IQ), Pond Inlet (PI), Pangnirtung (PN), Resolute (RS), Sanikiluaq (SK), Kangirsuk (KG), Kangiqsualujjuaq (KQ), Puvirnituq (PV), Hopedale (HP), Nain (NN).

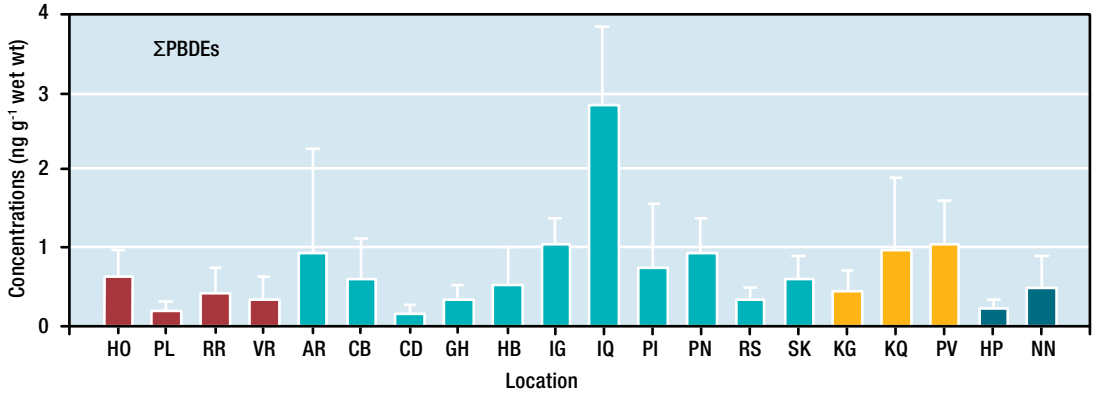

FIGURE 4.4

Mean (and standard deviation) concentrations of ΣPBDEs (sum of 14 BDE congeners) in sea-run char sampled at 20 locations over the period 2004–2009. See caption of Figure 4.2. for the full names of each location.

far south as Hudson Bay and the Labrador coast (see Figure 4.1. for sampling sites). ΣPBDE concentrations averaged 0.68 ± 0.58 ng g^{-1} in sea-run char sampled at 20 locations over this period. The highest concentrations were observed at Iqaluit (Figure 4.4, Annex Table A4-1). No other clear spatial trends were evident. The range of average ΣPBDE concentrations (0.1–2.6 ng g^{-1} ww) in sea-run char over was similar to landlocked arctic char, 0.09–9.9 ng g^{-1} ww (Annex Table A4-2). PBDE concentrations in sea-run char were not strongly associated with any variable, e.g., length, age and lipid content.

As observed in other fishes, BDE-47 was the major congener in sea-run char. Other congeners detected in almost all samples were BDE-28, -99, -100, -153, -154, and -209. No other BFRs were detected in sea-run char.

PFASs were determined in sea-run char muscle from Cambridge Bay, Pond Inlet and Nain. PFOS was detectable in all samples along with PFOA, PFNA, PFDA, PFUnA, PFDoA, and PFTriA (Annex Table A4-1). PFOS and ΣPFCA concentrations were very low averaging 0.04 ± 0.014 ng g^{-1} ww and 0.12 ± 0.03 ng g^{-1} ww, respectively, at Cambridge Bay and 0.07 ± 0.06 ng g^{-1} ww and 0.12 ± 0.15 ng g^{-1} ww, respectively, at Pond Inlet. The range of PFAS concentrations in sea-run char was 2- to 3-fold lower than in landlocked arctic char in Lake Hazen and Amituk Lake, which are remote lakes (Annex Table A4-2).

Endosulfan isomers and endosulfan sulfate were determined in sea-run arctic char muscle from a subset of sampling locations. Low sub ng g^{-1} concentrations of Σendosulfan were detectable in sea-run char and overall higher concentrations were present in char from most eastern Arctic locations (Pond Inlet, Nain, Puvirnituq; mean 0.45–1.1 ng g^{-1} ww) than in the western Arctic (Cambridge Bay, Ulukhaktok; means of 0.26 ng g^{-1} ww and 0.31 ng g^{-1} ww, respectively) (Figure 4.5). While α-endosulfan and sulfate were the major components of Σendosulfan, β-endosulfan was more frequently detected in the eastern arctic char and was undetectable in the samples from the two western arctic locations.

Chlorinated paraffins were determined in sea-run char collected near Iqaluit (Dick et al. 2010) as part of a study that investigated local sources of short-chain (SCCP) and medium chain (MCCP) chlorinated paraffins. Char from the mouth of the Sylvia Grinnell River (Kagnitsuatsia) had SCCP concentrations of 7.8 ± 17.0 ng g^{-1} ww (range: non-detectable–96.0 ng g^{-1}) for SCCPs and 6.8 ± 11.1 ng g^{-1} ww (range: non-detectable–54.5 ng g^{-1}) for MCCPs. Char collected east of Iqaluit (Peterhead Inlet) had lower concentrations (SCCPs = 1.6 ± 2.8 ng g^{-1}; MCCPs = 3.7 ± 1.8 ng g^{-1}) while a single landlocked arctic char from Iqalugaajuruluit Lake near Iqaluit had SCCP and MCCP concentrations of 12 and 13 ng g^{-1} ww, respectively. The results suggest that there are low background concentrations of SCCP and MCCPs in sea-run char and that further study is needed to examine spatial and temporal

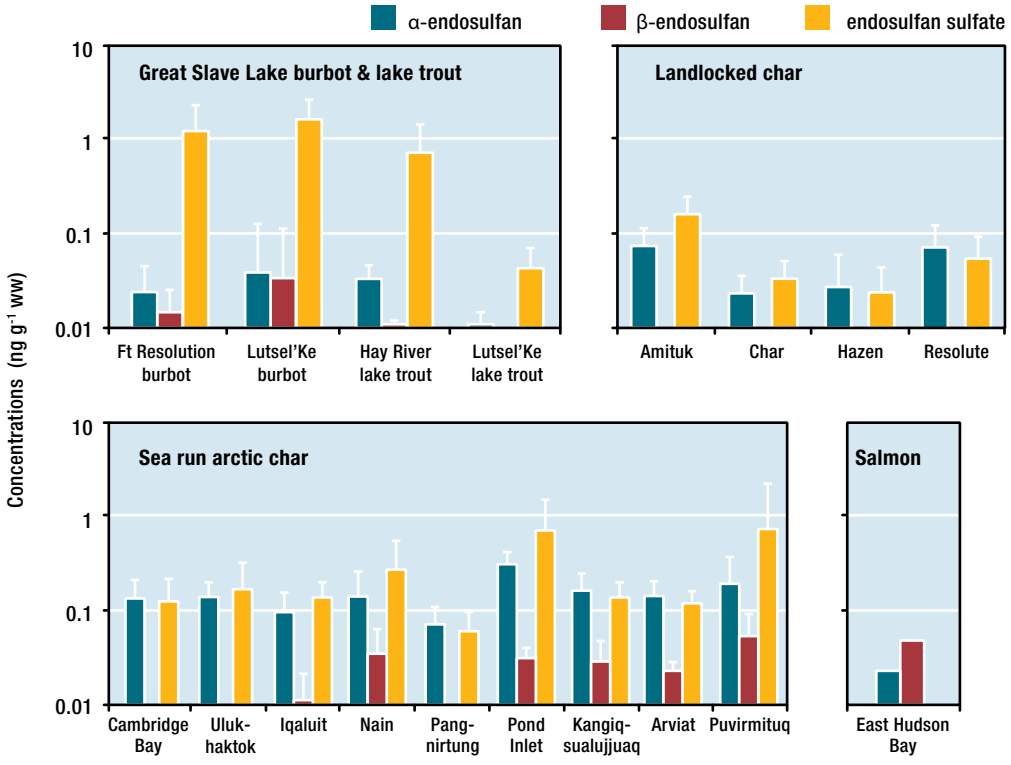

FIGURE 4.5

Mean (and standard deviation) concentrations of α- and β-endosulfan and endosulfan sulfate in Great Slave Lake burbot liver and lake trout muscle, landlocked arctic char muscle, sea-run char muscle and salmon from east Hudson Bay (Kelly et al. 2007). Results from Kelly et al. (2007) are geometric means converted to wet weight.

variation. SCCP and MCCP contamination of sediments, soils and surface water in Iqaluit is discussed further in Chapter 2, section 2.3.7.3.

4.1.2.1.2. Burbot and lake trout from NWT and Yukon lakes

POPs were determined in liver of burbot at Fort Good Hope and at two locations in Great Slave Lake over the period 2003–2011 (see map Figure 4.1). Sam-pling of burbot has occurred annually at these locations since 2000, with the exception of Great Slave Lake in 2003. Lake trout have also been collected annually since 2004 from two locations in Great Slave Lake and results for collections made in 2002 and 2007 in Great Bear Lake were also available for this assessment. While the main focus of the studies at Fort Good Hope and Great Slave Lake has been on temporal trends, the average concentrations and differences in patterns of major POPs are of interest and are briefly compared below.

In Great Slave Lake, POPs monitoring occurs in two regions: the West Basin, which is relatively shallow, warm and productive, and the East Arm which is deeper, colder, and less productive (Fee et al. 1985, Rawson 1955). These basic features will affect contaminant pathways in a number of ways. For example, concentrations of POPs are likely to be higher in biota in the low productivity waters of the East Arm than in the higher productivity waters of the West Basin based on observations of lake trout in Ontario (Bentzen et al. 1996) and other Canadian and northeastern USA lakes (Guildford et al. 2008, Houde et al. 2008, Bentzen et al. 1996, Berglund et al. 2001, Houde et al. 2008). Differences in fish growth and feeding characteristics between the two basins will also affect contaminant levels in fish. The Slave River formed by the confluence of the Peace and Athabasca Rivers, and is influenced by downstream activities such as pulp and paper mills, agriculture, and urban development. Some differences in contaminant levels between the two areas of the lake may be associated with these influences. However, sediment coring studies (Evans et al. 1998, Mudroch et al. 1992) determined that increases in contaminant loadings with time were small and in the general order observed elsewhere in undeveloped systems. No other results for POPs in lake trout or burbot from NWT, Nunavut or Yukon lakes have been published over the period 2003–2010.

Previous reviews and studies of POPs in burbot and lake trout from Yukon lakes noted the wide range of concentrations between lakes (Evans et al. 2005, Ryan et al. 2005) with the highest concentrations observed in fish from Lake Laberge. Over the period 2003–2010, sampling for the analysis of POPs focussed on lake trout in Lake Laberge and Kusawa Lake. The NCP "Blueprint" (INAC 2004, Macdonald 2004) redefined the focus to lake trout as the single species of fish for traditional foods monitored in the Yukon.

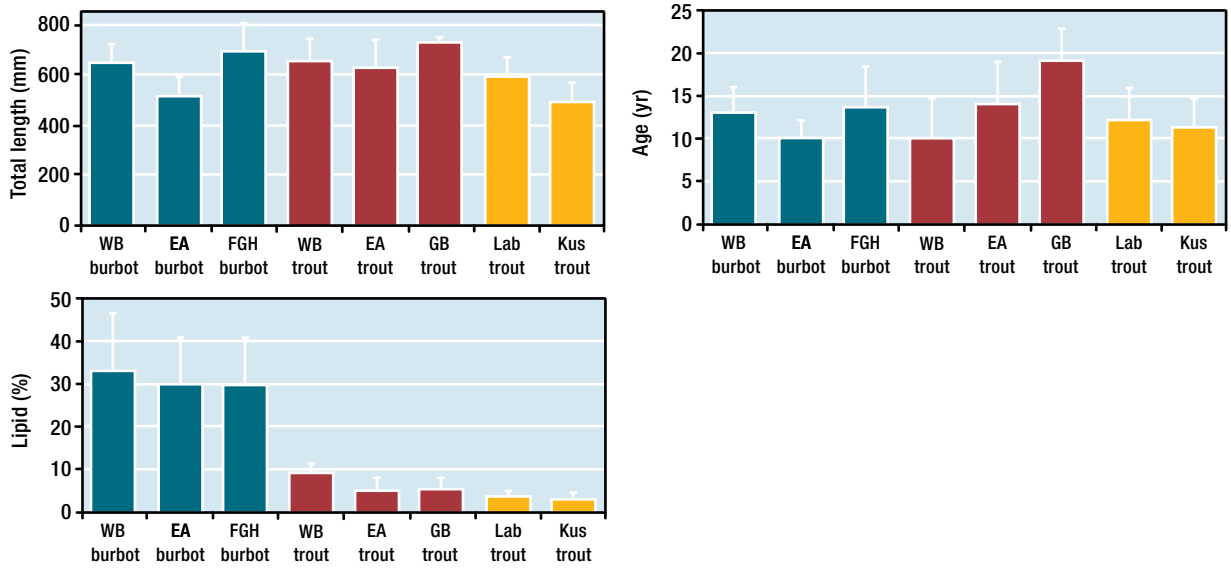

FIGURE 4.6

Mean biological attributes of burbot collected (2003–2010) from Great Slave Lake, West Basin (WB, Fort Resolution) and East Arm (EA, Lutsel K'e), and Fort Good Hope (FGH, Mackenzie River). Lake trout was collected from Lake Laberage (Lab), Kusawa Lake (Kus), from the West Basin (Hay River) and East Arm (Lutsel K'e), and from Great Bear (GB) Lake (2002). Data are shown as mean + one standard deviation. Lipid percent (fat content) is based on the liver for burbot and fillet for lake trout.

Lake trout is a pelagic cold-water stenotherm, which is only found in lakes that are sufficiently deep and low in productivity, for cold and well-oxygenated water to persist through the summer. Burbot is also a predator but more tolerant of warmer waters and is found not only in large lakes such as Great Slave Lake and Great Bear Lake but also in many northern rivers (Scott and Crossman 1998). Studies of the two species, and in the two ecological regions of Great Slave Lake, provide for an improved scientific understanding of the factors affecting contaminant levels that can then be generalized to the other broader regions of the Arctic. Lake trout and burbot differ in their biological features. Within each species, there are differences in their West Basin and East Arm populations. Lake trout are similar in size in the West Basin and East Arm but fish in the West Basin are younger and have more lipid in their fillet. Such differences suggest a faster growth rate and a richer food supply for West Basin trout compare to East Arm trout (Figure 4.6). Burbot tend to be larger, older, and with more lipid-rich livers in the West Basin than in the East Arm. Lake trout in Great Bear Lake were also large and older than in the West Basin of Great Slave Lake.

4.1.2.1.2.1. POPs in burbot and lake trout from NWT and Yukon lakes

Toxaphene and PCBs are the more prominent POPs in burbot (liver) and in lake trout in NWT and Yukon sampling locations (Figure 4.7). The overall ranking of average wet weight concentrations in burbot liver is toxaphene ≥ PCBs >> ΣCHL > ΣDDT > ΣCBz > ΣHCH. All POPs were generally higher in burbot liver than in lake trout fillet as expected given the high lipid content of burbot liver (Figure 4.6). In

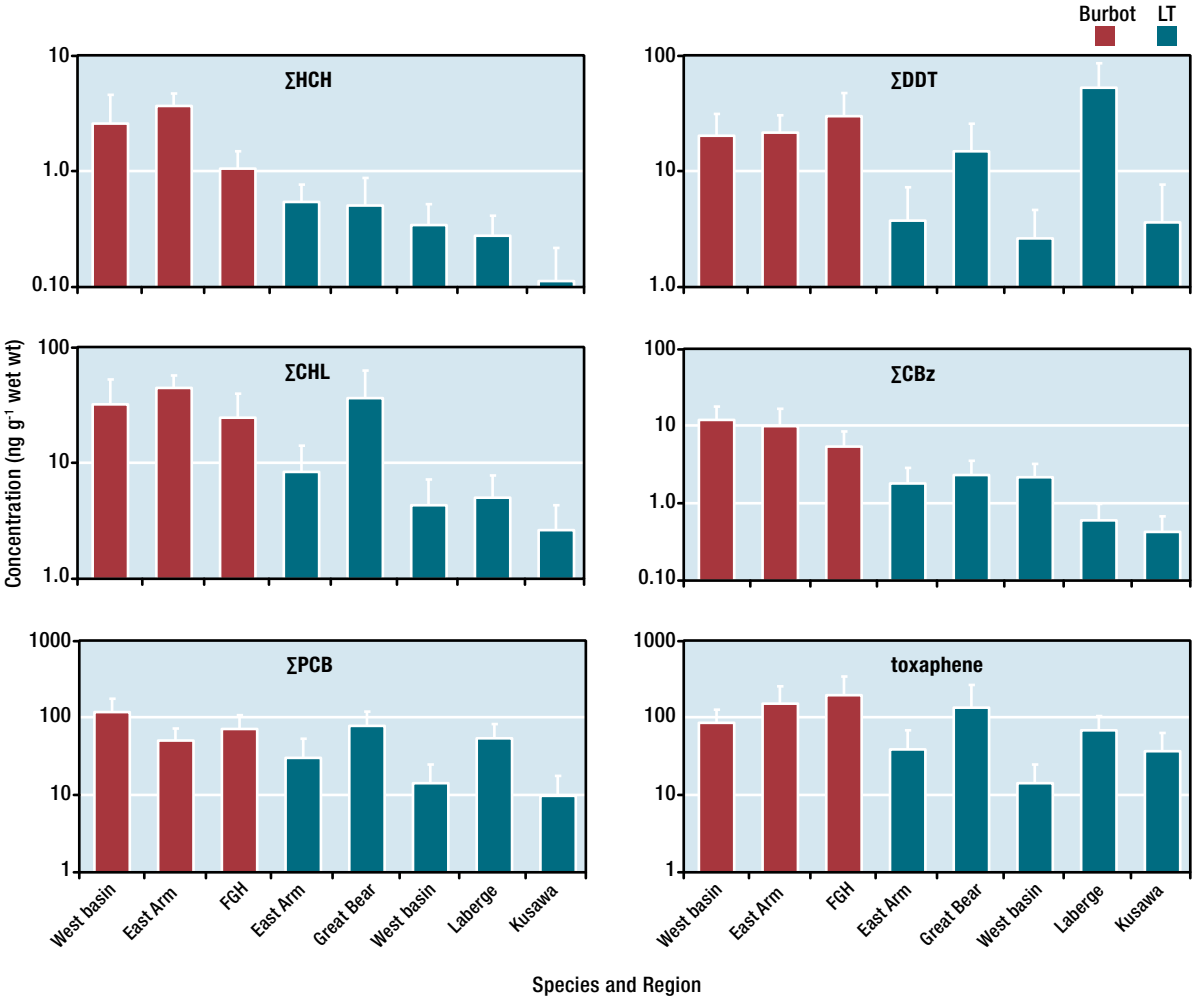

FIGURE 4.7

Mean (and standard deviation) of major legacy POPs in liver of burbot collected from the Great Slave Lake West Basin and East Arm, and at Fort Good Hope (FGH), as well as lake trout collected from the West Basin and East Arm of Great Slave Lake and from Lake Laberge and Kusawa Lake in the Yukon over the period 2003–2009 and from Great Bear Lake (2007).

Great Slave Lake, ΣHCH and ΣCBz in lake trout occurred in similar concentrations in the West Basin and East Arm, whereas ΣCHL, ΣDDT, and ΣPCB concentrations were higher in the East Arm than in the West Basin lake trout (Figure 4.7). Higher concentrations in East Arm lake trout may be related to the greater age and slower growth rates of these fish at this location. ΣHCH occurred in similar concentrations in the two regions of Great Slave Lake while ΣCBz, ΣDDT and ΣPCB concentrations were only slightly lower in East Arm than in West Basin burbot. Fort Good Hope burbot have very similar mean (ww) concentrations of ΣPCBs, ΣDDT and toxaphene as Great Slave Lake burbot and lower concentrations of ΣHCH, ΣCHL and ΣCBz. On a lipid adjusted basis, POPs are higher in East Arm and Fort Good Hope burbot (data not shown) due to lower percent lipid in liver. The higher levels of very bioaccumulative POPs such as PCBs, DDT and toxaphene are therefore associated with the lower productivity environment.

Average (ww) concentrations of legacy POPs in lake trout from Lake Laberge and Kusawa Lake for the period 2003–2009 are shown in Figure 4.7. Concentrations of ΣDDT in lake trout from Lake Laberge remain higher than those in Great Slave Lake and at Fort Good Hope as they were in the 1990s (Fisk et al. 2003) while PCBs and toxaphene levels were similar to those in Great Slave Lake (East Arm) and Great Bear Lake. There are no recent data from Lake Laberge or Kusawa Lake for burbot. Temporal trends of POPs in lake trout from these lakes are discussed in section 4.2.2.5.

4.1.2.1.2.2. New POPs in burbot and lake trout from NWT and Yukon lakes

Lake trout and burbot in Great Slave Lake have been analyzed for PBDEs and other BFRs including PBEB, HBCDD, and BTBPE (Evans and Muir 2009). PBDEs have also been determined in lake trout and burbot from Fort Good Hope and Lake Laberge and Kusawa Lake in the Yukon (Stern et al. 2012b, Stern et al. 2010b). The combined results for total PBDEs (sum of selected tri-decaBDEs) and HBCDD are shown in Figure 4.8.

PBDEs occurred at slightly higher concentrations in East Arm than West Basin burbot liver and lake trout. However, concentrations were low compared to PCBs and toxaphene (Figure 4.7). PBDE concentrations were higher in Great Slave burbot liver than in Fort Good Hope burbot liver. The highest concentrations of PBDEs in lake trout were found in Lake Laberge and Kusawa Lake fish, while those from Great Slave Lake and Great Bear Lake had about 10-fold lower concentrations (Figure 4.8).

The actual pattern of PBDEs in burbot liver and lake trout muscle from Great Slave Lake is illustrated in Figure 4.9. The proportion of tetra- and penta-BDEs was higher in the East Arm than in the West Basin for both species. This was mainly due to higher deca-bromodiphenyl ether (deca-BDE) in the West Basin fish. The detection of deca-BDE was unexpected, as it does not have a high bioaccumulation potential due to its high molecular weight and potential for debromination (Environment Canada 2010).

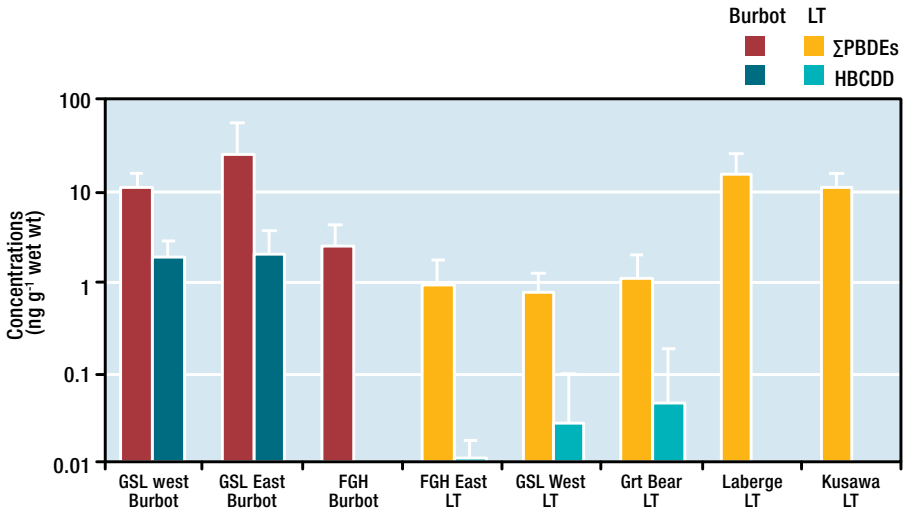

FIGURE 4.8

Concentrations of ΣPBDEs (sum of tri-decabromidiphenyl ether) and hexabromocyclododecane (HBCDD) in burbot liver and lake trout (LT) (skin-on muscle) from Great Slave Lake (GSL), Mackenzie River at Fort Good Hope (FGH), Great Bear Lake, Lake Laberge and Kusawa Lake in the Yukon. Bars represent mean + standard deviation for samples from the period 2003–2009. HBCDD was not determined in FGH burbot or in lake trout from Lake Laberge or Kusawa Lake.

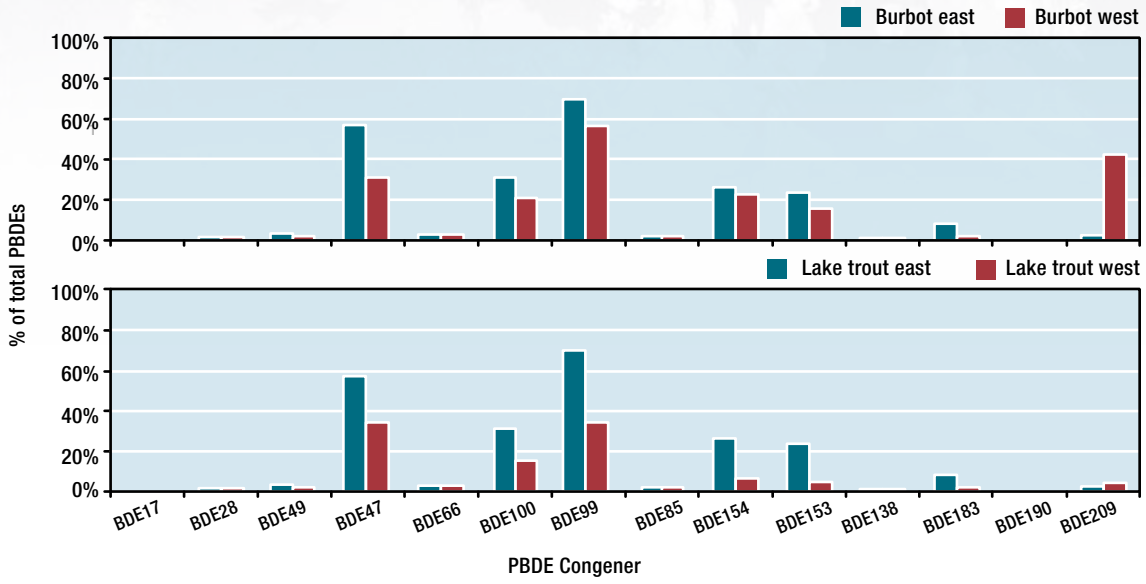

FIGURE 4.9

Relative proportions of individual PBDEs (tribromo to decabromidiphenyl ethers) in burbot and lake trout from Great Slave Lake.

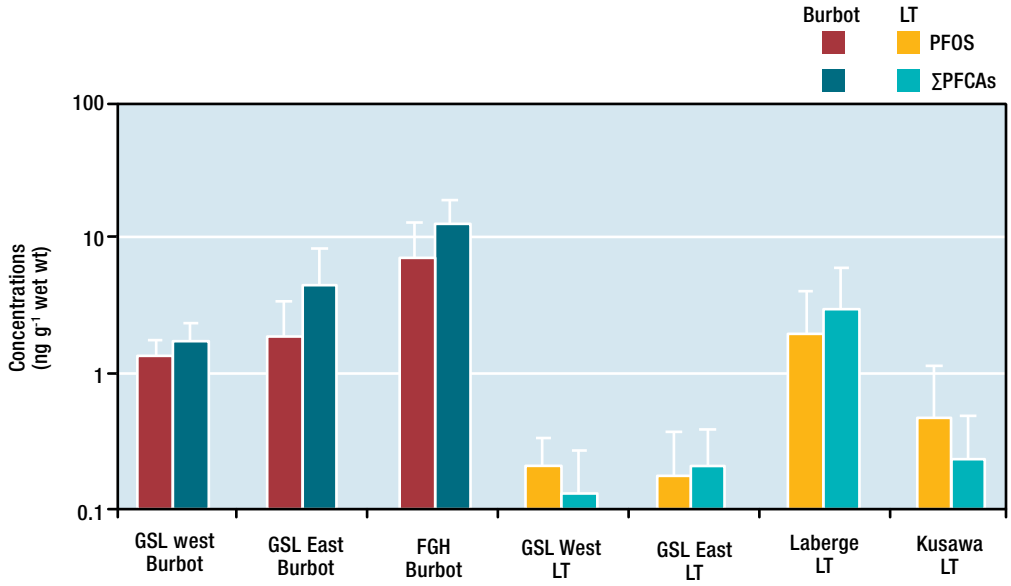

FIGURE 4.10

Concentrations of PFOS and total ΣPFCAs (PFHpA-PFDoA) in burbot liver and lake trout (LT) muscle from fish in Great Slave Lake (GSL), Mackenzie River at Fort Good Hope (FGH), Lake Laberge and Kuzawa Lake. Bars represent mean + standard deviation for samples from 2003–2009.

HBCDD was detected at low concentrations in burbot liver and in Great Slave Lake lake trout. It is quantified based on a γ-HBCDD standard by GC-MS and reported as total HBCDD. No measurements of HBCDD have been reported for the other locations in Figure 4.8. HBCDD levels were generally higher in burbot liver in the East Arm (2.4 ± 1.9 ng g^{-1} ww) than in the West Basin (1.4 ± 1.1 ng g^{-1} ww). For lake trout, HBCDD concentrations were similar in the West Basin and East Arm (0.04 ± 0.08 ng g^{-1} ww vs. 0.04 ± 0.09 ng g^{-1} ww), however, variability was also high (Figure 4.8).

PFASs in burbot and lake trout are shown in Figure 4.10. The spatial pattern of PFOS and total ΣPFCAs (sum of perfluoro hepta- to dodecanoate) in burbot liver was quite different from PBDEs with the highest concentrations in samples from Fort Good Hope. Lake trout from Lake Laberge had the highest levels

of PFOS and ΣPFCAs (Figure 4.10). PFAS was higher in burbot from Great Slave Lake East Arm than those in the West Basin. PFOS concentrations in lake trout (muscle) from Great Slave Lake over the period 2003–2009 were low, ranging from < 0.01 – 0.58 ng g^{-1} ww and did not differ between the East Arm and West Basin.

Endosulfan was detectable in burbot liver and lake trout from Great Slave Lake (Figure 4.5). Starting with 2008 collections, α-endosulfan, β-endosulfan and endosulfan sulfate were quantified in both burbot and lake trout samples using GC-negative ion MS rather than GC-ECD on which much of the previous measurements of endosulfan in Canadian arctic biota were based (Weber et al. 2010). Burbot liver had higher concentrations of endosulfan related compounds than lake trout. Endosulfan sulfate, the stable degradation product of endosulfan, was the major component, accounting for 95% of Σendosulfan in burbot liver and 89% of the total in lake trout muscle.

4.1.2.1.3. Landlocked arctic char

Concentrations of POPs in landlocked arctic char have been studied since 2003 in samples collected from Resolute, Char and Amituk Lakes on Cornwallis Island and from Lake Hazen in Quttinirpaaq National Park on Ellesmere Island. These locations were chosen because of the availability of previous data on POPs from these lakes (Evans et al. 2005, Muir and Lockhart 1994a) and of archived samples in the case of Lake Hazen (Gantner et al. 2009). Over the period 2003–2010, annual collections were made from Resolute Lake. It was less frequent for the other 3 lakes (7 out of 8 years) due to limited access (Lake Hazen) and lack of fishing success in some years (Char Lake, Amituk Lake).

4.1.2.1.3.1. POPs in landlocked arctic char

Toxaphene is the most prominent POP in landlocked arctic char from the Amituk and Hazen lakes while ΣPCBs outrank toxaphene in Char and Resolute lakes (Figure 4.11). The slightly higher ΣPCBs in Resolute (93 ± 67 ng g^{-1} ww; n=72) and Char lakes (74 ± 67 ng g^{-1} ww, n=32) compared to Amituk Lake which is 40 km north of Resolute and completely isolated (ΣPCB 29 ± 18 ng g^{-1} ww), may be a legacy of their proximity to the Resolute Bay airport and former military base (North Base) where PCBs could have been used in the 1950s and 1960s as they were at other military sites in the Canadian Arctic (Bright and Reimer 1993). While both lakes Resolute and Char are ultraoligotrophic, and have been since the first studies in the 1970s (Rigler 1975), they could

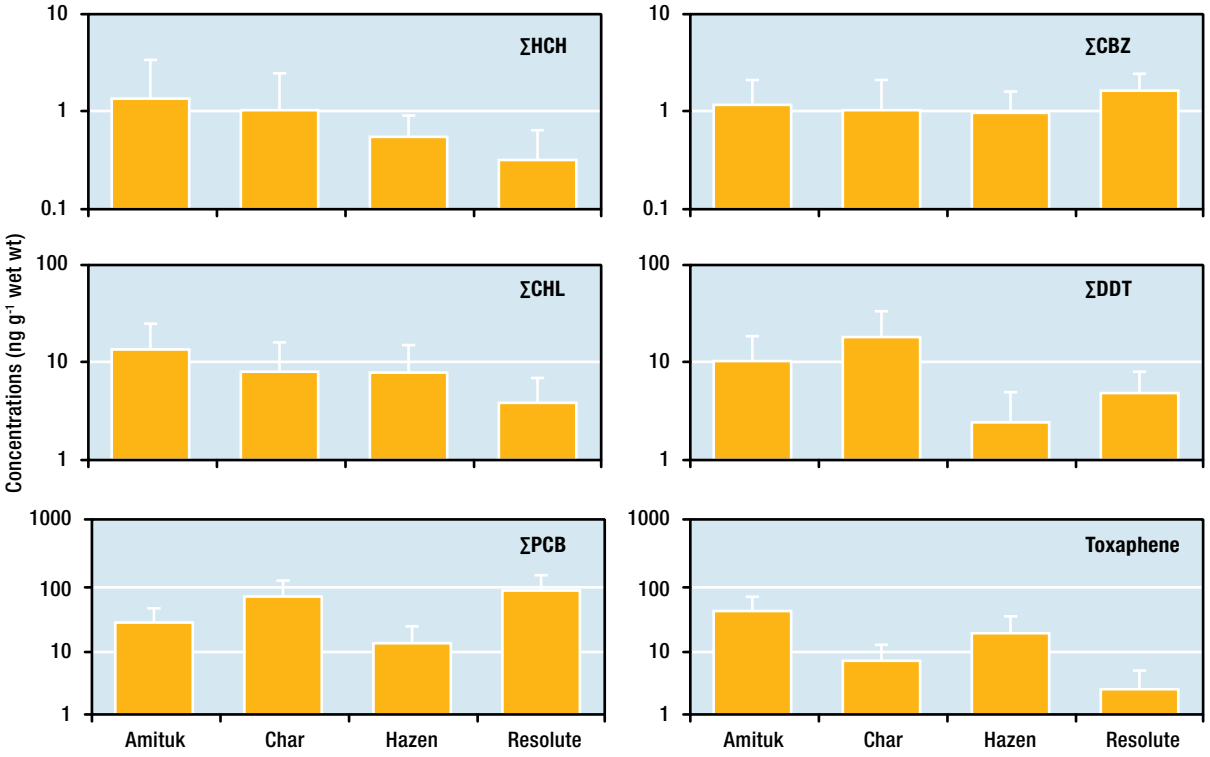

FIGURE 4.11

Mean concentration (and standard deviation) of major legacy POPs in landlocked arctic char (muscle+skin) samples from four arctic lakes over the period 2003–2009.

receive windblown dust from the building sites and unpaved roads that are within a 1–2 km radius. Resolute Lake is downstream of Meretta Lake that was impacted by wastewater discharges from the airport and miltary base (Michelutti et al. 2007) until 1998 when new wastewater facilities were built at the airport. Char Lake is more isolated from roads and development. PCB congener patterns were similar in Amituk, Char and Resolute lakes, with CB153 and CB138 predominating (together averaging 21, 28.5 and 25% of ΣPCBs). However, in Lake Hazen the proportion of these two hexachlorobiphenyl congeners was lower (14.7%) and tri- and tetrachloro-congeners were higher, reflecting the importance of atmospheric inputs of more volatile congeners to this high arctic lake (D. Muir, Environment Canada, unpublished data).

4.1.2.1.3.2. New POPs in landlocked arctic char

Landlocked arctic char have been analyzed for the same suite of new chemicals (Annex Table A4-2) determined in burbot, lake trout and sea-run char. PBDEs were detectable in all landlocked arctic char with mean concentrations for the period 2003–2009 ranging from 0.11 ng g^{-1} ww (n=50) in Lake Hazen to 4.6 ng g^{-1} ww in Char Lake (n=36) (Figure 4.12). BDE-47 was the major congener representing from 29% of ΣPBDEs in Lake Hazen to 49% of ΣPBDEs in char from Char Lake. HBCDD was also detectable at low concentrations (> detection limits of approximately 0.01 ng g^{-1} ww) in char from all 4 lakes, with highest concentrations observed in Char and Resolute Lakes. However, detection frequency was particularly low in Amituk Lake (15%) and Lake Hazen (4%). No other BFRs were detectable in landlocked arctic char.

PFASs were detectable in all landlocked arctic char in all lakes sampled to date (Figure 4.13). However, unlike all other new chemicals measured in fish, there was evidence for local contamination in Resolute Lake and in nearby Meretta Lake (Figure 4.13). As discussed in section 4.1.2.1.3.1, the Resolute Bay airport is within the catchment and Meretta Lake was impacted by wastewater discharges from the airport and miltary base (Michelutti et al. 2007) until 1998. Fire-fighting foams (aqueous film forming foams) containing PFOS as well as related compounds such as PFHxS were used in airports and military bases (Moody and Field 2000, Schultz et al. 2003) including Canadian Department of National Defense (DND) bases (Scott et al. 2007) and until 1998, waste water from the airport would likely have been washed into the waste water system and eventually getting into Meretta Lake. Measurements of lake water have also shown much higher levels of PFOS, PFHsS and PFOA in both Resolute and Meretta lakes than in nearby Char Lake (Stock et al. 2007)

The pattern of PFASs in the landlocked arctic char from eight arctic lakes shows that there are very similar concentrations of ΣPFCAs in most lakes (sum of PFOA-PFDoA) including Resolute Lake and Meretta Lake, indicating that the contamination is almost entirely due to products containing PFOS and related compounds. While Stock et al. (2007) found higher PFOA in water in Resolute and Char Lakes, this was not apparent in landlocked arctic char due to the low bioaccumulation potential of PFOA (Martin et al. 2003b). ΣPFCAs in char from Lac Pingualuk, the crater lake in Nunavik, were about 10 times lower than for other locations (0.018 ± 0.013 ng g^{-1} ww) including nearby Lac Laflamme (0.064 ± 0.061 ng g^{-1} ww) (Gantner et al. 2012).

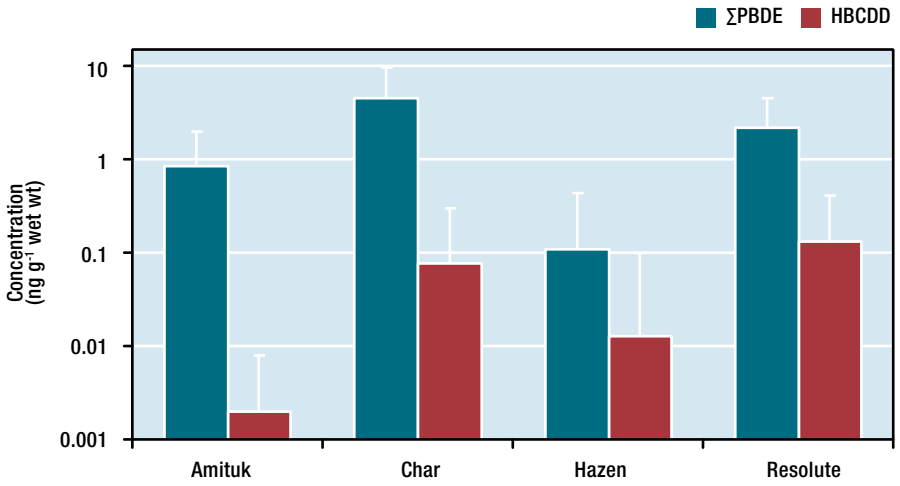

FIGURE 4.12

Mean concentrations (and standard deviations) of ΣPBDEs and HBCDD in muscle and skin of landlocked arctic char (2003–2009).

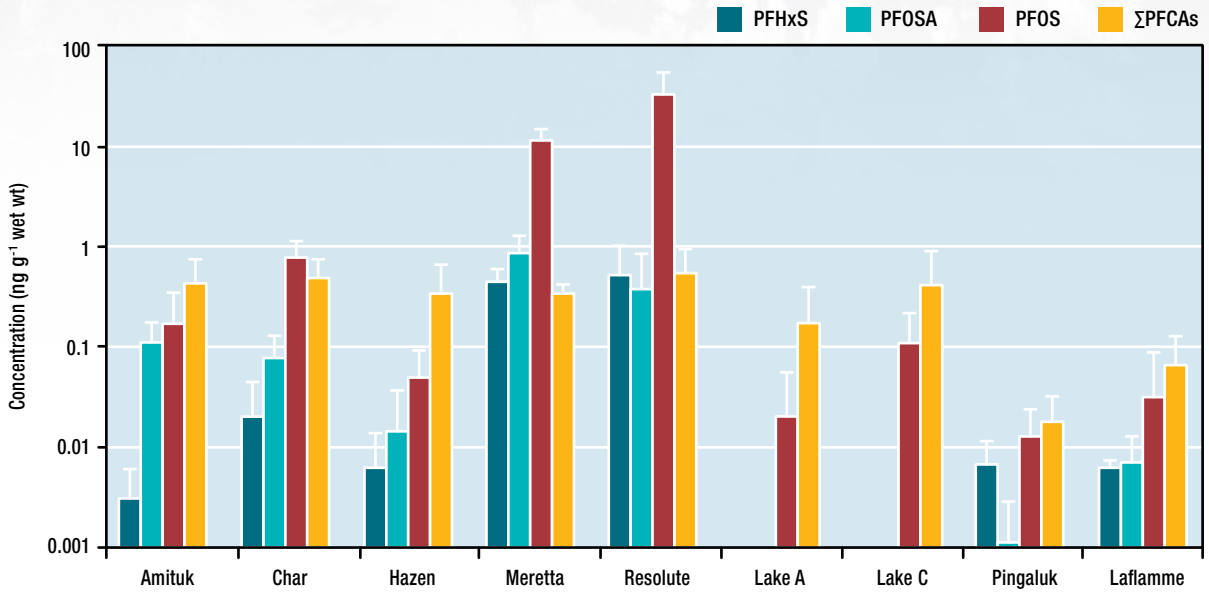

FIGURE 4.13

Mean concentrations (and standard deviation) of PFASs in landlocked arctic char muscle from eight arctic lakes over the period 2003–2010.

Unlike the other lakes, Lac Pingualuk, lacks a catchment. Thus inputs are entirely from the atmosphere compared with other lakes that have annual snow melt runoff, as well as glacial inputs in the case of Lake Hazen. Char in Lakes A and C from northern coastal Ellesmere Island had similar concentrations of PFOS and ΣPFCAs as char in Lake Hazen (Figure 4.13) (Veillette et al. 2012) suggesting relatively uniform contamination over a broad area of the High Arctic.

Endosulfan was determined in landlocked arctic char by GC-negative ion MS over the period 2003–2009. Unlike in lake trout and burbot liver, α-endosulfan and endosulfan sulfate were present at similar sub-ng g^{-1} concentrations while β-endosulfan was below detection limits (Figure 4.10.). No effect of distance from sources or from lake location relative to the village of Resolute Bay or the airport, was apparent since char from remote Amituk Lake (40 km north of Resolute Bay) had 3 times higher concentrations of total endosulfan than in Char Lake.

4.1.2.1.4. New POPs in other freshwater and anadromous fish

Martin et al. (2004a) determined PFASs in several freshwater species sampled in 2002 from the mouth of the Great Whale River at Kuujjuarapik in Quebec. PFOS and PFOSA were the dominant PFA in the liver of fish with mean concentrations of PFOSA ranging from 14 ng g^{-1} ww in lake whitefish (*Coregonus* sp) to 2.8 ng g^{-1} ww in brook trout.

Mean PFOS concentrations were greatest in brook trout (39 ng g^{-1} ww) and smallest in northern pike 5.7 ng g^{-1} ww. Although sample sizes in this study were limited, in general, for the PFCAs, the rank order of concentrations were PFUnA > PFNA ≈ PFTrA > PFDA ≈ PFDoA > PFTA > PFOA > PFPA.

Tomy et al. (2009b) determined PBDEs, HBCDD and PFASs in cisco (*Coregonus autumnalis*), an anadromous species, from the southern Beaufort Sea area. HBCDD was detectable in cisco averaging 1.0 ng g^{-1} (lw). For PFASs, the PFCAs predominated in cisco along with PFOSA.

Endosulfan isomers and endosulfan sulfate were determined salmon in eastern Hudson Bay using GC-high resolution MS and reported in supporting information published by Kelly et al. (2007). ΣEndosulfan, consisting mainly of α-endosulfan, was detectable in salmon muscle (Figure 4.10). Concentrations in salmon were lower than those reported for sea-run char in Hudson Bay (Arviat, Puvirnituq) and the pattern also differed, with endosulfan sulfate undetected in salmon but prominent in char.

4.1.2.2. Assessment of spatial trends in freshwater biota

- The rank order of concentrations of legacy POPs (PCBs, OCPs) in all arctic freshwater fish sampled between 2003 and 2010 was generally: toxaphene > ΣPCBs > ΣDDT > ΣCHL >> ΣCBz and ΣHCH. This order remained unchanged from the previous assessment period of 1998–2002 (Fisk et al. 2003).

- An exception to this ranking is in Resolute Lake and Char Lake where ΣPCBs > toxaphene. ΣDDT concentrations in lake trout in Lake Laberge were also similar to ΣPCBs and toxaphene. For Lake Laberge, as well as Char and Resolute Lakes, past contamination due to local use of DDT and PCB is the likely the reason for the different ranking.
- However, other variations between locations are also due to biological factors such as lipid content of the samples, age and growth rates. These factors have not been thoroughly evaluated in this assessment but are being examined by contributors responsible for the various studies.
- Toxaphene was the most predominant legacy POP in sea-run char, however, ΣHCH and ΣCBz concentrations were higher than ΣDDT. This may reflect the predominance of ΣHCH and HCB in seawater relative to other legacy POPs (see Chapter 3, section 3.2.2). The results for sea-run char represent the first comprehensive spatial trends information on this widely consumed species, since the late 1980s. No major geographic trends were evident in the legacy POPs in sea-run char.
- PBDEs, PFASs, along with Σendosulfan were the major "new" POPs detected in freshwater fish and sea-run char. ΣPBDEs were ≈ ΣCBz > ΣHCH in burbot liver and lake trout while Σendosulfan ≈ ΣPBDEs and PFASs in lake trout. All 3 groups of "new POPs" were present at much lower concentrations than toxaphene, ΣPCBs, ΣDDT and ΣCHL. An exception was in Kusawa Lake where ΣPBDEs were > ΣDDT and ΣCHL.
- No major geographic trends in ΣPBDEs in sea-run char were evident, except for slightly elevated concentrations in samples from Iqaluit which could be due to local sources given the relative size of the community compared to all the other sampling locations. However, legacy POPs were not elevated in the same samples.
- ΣPFCAs were greater than PFOS concentrations in all landlocked arctic char except in Resolute and Meretta Lakes; the latter explained by local contamination. ΣPFCA concentrations were similar in all 6 lakes within the Arctic Archipelago suggesting relatively uniform contamination over a broad area of the High Arctic. Compared with legacy POPs, ΣPFCAs were generally similar to ΣHCH and ΣCBz and much lower than PCBs or toxaphene. There are too few locations where sea-run char was analyzed for PFASs to assess spatial trends.
- Spatial coverage for legacy and new POPs in freshwater fish is limited. Coverage for lake trout was only in the Yukon, lake trout and burbot only in the Great Slave Lake, and for burbot at Fort Good Hope. No data were available for these species in other regions covered by the NCP.
- For anadromous fishes, geographical coverage was better with sea-run arctic char from 20 communities and studies that included salmon and cisco.

4.1.3. Terrestrial biota

4.1.3.1. Introduction

Evaluation of POPs in terrestrial animals and food chains has been less extensive than contaminant analyses in freshwater and marine organisms, presumably given the general trend of lower POP concentrations in arctic terrestrial biota (Braune et al. 1999, Gamberg et al. 2005). However, contamination of terrestrial biota is pertinent to understanding contaminant pathways, particularly for organisms that may be receiving predominantly atmospheric inputs. Furthermore, terrestrial biota comprise a key food source for people inhabiting the north.

Levels and spatial trends of POPs in terrestrial biota from the Canadian Arctic have been summarized in previous editions of CACAR and in related review articles. Braune et al. (1999) reviewed the literature to 1997 while Gamberg et al. (2005) reviewed the limited data published for the period of 1998–2003. A summary of POPs in terrestrial biota during the period 2003–2010 as well as earlier studies which were not reviewed in CACAR I and CACAR II is presented here. Data on contaminants in plants, mammals and birds are included. In addition, comparisons are made where possible between measurements in biota sampled in Canada vs. other Arctic areas. Figure 4.14 illustrates the locations of biota that were sampled. Studies of biomagnification of POPs in the arctic terrestrial food web are discussed in section 4.1.4.

4.1.3.2. Terrestrial plants and lichens

4.1.3.2.1. Legacy POPs in vegetation

Terrestrial vegetation in the arctic ecosystem occupies the base of the food web for many organisms. Plants are often consumed by local terrestrial herbivores and omnivores including moose, beaver, muskrat and migratory waterfowl.

Lichen (*Cladonia rangiferina* and *Cetraria nivalis*) and willow leaves (*Salix glauca*) were collected in 1997 and 1998 as a part of a terrestrial food web study in the Bathurst Inlet area of Nunavut (Kelly and Gobas 2001). The major contaminants detected in lichen and willow leaves were α-HCH and γ-HCH

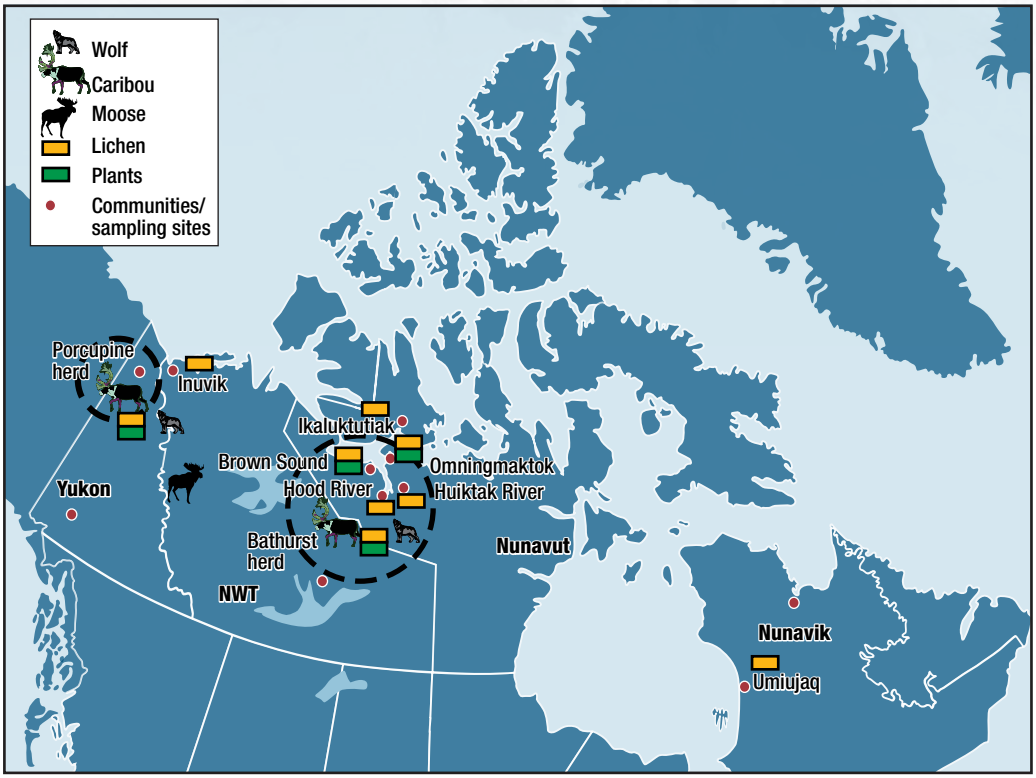

FIGURE 4.14

Sampling locations of terrestrial plants, lichen and mammals sampled in studies by Kelly and Gobas (2001), Kelly et al. (2007), Müller et al. (2011) and Morris et al. (2010b).

isomers, HCB, *p,p'*-DDT, and PCBs (congeners 52, 66/95, 153, 138, 110, 101, 118, 170/190). Concentrations of major groups of legacy POPs in lichen collected in summer are shown in Figure 4.15. Lichen had higher concentrations of all POPs than willow leaves. *C. nivalis* had higher concentrations than *C. rangiferina*. Both lichen form thick carpets over arctic soils.

Kelly and Gobas (2001) also analyzed lichen that was sampled in the spring during the snowmelt period. They found much higher concentrations of all POPs, particularly PCBs which were 100 times higher than in collections taken in summer in the same area (Bathurst Inlet). They hypothesized that snow sublimation could concentrate less volatile contaminants such as PCBs and release relatively volatile pollutants such as HCHs and HCB. This hypothesis was confirmed by measuring the fugacity of POPs and the result of PCB partitioning from spring melt-water to lichen. In more recent work, Kelly et al. (2007) reported a similar suite of legacy POPs in lichen from the Umiujaq area in Nunavik. Concentrations (compared on a ng g^{-1} dw basis) were generally lower in the Nunavik samples than in the Bathurst area (Figure 4.15).

Choy et al. (2010) measured PCBs and DDTs in jewel lichen (*Xanthoria elegans*) and worm lichen (*Thamnolia vermicularis*) in Cape Vera on Devon Island and Cape Herschel on Ellesmere Island, both in Nunavut, Canada. These samples had variable congener profiles of PCBs but were dominant in PCB-153, -138/163, -180, and -118. Lower concentrations of PCBs and DDTs were noted in lichen sampled away from the seabird colony, potentially suggesting that breeding seabirds were responsible for transporting and depositing these pollutants into lichen and plants at the base of the terrestrial food web at this location. Further discussions on the results of this study are given in section 4.1.4.3.

4.1.3.2.2. New chemicals in vegetation

PBDEs, PFASs and current use pesticides (CUPs) have recently been reported in arctic plants and lichen. Kelly et al. (2008a) reported detectable concentrations of PBDE congeners (9.3 ng g^{-1} lipid; n=11) in lichen (*C. rangiferina*) from the Umiujaq area in Nunavik. BDE-47 represented about 39% of ΣPBDE (sum of di-heptaBDEs).

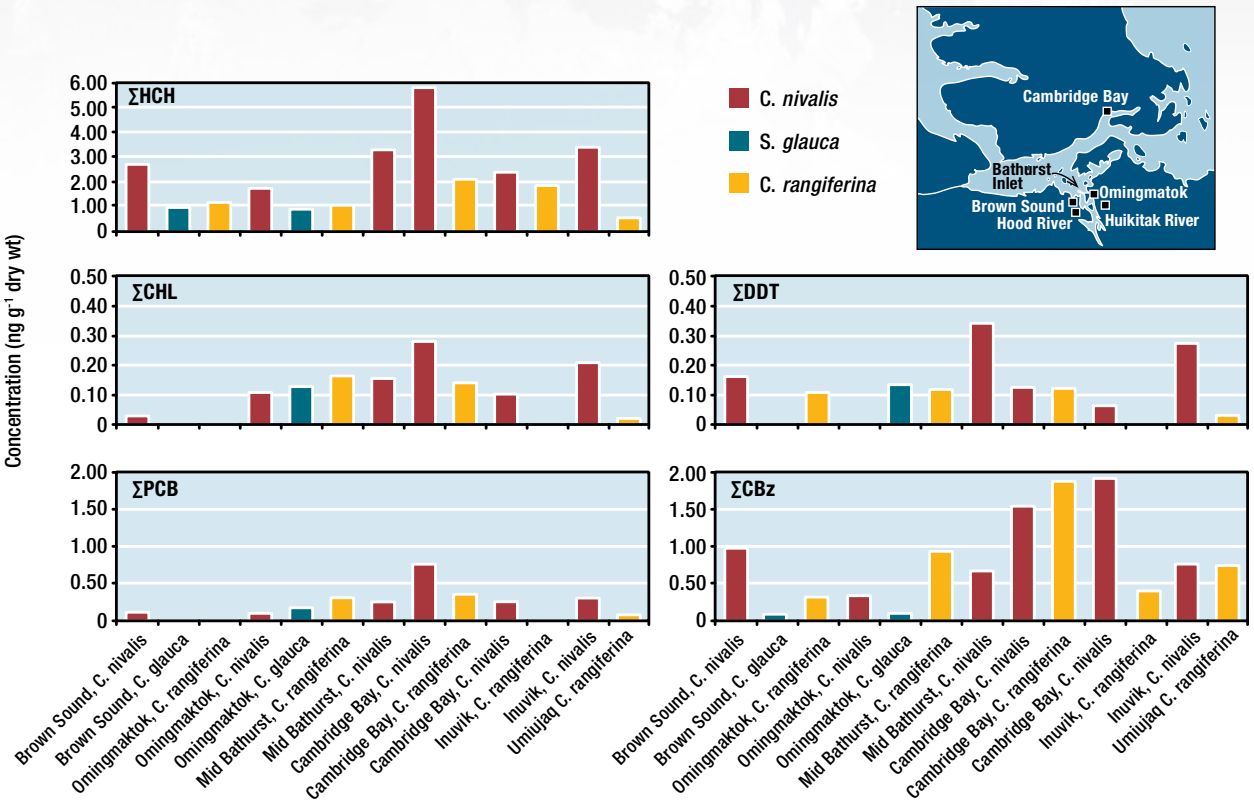

FIGURE 4.15

Geometric mean concentrations (ng g^{-1} dw) of legacy POPs in lichen (*C. nivalis, C. rangiferina*) and willow leaves (*S. glauca*) from the Bathurst Inlet, Cambridge Bay and Inuvik areas analyzed from 1994 to 2001 and from the Umiujaq area for the period 1999–2002. Calculated with results from (Kelly and Gobas 2001; Kelly et al. 2007).

Morris et al. (2010b) analyzed PBDEs and CUPs in vegetation including reindeer lichen (*C. rangiferina*), stunted willow (*Salix sp.*), mosses (*Rhytidium sp., Polytrichium sp.*) mushrooms, and grasses collected in August 2009 in the Bathurst Inlet area (Figure 4.16) as part of a terrestrial food web study. Five CUPs were detectable in all plants and lichen: pentachloronitrobenzene (PCNB), chlorothalonil chlorpyrifos, dacthal and α- and β-endosulfan isomers along with endosulfan sulfate. The average concentrations of the 5 CUPs were in the ranged from 1 to 80 pg g^{-1} ww with lichen having highest levels. In the same samples, ΣPBDEs (BDE-28, -47, -99, -100, -138, -154, -183) and BTBPE were detectable in moss, lichen, grass and willow. Average concentrations of ΣPBDEs ranged from 438 pg g^{-1} ww in mushrooms to 940 pg g^{-1} ww in lichen. Further details are given in Annex Table A4-3.

Katz et al. (2009) and Müller et al. (2011) detected low levels of PFASs in plants and in the lichen from locations in the northern Yukon and from western Nunavut near Bathurst Inlet. Overall average concentrations of PFOS and ΣPFCAs in lichen (*C. rangiferina*) in the two regions were similar. However, unlike the results for CUPs and PBDEs reported by Morris et al. (2010b) the pattern of PFASs differed widely between vascular plants and lichen (Figure 4.17). Lowest average ΣPFCA concentrations were found in water sedges and cottongrass in the northern Yukon (0.01–0.02 ng g^{-1} ww), while the cottongrass in the Bathurst Inlet area had higher average concentrations (0.12 ± 0.04 ng g^{-1} ww). Higher ΣPFCA concentrations were found in lichen (0.17–0.22 ng g^{-1} ww) and willow (0.08–0.26 ng g^{-1} ww) and were similar in both areas investigated. The PFCA composition differed among types of vegetation. All plants (grass, sedge, willow and moss) are dominated by perfluorooctanoate (PFOA), while both lichen species showed a dominance of the odd carbon chain lengths ($C_8 < C_9$ $C_{10} < C_{11}$ $C_{12} < C_{13}$).

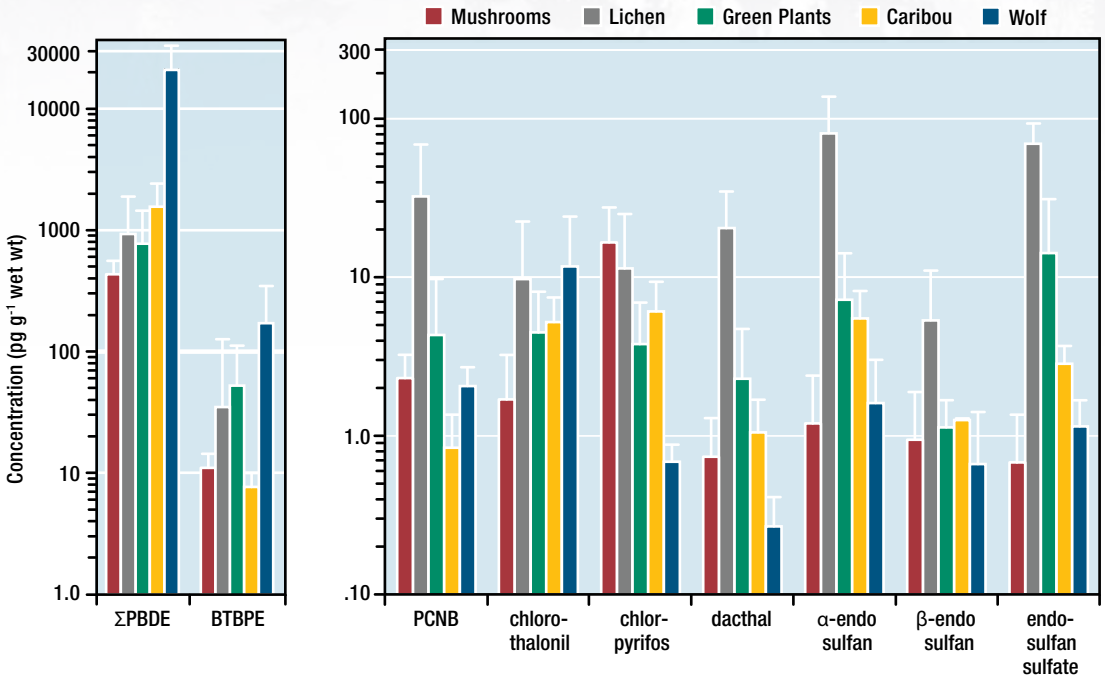

FIGURE 4.16

(A) PBDEs and BTBPE and (B) current use pesticides in all plants and lichen, caribou and wolf samples from the Bathurst Inlet area (Morris et al. 2010b). Bars represent mean concentrations (+ standard deviation). For caribou and wolf concentrations represent a whole body basis (A. Morris, University of Guelph, unpublished data).

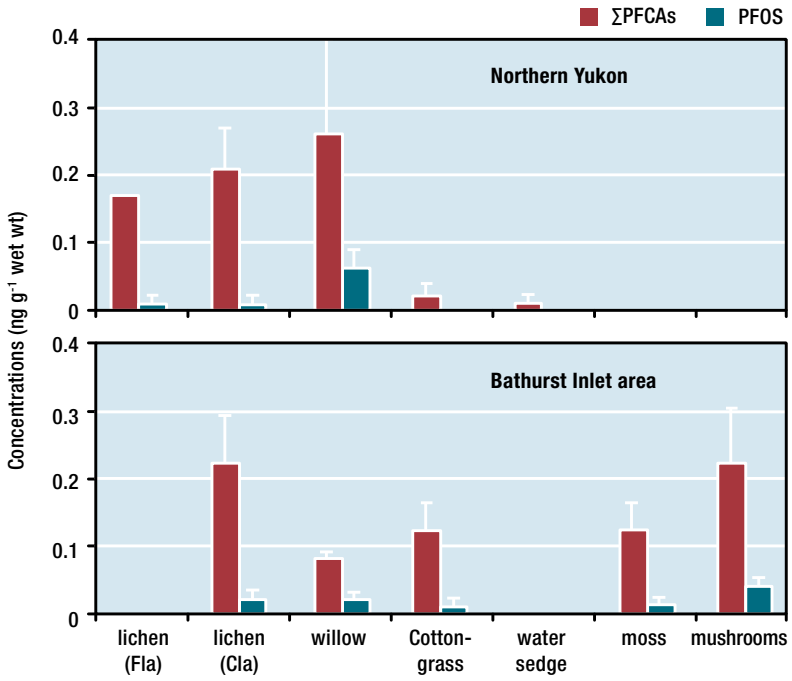

FIGURE 4.17

Concentrations (and standard deviation) of ΣPFCAs (sum PFOA, PFNA, PFDA, PFUnA, PFDoA) and PFOS in plants and lichen from the summertime Porcupine herd area of northern Yukon and the Bathurst herd area of NWT and western Nunavut. Lichen (Fla) = *Flavocetratia nivalis/cucullata* (N. Yukon only); lichen (Cla) = *Cladina mitis/rangiferina*; willow = *Salix pulchra*; cottongrass = *Eriophorum vaginatum*; water sedge = *Carex pulchra*; moss = *Rhytidium rugosum*; mushrooms (unidentified species). From Müller et al. (2011).

4.1.3.3. Legacy POPs in terrestrial mammals

4.1.3.3.1. Terrestrial carnivores

Studies on POPs in terrestrial carnivores including wolf, arctic fox, wolverine, marten, and mink were included in reviews by Braune et al. (1999) and Gamberg et al. (2005). No new studies were conducted specifically on legacy POPs in terrestria carnivores during the period 2003–2011. Thus previous results are briefly summarized here and studies on new POPs are discussed separately.

4.1.3.3.1.1. Legacy POPs

Gamberg and Braune (1999) measured 22 organochlorine pesticides (OCPs) and 97 PCB congeners in liver from wolves (*Canis lupus*) sampled in 1993 and 1994 in southern Yukon. In general, organochlorines were lower in wolf liver compared to prey species moose and caribou. (reviewed in Braune et al. (1999). Chlorobenzenes (CBzs) were observed at 3.7–4.9 ng g^{-1} ww in liver, of which 55% was dichlorobenzene and 36% was HCB. ΣCHL ranged from 0.5 ng g^{-1} ww to 4.9 ng g^{-1} ww. PCBs were abundant (0.7 ng g^{-1} ww to 15.1 ng g^{-1} ww) and hexa- and hepta-chlorinated congeners were the major homolog group. The ΣPCB concentrations in wolf liver reported by Gamberg and Braune were significantly less than in livers of mink and marten from the NWT, reported by Poole et al. (1995). Comparing the same samples, dieldrin and ΣCHL were similar and HCB was higher in the Yukon wolves. Their dietary habits and habitat may account for some of these differences; marten and wolves are both terrestrial carnivores while mink may also consume fish. Gamberg and Braune (1999) noted that many terrestrial herbivores are marked by PCB congener profiles where tri- and tetra-chlorinated PCBs dominate, highlighting that this could be due to the lower rates of metabolism of more chlorinated PCBs in higher trophic level animals.

In their food chain study, Kelly and Gobas (2001) utilized data first reported by Elkin (1994) for OCPs and PCBs in wolf liver, muscle and fat from the Bathurst caribou herd area northeast of Yellowknife, and from Cambridge Bay and Inuvik areas. Mean (lipid weight) concentrations of major POPs (HCB, ΣHCH, ΣCHL and ΣPCBs) were very similar in wolves from all three regions.

Exposure of arctic fox to POPs has been extensively studied in Svalbard with wild foxes (Fuglei et al. 2007) and captive studies (Sonne et al. 2009). However, there has been no further study of contaminants in arctic fox in Canada since the work of Hoekstra et al. (2003b) which was included in CACAR II and reviewed by Gamberg et al. (2005).

4.1.3.3.1.2. New POPs

PBDEs, PFASs and current use pesticides (CUPs) have recently been reported in arctic wolves (Morris et al. 2010b, Müller et al. 2011) and are briefly discussed here. See the Terrestrial Food web (section 4.1.4) for discussion of trophic bioaccumulation of these new POPs.

Morris et al. (2010b) analyzed PBDEs in wolf muscle and liver from the Porcupine herd grazing area of northern Yukon and the Bathurst herd range in NWT-western Nunavut. Major PBDE congeners in wolf tissues were BDE-47, -99, -100 and ΣPBDEs averaged 21,000 pg g^{-1} ww (Figure 4.16). BTBPE was also detected in wolf liver and muscle at low pg g^{-1} levels (Figure 4.16).

Morris et al. (2010b) detected the CUPs, dacthal, chlorpyrifos, chlorothalonil, pentachloronitrobenzene (PCNB) and endosulfan (α- and β- isomers and sulfate) in wolf tissues at low pg g^{-1} ww concentrations. Endosulfan sulfate was the major form of endosulfan in wolf tissues, averaging 3.6 pg g^{-1} ww, while α-endosulfan was present at 1.5 pg g^{-1} ww (Figure 4.16). Morris et al. (2010b) included a larger suite of CUPs that were analysable by GC-negative ion MS, but all the others were not detected in wolf tissues.

Müller et al. (2011) determined PFASs in wolf muscle and liver from the Porcupine herd grazing area of the northern Yukon and the Bathurst herd range in NWT-western Nunavut. Wolves had concentrations of ΣPFCAs and PFOS in the low ng g^{-1} ww range. Highest concentrations in liver were observed for PFNA (4.7 ± 0.9 ng g^{-1} ww and 7.4 ± 1.3 ng g^{-1} ww for Yukon and Bathurst, respectively) and PFUnA (2.4 ± 0.4 and 6.4 ng g^{-1} ww ± 1.2 ng g^{-1} ww, respectively). PFOS was a relatively minor component (1.4 ng g^{-1} ww ± 0.3 ng g^{-1} and 1.7 ± 0.1 ng g^{-1} ww, respectively). Concentrations of PFOS present in wolf liver were 5 to 15 times higher compared to muscle, and the contribution of liver concentrations to the whole body burden was about 10% to 40%. Concentrations of PFDA and PFUnA were higher in the Bathurst wolves. Concentrations of PFASs in wolf liver and muscle were not significantly correlated with age so it was unlikely to explain the geographical differences.

As part of an assessment of PFASs in a diverse sample set from the Canadian Arctic, Martin et al. analyzed arctic fox from Arviat and mink from the Watson Lake Area of the Yukon (Martin et al.

2004a). Both sample sets were collected in 2001. Similar to arctic fox, mink cannot be considered to have a solely terrestrial dietary feeding strategy since there are aquatic-based inputs too. In all of the organisms analyzed for this study, which included polar bears, ringed seals, bearded seals, fish and marine birds, total perfluoroalkylsulfonates (ΣPFSAs) exceeded ΣPFCAs. PFOS was the dominant PFSA congener and is bioaccumulative. The mean concentration of perfluorononanoate (PFNA) in mink exceeded that reported in ringed seals, birds, and fish but was less than PFNA measurements in polar bears and fox (Martin et al. 2004a; Butt et al. 2010). Interestingly, mink was the only species in the survey in which PFNA was greater than PFOS. The higher PFCAs in mink and wolves, compared to animals feeding in the marine environment, may imply differences in sources.

4.1.3.3.2. Terrestrial herbivores

The studies by Elkin and Bethke (1995) on PCBs and OCPs and studies by Hebert et al. (1996) on PCDD/Fs and co-planar PCBs remain the only large scale studies of POPs in caribou in the Canadian Arctic. Elkin and Bethke (1995) included samples from the Bathurst, Qamanirjuaq (Arviat), Southampton Island, Cape Dorset and Kimmirut herds. Caribou from the Cambridge Bay and Inuvik areas were also sampled and results reported in Kelly et al. (2001), while Hebert et al. (1996) included the Finlayson, Tay and Bonnet Plume herds from southern Yukon. The major compounds in caribou were α-HCH, β-HCH, 1,2,4,5-TCB, HCB, oxychlordane, *p,p'*-DDE, and PCB congeners (118,138,153,180). Both Hebert et al. (1996) and Elkin and Bethke (1995) showed that a distinct geographical trend existed for HCB, ΣCHL, ΣPCBs and ΣPCDD/Fs, with higher concentrations in samples (fat) in the two Baffin Island herds. Dieldrin, ΣHCH, ΣDDT did not show clear trends.

4.1.3.3.2.1. Legacy POPs

Larter et al. (2011) determined PCBs and OCPs in moose liver from the Dehcho Region of the Northwest Territories. ΣPCBs were the major legacy POP in moose liver with concentrations ranging from 0.36–2.6 ng g^{-1} ww. The relative ranking of POPs in moose was ΣPCBs > toxaphene > ΣCBz > ΣHCH> ΣCHL > ΣDDT. Compared on a lipid basis, the ΣPCBs in moose liver were similar to results for caribou from the Bathurst herd (Elkin and Bethke 1995, Kelly and Gobas 2001). A study of POPs in moose in Finland (Suutari et al. 2009) reported PCBs (the sum 37 congeners) averaging 5.4 ± 2.8 ng g^{-1} lw which was almost identical to the Dehcho moose when the sum of same congeners (4.7 ± 1.7 ng g^{-1} lw) was calculated. However the PCB congener pattern appeared to be different with lower chlorinated congeners representing a higher proportion of the ΣPCBs in the Dehcho moose than in those from Finland. Results for other legacy POPs in moose liver from the Dehcho are summarized in Annex Table A4-4.

Photo: Yukon government

In addition to vegetation analysis, Choy et al. (2010) measured PCBs, DDT, and DDT-derivatives in terrestrial wildlife in Cape Vera, Devon Island (Nunavut, Canada). Sampled organisms consisted of northern collared lemmings, snow bunting and ermine. Snow buntings were the most contaminated, followed by ermine and lemmings. PCB levels in these buntings exceeded those reported in buntings in Rankin Inlet in the early 1990s (Johnstone et al. 1996) by approximately eight-fold. The buntings feed on the invertebrae chironomids, which likely accumulate POPs at the aquatic larval stage via sediment. Although ermine are a top predator that feed primarily on lemmings, lower concentrations of legacy POPs were found than for those in buntings. Lemmings had PCB and DDT concentrations that were near the limit of detection. Biomagnifying PCBs (PCB-153, -118, -138/163, -180, and -99) were dominant congeners in snow buntings and ermine. Lemmings also had high proportions of PCB-153, PCB-138/163, and PCB-180, but had more variation in their congener profiles.

4.1.3.3.2.2. New POPs

Larter et al. (2011) analyzed PBDEs and PFASs in the liver of moose from the Dehcho Region. PFASs were the major POPs in moose liver ranking ahead of PCBs and PBDEs (ΣPFCAs > PFOS > ΣPCBs > ΣPBDEs). Concentrations of PFASs in moose liver ranged from < 0.01–1.1 ng g^{-1} ww for PFOS and from 2.2–4.3 ng g^{-1} ww for ΣPFCAs. This is the first report of PFASs in moose but the relative prominence of the PFASs was anticipated based on results for caribou liver from the Canadian Arctic, where they are also present at low ng g^{-1} ww concentrations (Ostertag et al. (2009) discussed below). The pattern of individual PFASs in moose is compared with caribou, and wolves in Figure 4.18. In all species, the 9 to 11 carbon perfluorocarboxylates PFNA-PFUnA predominated.

Morris et al. (2010b) detected five CUPs at low pg g^{-1} concentrations in caribou muscle and liver from the Bathurst herd (Figure 4.16). Endosulfan sulfate was the most prominent CUP in liver averaging 92 pg g^{-1} ww and 2.5 pg g^{-1} ww on a whole body basis (Figure 4.16). In muscle, chlorothalonil, chlorpyrifos, and α-endosulfan were present at 8, 9 and 9 pg g^{-1} ww, respectively, while ES was less prominent (2.5 pg g^{-1}).

Müller et al. (2011) measured PFASs in the liver and muscle of caribou from the Porcupine herd in the northern Yukon and the Bathurst herd from NWT-western Nunavut as part of a terrestrial food web study (see section 4.1.4.4). Highest PFAS liver concentrations were found for PFNA (2.2 ± 0.2 ng g^{-1} ww and 3.2 ± 0.4 ng g^{-1} ww for the Porcupine and Bathurst herd, respectively) followed by perfluorodecanoate (PFDA, 1.9 ± 0.1 ng g^{-1} ww and 2.2 ± 0.2 ng g^{-1} ww, respectively) and perfluoroundecanoate (PFUnA, 1.7 ± 0.1 ng g^{-1} ww and 3.2 ± 0.2 ng g^{-1} ww, respectively). The Bathurst caribou had relatively high PFOS concentrations (2.2 ± 0.3 ng g^{-1} ww) compared to the Porcupine herd. In general, ΣPFCAs and PFOS were about 2-fold higher in the Bathurst herd. This geographical difference may be due to the more remote location of the Porcupine herd relative to sources of PFASs although concentrations in lichen were similar (Figure 4.17). Differences in diet may also play a role.


Photo: Eric Loring

Many terrestrial organisms comprise a portion of traditional diets in the Canadian north and this introduces concern for human exposure to contaminants. Ostertag et al. (2009) measured PFAS in terrestrial mammals collected in Nunavut in order to estimate human exposure via a traditional Inuit diet. Caribou, ptarmigan, arctic hare and snow goose were caught in Nunavut in 1997–1998 from Chesterfield Inlet, Igloolik, Pond Inlet and Qiqiktarjuaq. The following tissues from caribou were analyzed: liver, meat, bone marrow, heart, blood, fat, kidneys, stomach and tongue. For ptarmigan, hare and goose, PFASs in meat or whole body homogenate were measured. Caution should be taken in interpreting the results of the study since the sample size was small, typically consisting of n=1 to n=3. Caribou liver was the most contaminated, comprised of 5.0 ng g^{1} ww PFOS, 0.7 ng g^{-1} PFOA, 1.6 ng g^{-1} PFNA, 0.6 ng g^{-1} PFDA, and 1.1 ng g^{-1} PFUnA.

The PFAS burden in caribou meat (muscle) was considerably less, with most analytes not observed above detection limits with the exception of PFNA that ranged from 0.3 ng g^{-1} to 1.0 ng g^{-1}. PFASs in other caribou tissues were all generally < LOD. In addition, PFASs were not observed in ptarmigan, arctic hare or snow goose, except for 1.2 ng g^{-1} PFNA in snow goose meat. With the exception of caribou meat, marine organisms in the traditional Inuit diet contained higher concentrations of PFASs, particularly blood and liver from ringed seal and polar bears where ΣPFC ranged from 5.0–7.7 ng g^{-1} ww.

Larter et al. (2011) also detected PBDEs in moose liver ranging from 0.01–0.93 ng g^{-1} ww. Decabromodiphenyl ether (BDE-209) was the major PBDE detected in all samples representing an average of 44% of ΣPBDEs. Mariussen et al. (2008) reported ΣPBDE concentrations in moose from Norway ranging from 0.42–9.4 ng g^{-1} lw which was comparable to the Dehcho moose (0.2–14.6 ng g^{-1} lw). They observed BDE-209 but could not distinguish it from blank values. Similarly Larter et al. (2011) noted greater uncertainty in the detection of BDE-209 due to its presence in laboratory blanks.

4.1.3.4. Contaminants in terrestrial birds

Braune and Malone (2006) analyzed legacy POPs in autumn-harvested game birds collected between 1991 and 1994 from northern Canada including locations in the Yukon, Northwest Territories, Nunavut and northern Quebec. The bird species were comprised of rock ptarmigan, willow ptarmigan, ruffed grouse, spruce grouse and sharp-tailed grouse. Both ptarmigan and grouse are not considered migratory birds and contaminant levels were interpreted as reflecting environmental levels for the corresponding regions. In this research, pectoral muscle (breast tissue) was analyzed as a means of assessing human exposure. With a detection limit of 0.1 ng g^{-1} ww and a limit of quantitation (LOQ) of 1.0 ng g^{-1}, most samples were below or at the LOQ for ΣPCB, ΣDDT, ΣCBz, ΣCHL, ΣHCH, Σmirex, and dieldrin. Of the species in this study, spruce grouse had the highest observed maxima wet weight concentrations for ΣPCB (8.0 ng g^{-1}), ΣDDT (2.0 ng g^{-1}), ΣCBz (2.0 ng g^{-1}), ΣCHL (3.0 ng g^{-1}), and dieldrin (5.0 ng g^{-1}). In comparison, breast tissue collected from American woodcock (*Scolopax minor*) near Montreal had much higher concentrations of ΣPCB (max 12 ng g^{-1} ww) and

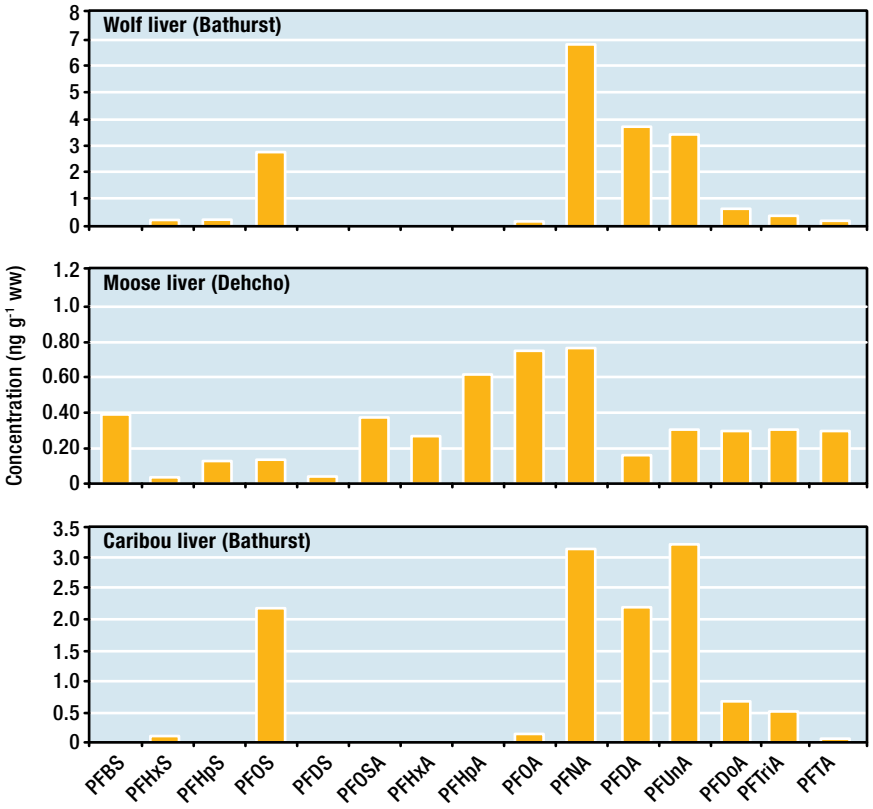

FIGURE 4.18

Mean concentrations of PFASs (ng g^{-1} ww) in wolf liver, caribou liver and moose liver from the Northwest Territories, illustrating the relative proportions of each.

ΣDDT (max. 22 ng g^{-1} ww). This is indicative of lower concentrations of organochlorines in these remote areas compared to lower latitudes and urbanized regions. Ptarmigan and grouse occupy a low trophic position and feed on terrestrial vegetation and some insects. In addition, the results suggest that breast muscle is not a target tissue for these contaminants.

Tsuji et al. (2007) determined legacy POPs in game birds harvested during the spring months (March to May) in western James Bay with the rationale that most birds for human consumption are caught in the springtime. Breast tissue was analyzed in mallard ducks, northern pintails, Canada geese, and lesser snow geese. Both mallard ducks and pintail ducks had detectable levels of most POPs compared to snow geese, Canada geese and godwits, which were less contaminated. Consistent with previous findings by Braune and Malone (2006), ΣPCBs and ΣDDT were the most frequently detected and HCH was the least frequently observed. The results by Tsuji et al. highlight the importance of the sampling season since PCBs were elevated in spring-sampled mallards compared to those harvested in the fall season. Percent lipid levels were not statistically different for these species between the two seasons. Trophic level and feeding habits were proposed to account for inter-species differences whereby dabbling ducks had higher levels of organochlorines compared to grazing geese.

Concentrations in the breast tissue analyses of terrestrial game birds by Braune and Malone (2006) or Tsuji et al. (2007) indicated overall low legacy POPs concentrations, similar to terrestrial herbivores such as moose, and lower than in caribou. Other studies of arctic terrestrial birds have also found low concentrations of POPs. Vorkamp et al. (2004) measured chlorinated compounds in ptarmigan (*Lagopus mutus*) sampled in Greenland in 2004. Concentrations of OCPs (heptachlor, dieldrin, aldrin and endrin pesticides) were higher in ptarmigan and hares compared to caribou, lamb and muskox. However dieldrin and mirex concentrations in ptarmigan from Greenland were < 0.1 ng g^{-1} ww for both liver and muscle. By contrast, for ptarmigan from the Candian Arctic, mirex and dieldrin levels ranged from 1–5 ng g^{-1} ww (de March et al. 1998).


Photo: Adam Collingwood/ArcticNet

4.1.3.5. Assessment of levels and spatial trends of POPs in terrestrial biota

- Limited data for POPs in terrestrial game birds and waterfowl, caribou, moose, and wolves confirms much lower levels of most POPs compared with those in top predator fish, seabirds and marine mammals.
- An exception are the PFASs, where concentrations in liver of caribou are comparable to levels of PFASs in fish muscle and ringed seal liver. PFASs were the major POPs in caribou and moose with concentrations in liver ranking ahead of PCBs and PBDEs (ΣPFCAs > PFOS > ΣPCBs > ΣPBDEs).
- PFOS and other perfluorinated compounds were higher in caribou liver than in muscle and this was found to be the case for other mammals in the traditional diet as well.
- Concentrations of PCBs and OCPs in the breast tissue of terrestrial game birds were low as well, similar to terrestrial herbivores such as moose, and lower than in caribou.
- Very limited data for new POPs, such as PFASs in terrestrial game birds, indicates low concentrations compared to legacy POPs.
- Spatial coverage of results for POPs in terrestrial biota is limited. There are limited or no data for caribou in the eastern Arctic (Nunavik, Baffin, Nunatsiavut).
- There has been no further study of contaminants in arctic fox in Canada since the work of Hoekstra et al. (2003b). However, exposure of arctic fox to POPs has been extensively studied in Svalbard with wild foxes (Fuglei et al. 2007) and captive studies (Sonne et al. 2009). Further work with arctic fox should be considered.

4.1.4. Terrestrial food web studies

4.1.4.1. Introduction

Although many measurements have been made of POPs in terrestrial animals, studies on the bioaccumulation of POPs encompassing entire terrestrial food webs (Choy

et al. 2010, Katz et al. 2009, Kelly and Gobas 2001, Salisbury et al. 1992, Thomas et al. 1992) are limited compared to those involving freshwater and marine species and this has been a major gap in arctic contamination research. They were not reviewed in the previous CACAR (Fisk et al. 2003). The focus of most POPs measurements in terrestrial animals and vegetation in the Arctic has been on lichens, caribou and wolves. In general, this is considered a linear food chain whereas the tundra ecosystem receives contaminants from the atmosphere, which then partition from air to lichen, dry deposition and wet deposition (Figure 4.19). Further partitioning may occur during seasonal snowmelt periods. Some of these animals undergo pack migration and have seasonal movement, which introduces another mode of contaminant transport.

The terms biomagnification and bioaccumulation are used in this section as well as in the section on marine food web studies (section 4.16). Bioaccumulation is defined here as the process that causes an increased chemical concentration in an organism compared to that in its ambient environment, through all exposure routes including dietary absorption and transport across body surfaces. Biomagnification is a special case of bioaccumulation in which the chemical concentration in the organism exceeds that in its prey due to the dietary absorption occurring faster than the elimination. Trophic dilution is the less common case of declining concentrations with increasing trophic level (Borgå et al. 2012).

4.1.4.2. Lichen-caribou-wolf food chain studies with legacy POPs

Kelly and Gobas (2001) measured PCBs and OCPs in the lichen-caribou-wolf food chain in the Canadian central (Bathurst Inlet area) and western Arctic (Inuvik). Their dataset consisted of POPs in lichen samples from Bathurst Inlet, Cambridge Bay and Inuvik, sampled by Government of Northwest Territories (GNWT) scientists between 1992 and 1995, and lichen (*C. rangiferina and C. nivalis*) and willow samples from several locations close to Bathurst Inlet and Cambridge Bay collected in 1997–1998. Data for caribou were based on liver, muscle and fat tissues of male and female caribou and wolves were collected between 1992 and 1995 by GNWT from the Bathurst, Bluenose and Victoria Island caribou herds. The principal contaminants detected in vegetation samples were α-HCH, β-HCH, HCB, *p,p'*-DDT, and PCB congeners 153, 138, 110, 101, 118, 170/190, and 66/95. The predominant compounds detected in caribou tissue were α-HCH, β-HCH, 1,2,4,5-TCB, HCB, oxychlordane, *p,p'*-DDE, and PCB congeners 118, 138, 153, and 180 while they were α-HCH, β-HCH, 1,2,4,5-TCB, HCB, oxychlordane, and PCB congeners 153, 138, and 180 in wolves.

Biomagnification factors (BMFs) were calculated from the ratio of the fugacity in the wolves or caribou and the fugacity in the diet of the caribou (i.e., 100% lichen) or in the diet of the wolf or the wolves (50%

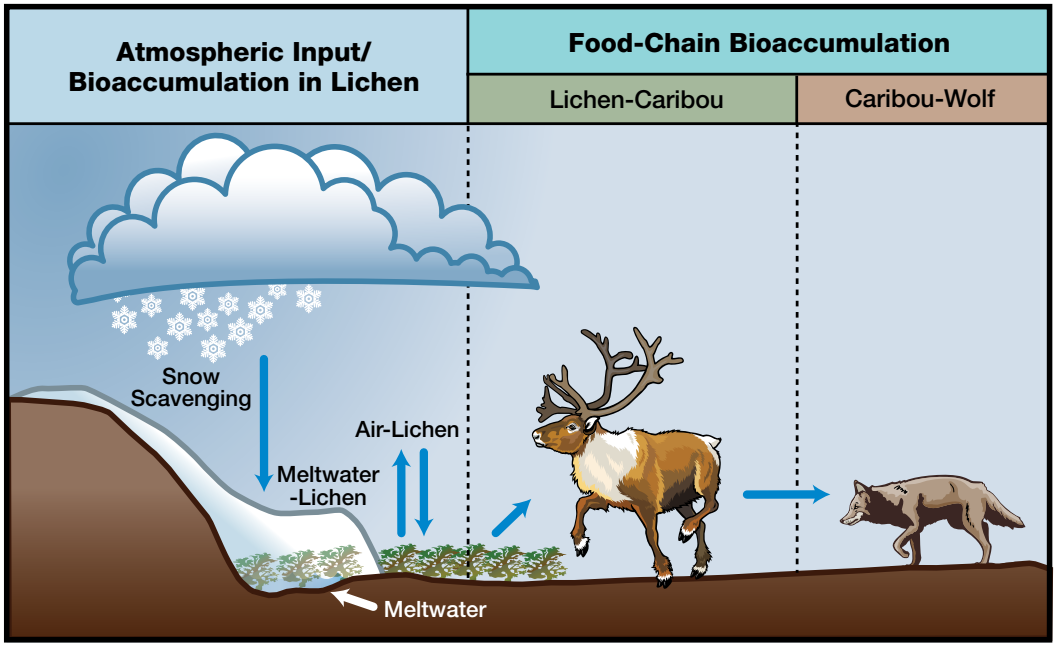

FIGURE 4.19

Pathways of accumulation of POPs in the lichen and terrestrial vegetation-caribou-wolf food chain from Kelly and Gobas (2001). Adapted with permisson. Copyright (2001) American Chemical Society.

female and 50% male, adult caribou). The fugacity ratio is approximately the same as the ratio of the lipid adjusted concentrations.

BMFs of β-HCH for male wolves ranged from 3.4 for animals sampled at Cambridge Bay to 16 and 28 for wolves at Bathurst Inlet and Inuvik, respectively. No substantial biomagnification or trophic dilution of α-HCH was observed. It appears that both caribou and wolves can efficiently eliminate γ-HCH and to a smaller extent α-HCH, but not β-HCH. In both caribou and wolves, oxychlordane attained greater fugacities than other chlordane-related compounds. BMFs of oxychlordane for male wolves ranged from 9.0 for animals at Cambridge Bay to 92 and 158 for animals at Bathurst Inlet and Inuvik, respectively. The BMF of *trans*-nonachlor for male wolves at Bathurst Inlet was 13. Evidence of biomagnification for 1,2,4,5-TCB and HCB is shown in lichen-caribou-wolf food chains of Canada's central and western Arctic region. The BMFs of HCB for male caribou in the fall at Bathurst Inlet, Cambridge Bay, and Inuvik were 4.0, 6.2, and 6.9, respectively. The BMFs of HCB in wolves from Bathurst Inlet and Inuvik were 6.5 and 2.1, respectively.

PCB-153 and PCB-180 concentrations increased significantly with increasing trophic level whereas PCB-52 concentration was not statistically different between trophic levels, suggesting elimination and metabolization of this congener in both caribou and wolves. PCBs demonstrated congener specific bioaccumulation patterns in lichens, caribou and wolves. The PCBs that are most prevalent in lichens consist of lower chlorinated compounds such as PCB-52, PCB-66/95, and PCB-101. Caribou appear to bioaccumulate these congeners, in addition to various higher chlorinated congeners such as PCB-118, -138, -153, and PCB-180. In caribou, the hexachloro biphenyl congener (PCB-153) bioaccumulated to the greatest extent. The BMFs of PCB-153 in male caribou from Bathurst Inlet during the summer and fall were 13 and 2.0, respectively. Wolves seem to have the ability to metabolize many PCB congeners and only extensively accumulate the higher chlorinated PCBs: 153, 99, 118, 180, 170 and/or 190, 194, and 206. Of the persistent PCBs observed in wolves, the heptachloro congeners PCB-180 and PCB-170 and/or 190 demonstrated the greatest BMFs. For example, the BMFs of PCB-180, PCB-170 and/or 190 for adult wolves from Bathurst Inlet were 93 and 112, respectively.

Trophic magnification factors (TMF) are calculated using the natural logarithm of the concentration (C_{ww}) of individual organisms vs. their trophic level (TL) assigned using $\delta^{15}N$ values (Jardine et al. 2006) and provide information on the average change in contaminant concentration per relative trophic level. TMFs significantly > 1 indicate biomagnification is occurring. TMFs were calculated for the vegetation-caribou-wolf food chain in the Bathurst herd range using the data of Kelly and Gobas (2001). All results were first expressed as ng g^{-1} lipid weight and trophic levels for lichen, willow, caribou and wolves were assigned based on Müller et al. (2011). TMFs ranged from 0.54 ± 0.38 for α-HCH to 2.1 ± 1.8 for CB153 (Figure 4.20).

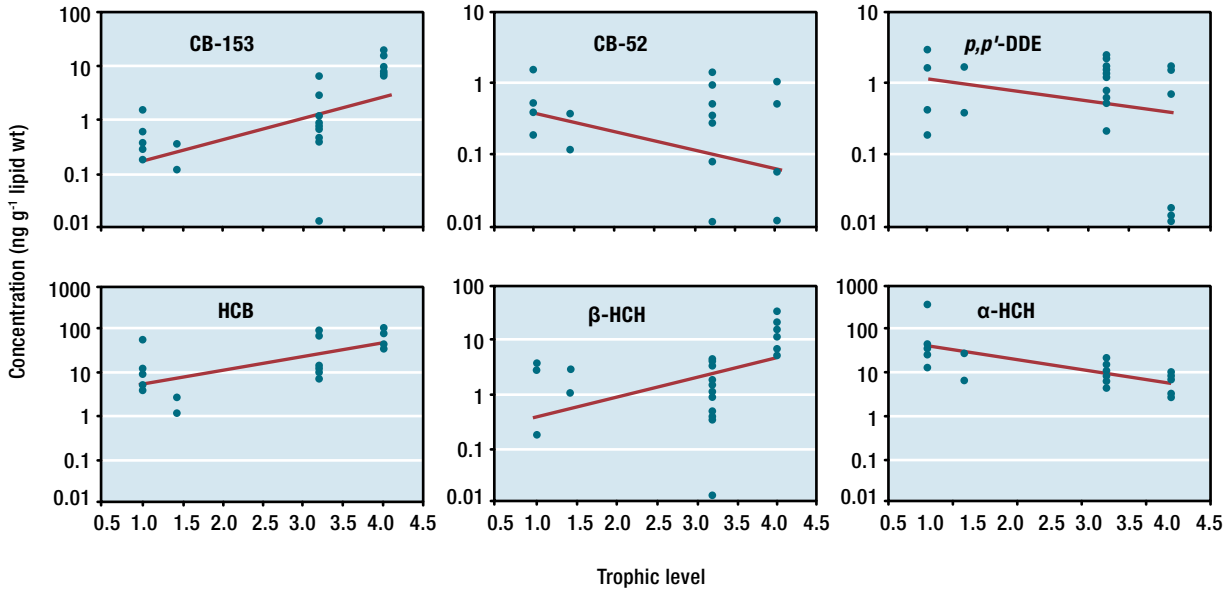

FIGURE 4.20

Biomagnification of selected legacy POPs in the vegetation-caribou-wolf food chain based on samples in the Bathurst herd range. Symbols represent geometric mean concentrations (lipid weight) from Kelly and Gobas (2001).

These TMFs indicate that even some highly bioaccumulative compounds such as *p,p'*-DDE do not biomagnify in terrestrial food webs due to biotransformation in both prey (caribou) and predator (wolf). This behaviour for *p,p'*-DDE is similar to the marine food web where BMFs for polar bears consuming seals were < 1 (Muir et al. 1988).

4.1.4.3. Legacy POPs in the lichen-lemming-bunting food web

Choy et al. (2010) investigated contamination of an arctic terrestrial food web at Cape Vera, Devon Island (Nunavut) with marine-derived POPs transported by northern fulmars. The terrestrial and aquatic environment in the study area was contaminated by guano from the fulmar colony. Choy et al. (2010) found that concentrations of ΣDDT, ΣPCBs and PCB-153 were highest in snow buntings (106 ng g^{-1} ww, 168 ng g^{-1} ww and 64 ng g^{-1} ww, respectively) followed by ermine (37 ng g^{-1} ww, 54 ng g^{-1} ww and 18 ng g^{-1} ww, respectively), lichen (*X. elegans*) (0.3–2 ng g^{-1} ww, 0.94–3.3 ng g^{-1} ww and 0.12–0.54 ng g^{-1} ww, respectively) and lemmings (0.7 ng g^{-1} ww, 0.76 ng g^{-1} ww and 0.11 ng g^{-1} ww, respectively). There was an exponential relationship between log PCB (ng g^{-1} ww) and trophic level (measured with $\delta^{15}N$ values) for the terrestrial food web as illustrated for PCBs and DDT in Figure 4.21, but no TMF values were reported.

4.1.4.4. Lichen-caribou-wolf food chain studies with new POPs

The bioaccumulation of PFASs in the lichen vegetation-caribou-wolf food chain was studied by Katz et al. (2009) and Müller et al. (2011). This study included terrestrial food web samples from the range of the Porcupine herd in northern Yukon and from the Bathurst herd in the eastern NWT-Western Nunavut. In addition to lichens, plants, cottongrass, aquatic sedge and willow leaf samples from the Porcupine herd range, cottongrass, willow leaf, moss and mushroom from the Bathurst area were analyzed. More than half of the caribou winter diet comprises of lichen while more than half of its summer diet is comprised of sedges. This was the first study of PFASs in an entire terrestrial food web.

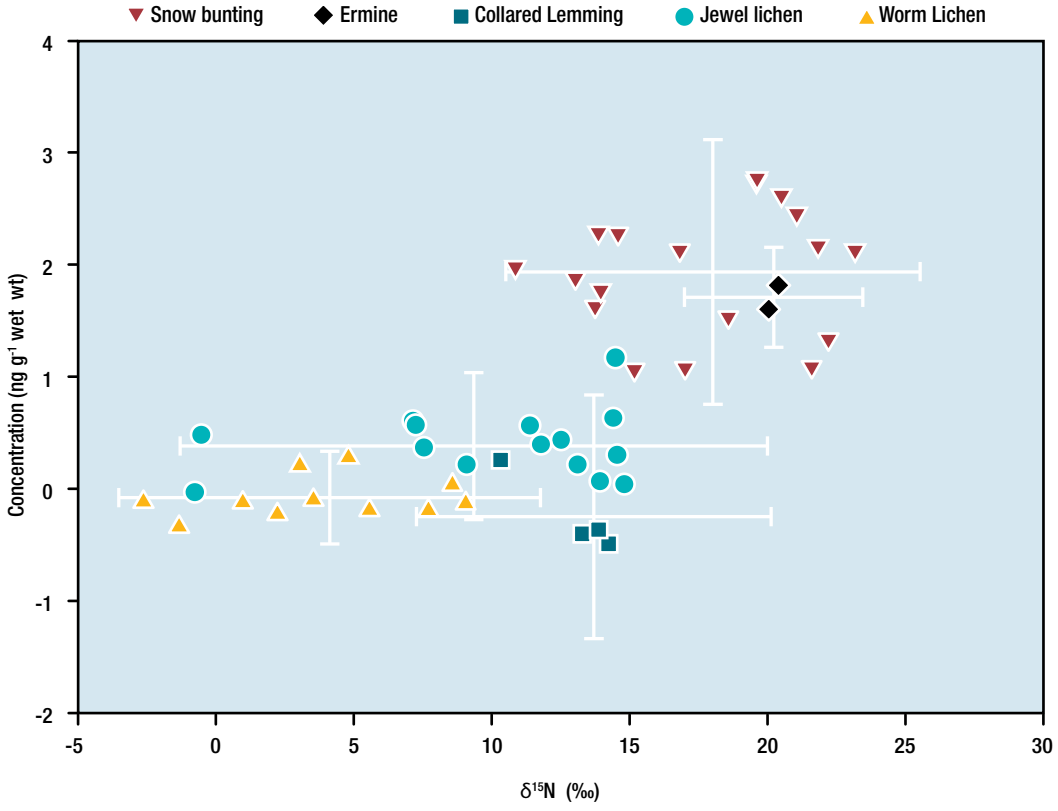

FIGURE 4.21

The relationship between log ΣPCB (ng g^{-1} ww) and $\delta^{15}N$ values among lichen, ermine, lemmings, and snow bunting at Cape Vera, Devon Island. Error bars represent the 95% confidence intervals surrounding the species means of PCBs and the $\delta^{15}N$ values for each species (redrafted from Choy et al. 2010).

Six PFCAs and perfluorooctane sulfonate (PFOS) were regularly detected in all species. Low but detectable ΣPFCAs concentrations were found for vegetation, 0.01 ng g^{-1} ww to 0.32 ng g^{-1} ww, and <0.003–0.045 ng g^{-1} ww for PFOS. Wolf liver showed highest concentrations in the 11 ng g^{-1} ww to 20 ng g^{-1} ww range for ΣPFCA and 0.97–2.68 ng g^{-1} ww for PFOS, followed by caribou liver (7 ng g^{-1} ww to 12 ng g^{-1} ww for ΣPFCA and 0.18–3.35 ng g^{-1} ww for PFOS). Results of carbon and nitrogen stable isotope analyses of vegetation as well as caribou and wolf muscle samples, showed that the caribou were feeding mainly on lichen and wolves were feeding mainly on caribou (Figure 4.22).

TMFs were highest for PFCAs with nine to eleven carbons (TMF = 2.1–2.9) as well as for PFOS (TMF = 2.3–2.8) and all but PFOA were significantly biomagnified, as illustrated in Figure 4.23.

The relationship of PFCA and PFSA trophic magnification factors with the chain length in the terrestrial food chain was similar to previous

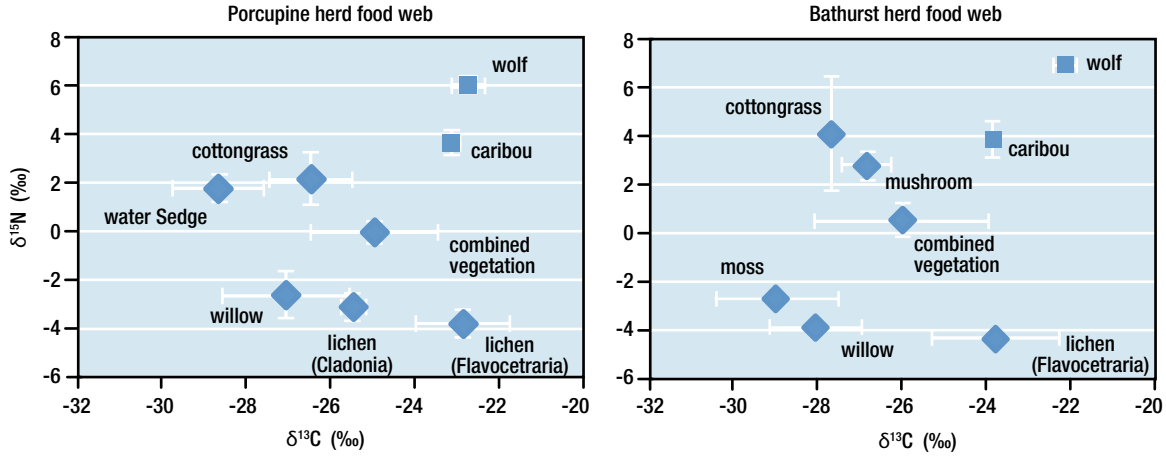

FIGURE 4.22

Stable isotope ratios $\delta^{15}N$ and $\delta^{13}C$ in the vegetation, caribou and wolf of the Porcupine and Bathurst herd ranges. Solid symbols are average values and lines are their corresponding standard deviations. (Müller et al. 2011).

Photo: Eric Loring

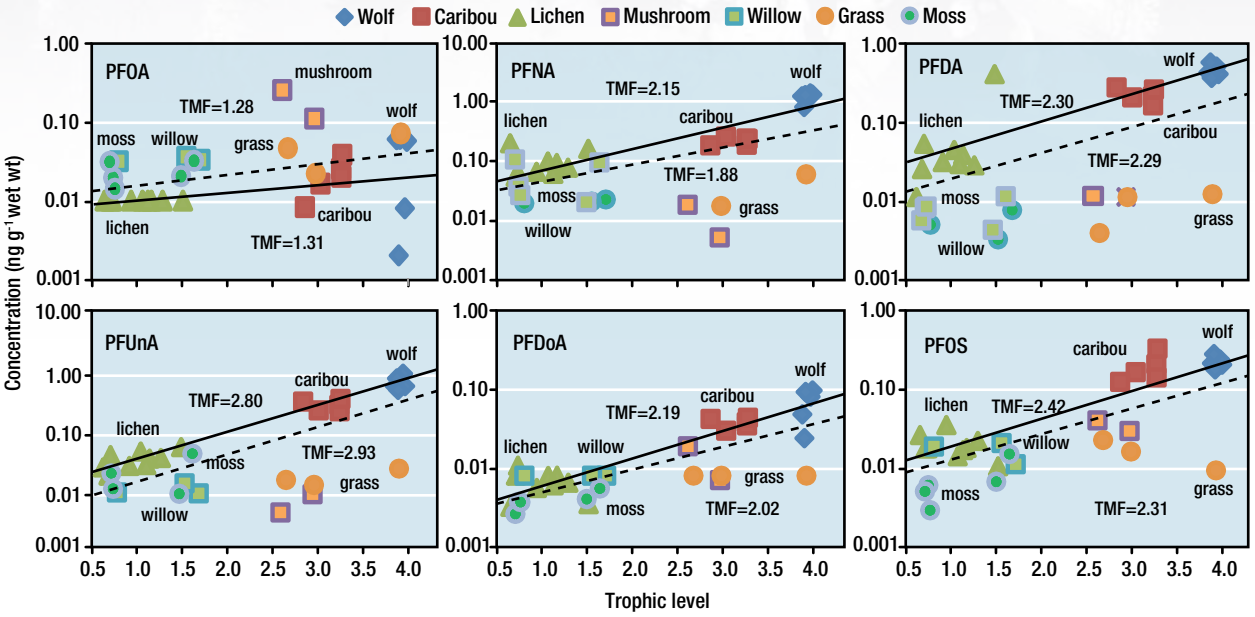

FIGURE 4.23

Biomagnification of PFCAs and PFOS in the terrestrial food web of the Bathurst caribou herd range. The solid line shows the regression with lichen only, the dashed line shows the regression with all vegetation samples (Müller et al. 2011).

studies for arctic marine mammal food webs, but the absolute values of TMFs were about two times lower for this study than in the marine environment.

4.1.4.5. Terrestrial food web modeling studies

Food chain bioaccumulation models play an important role in advancing our understanding of pathways and processes influencing the accumulation of POPs in wildlife and humans. Models that successfully predict levels of bioaccumulative contaminants in top predators can be used for environmental and human health risk assessment of new POPs and other less studied chemicals, as well as for site specific applications such as remedial cleanup efforts. Food chain models such as those described in Kelly and Gobas (2003), Kelly et al. (2007, 2009) and the ACC-Human model (Czub and McLachlan 2004, Czub et al. 2008) have been used to predict accumulation of POPs for hypothetical chemicals with arctic accumulation potential. Here we briefly describe the model from Kelly and Gobas (2003) because of its relevance to predicting bioaccumulation in terrestrial food webs. Food web models incorporating the marine food web are discussed in section 4.1.6.5.

Kelly and Gobas (2003) presented a model of the bioaccumulation of POPs in arctic terrestrial mammalian food chains to forecast concentrations of POPs in lichen-caribou-wolf food chains of Canada's central and western Arctic region from measured concentrations in air and snowpack meltwater. The model is illustrated schematically in Figure 4.24. The arctic terrestrial food chain bioaccumulation model consists of a series of mechanistic equations relating concentrations of POPs in air (gas phase and particles) and dissolved concentrations in snow pack, to resulting concentrations in arctic vegetation, herbivores and carnivorous predators. The model was used to estimate concentrations of POPs in vegetation (lichens and willows), caribou and wolves, from observed aerial and snowpack concentrations. Physical-chemical properties such as vapour pressure (VP_{SL}), octanol-water partition coefficient (K_{OW}) and octanol-air partition coefficients (K_{OA}) are key input parameters driving the model. For modeling studies, the availability of quality biomonitoring data is crucial for evaluating model performance. The data are discussed in section 4.1.4.2.

To simulate POPs bioaccumulation in caribou and wolves, it includes a two-compartment chemical bioaccumulation model, consisting of a gastrointestinal tract (GIT) and an organism compartment which represents the animal's overall contaminant storage (Figure 4.24). Also shown are the rate constants (k, h^{-1}) representing the various contaminant uptake and elimination processes. The model is based on the assumption that gastro-intestinal magnification is the primary mechanism for gastro-intestinal uptake and biomagnification of organic chemicals (Gobas et al. 1993).

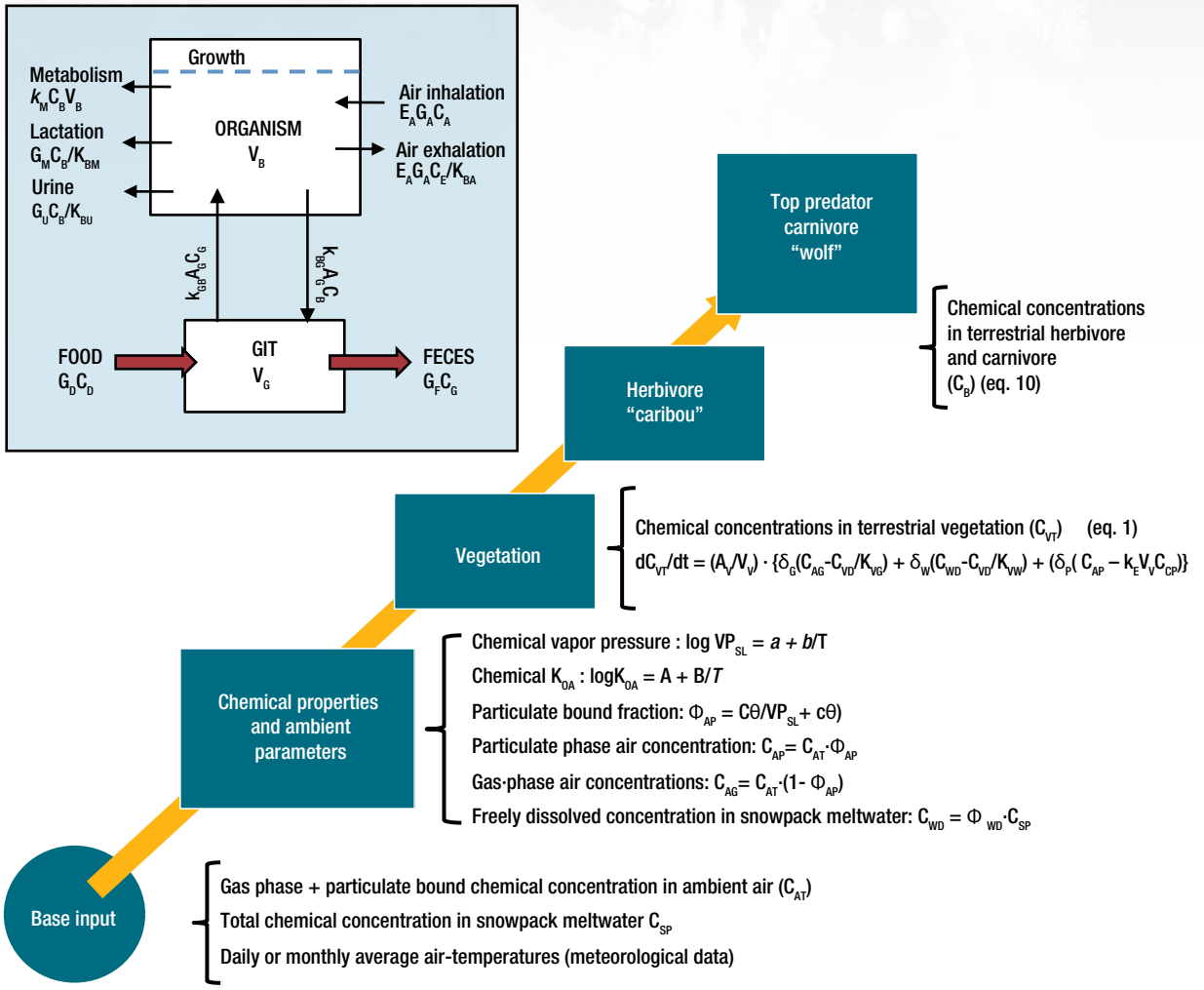

FIGURE 4.24

Schematic illustration of the modeling framework in the Kelly and Gobas (2003) terrestrial food web model, including base input parameters, chemical properties and ambient parameters combined with a two-compartment bioaccumulation model for caribou and wolf showing uptake and elimination processes.

The GIT compartment receives food at the rate of ingestion, i.e., the product of the ingestion rate G_D in $m^3\ h^{-1}$ and the dietary concentration C_D (mol m^{-3}) or $G_D C_D$ (mol h^{-1}) and eliminates fecal matter at a rate of $G_F C_G$ (mol h^{-1}), i.e., the product of the fecal egestion rate G_F ($m^3\ h^{-1}$) and the intestinal concentration C_G (mol m^{-3}). Diffusion at rates of $k_{GB} A_G C_G$ ($m^3\ h^{-1}$) and $k_{BG} A_G C_B$ ($m^3\ h^{-1}$) describe the exchange of chemical between the GIT compartment and the organism. k_{GB} and k_{BG}, are the mass transfer coefficients in units of (m h^{-1}) for diffusion from the GIT into the organism and from the organism to the GIT respectively and A_G (m^2) is the area over which diffusion occurs.

The degree of chemical accumulation in tissues of terrestrial mammals (i.e., caribou and wolves) is the result of competing rates of chemical uptake through air inhalation ($G_A E_A C_{AG}$) and absorption from the GIT ($k_{GB} A_G C_G$), and rates of chemical elimination through exhalation ($G_A E_A C_B / K_{BA}$), urinary excretion ($G_U C_B / K_{BU}$), fecal egestion ($k_{BG} A_G C_B$), milk excretion ($G_M C_B / K_{BM}$) and metabolic transformation $k_M V_B C_B$. Assuming continuous feeding and a steady state condition in the GIT (i.e., $N_G = 0$), the resulting mass balance equation representing the chemical flux (mol h^{-1}) into the organism (N_B) can be represented as:

$$N_B = d(V_B C_B)/dt = G_{AG} E_A C_{AG} + G_D E_D C_D - (G_A E_A / K_{BA} + (E_D / K_{BG}) G_F C_B + G_U / K_{BW} + G_M / K_{BM} + k_M V_B C_B) \times C_B$$

where V_B is the volume of the organism (m^3), G_A is the inhalation rate ($m^3\ h^{-1}$), E_A is the inhalation efficiency (no units), E_D is the dietary uptake efficiency, C_{AG} is the gaseous aerial concentration

(mol m^{-3}), G_U is the urinary excretion rate (m^3 h^{-1}), G_M is the milk excretion rate (m^3 h^{-1}) for female animals, k_M is the metabolic transformation rate constant (h^{-1}) and K_{BA}, K_{BU}, K_{BM} are the chemical's partition coefficients between organism and air, organism and urine and organism and milk respectively. A glossary of the terms used in the model is provided in Annex Table A4-5.

Lipid-to-air partitioning (K_{BA}) and gastro-intestinal magnification ($K_{DG} \cdot G_D / G_F$) are the main driving forces for bioaccumulation in this model. Biomagnification in the model occurs as a result of food digestion that (i) reduces the fecal egestion rate G_F below the dietary ingestion rate G_D and (ii) elevates the biota-to-GIT partition coefficient K_{BG} above the biota-to-diet partition coefficient K_{BD}. Elimination through air-exhalation, urine, milk and metabolic transformation combine to reduce the degree of biomagnification. Changes in the organism's biomass, which is particularly important for nursing newborns and fasting animals, are presented in the model as the time dependence of the weight of the animal, i.e., dV_B/dt in this time dependent model. In essence, this acts to reduce biomagnification during periods of growth (growth dilution) and increase biomagnification during periods of biomass loss (e.g., winter). The model assumes that concentrations of POPs among different tissues are at a chemical equilibrium and hence homogeneously distributed within the animal when expressed on a lipid weight basis.

The model was parameterized and applied to simulate POPs bioaccumulation in the lichen-caribou-wolf food chains of Canada's central and western arctic region (i.e., Bathurst Inlet Cambridge Bay and Inuvik). Measured concentrations of the 25 organic chemicals in arctic air (Stern et al. 1997, Bidleman et al. 1999, AMAP 1998, Bidleman et al. 1995) and snow pack meltwater (Bidleman et al. 1999, Strachan W. Environment Canada, Burlington ON, unpublished data) were used as input parameters to generate hourly concentrations (i.e., dt = 1 hour) in lichens, willows, caribou and wolves. Simulations were conducted for (i) male and female caribou and (ii) male and female wolves, generating hourly chemical concentrations (ng g^{-1} lw) in those individual animals. At the time of parturition for caribou (t_0= June) and wolves (t_0= May), the neonate was assigned a lipid equivalent concentration equal to that of the pregnant female. Post-parturition, maternal milk is ingested by the neonate over a specified nursing period. Chemical concentrations in milk (C_M) are assumed to equal normalized concentrations in the adult female (i.e., C_M

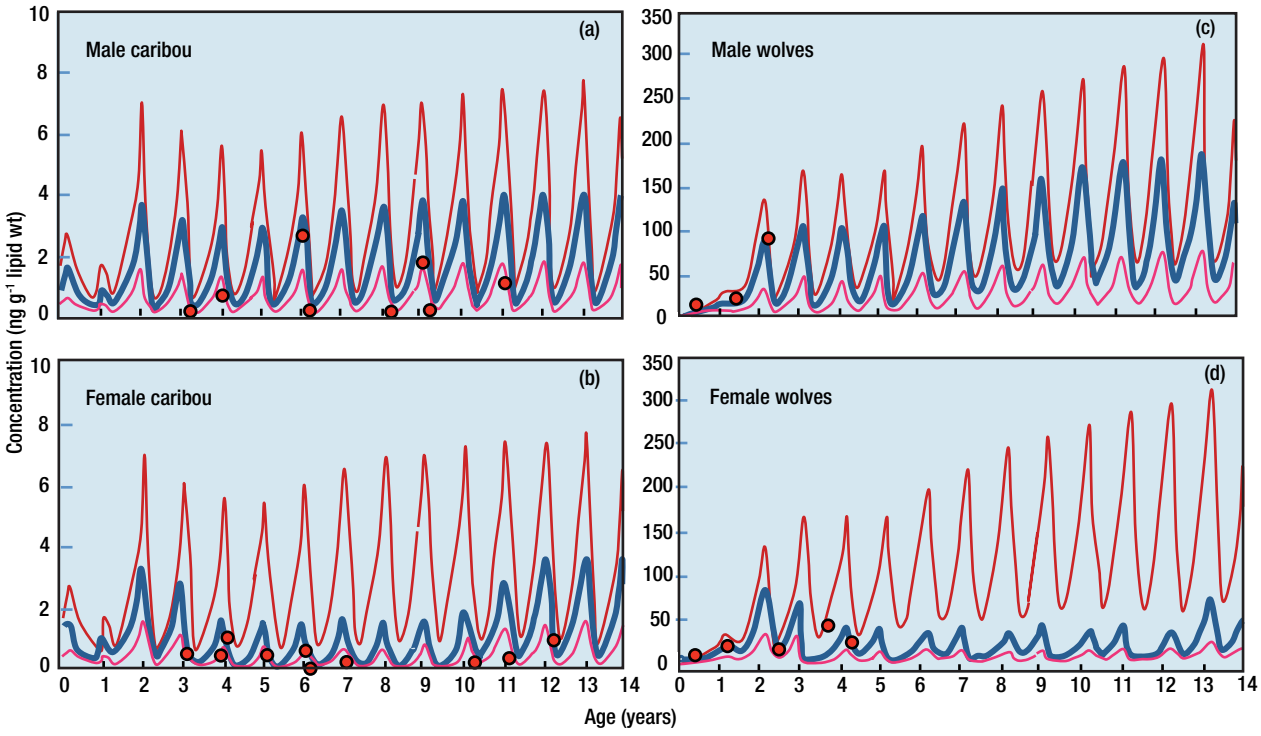

FIGURE 4.25

Predicted PCB-153 concentrations (ng g^{-1} lw; dark blue lines) in the tissues of (a) male caribou (b) female caribou (c) male wolves and (d) female wolves from Bathurst Inlet over a 14 year life-span. Data points (red dots) represent measured concentrations of PCB-153 in fat tissue of individual caribou and wolves from Bathurst Inlet (Kelly and Gobas 2001). Red lines above and below predicted value represent upper and lower 95% confidence intervals, calculated using Monte Carlo simulation.

= C_B). To assess the predictability of the model, forecasted concentrations (C_P) in caribou and wolf tissues (ng g^{-1} lw) were compared to the observed concentrations (C_O) in animals sampled from Cambridge Bay, Bathurst Inlet and Inuvik (Elkin and Bethke 1995, Kelly and Gobas 2001).

The model was evaluated by comparison of the model predicted and observed concentrations. Model predicted concentrations of 25 organic chemicals forecasted for caribou and wolves from Cambridge Bay, Inuvik and Bathurst Inlet are shown to be in good agreement with the observed data. Figure 4.25 illustrates model predicted tissue concentrations (ng g^{-1} lw) of PCB-153 over a 14 year life-span for (a) male caribou (b) female caribou (c) male wolves and (d) female wolves from Bathurst Inlet. Observed data for individual animals sampled near Bathurst Inlet are shown for comparison. Post-parturition, caribou calves (t_0=June) and wolf pups (t_0=May) are shown to experience only slight increases in tissue concentrations following maternal transfer, due primarily to the newborn's rapid growth rate which provides a dilution effect during this sensitive life-stage.

The successive cyclical fluctuations of tissue concentrations are primarily due to (i) seasonal changes in lipid content and body size and/or (ii) lactational excretion (females only). The increased body growth and lipid contents during the fall causes a dilution of chemical residues in the animal's tissues, resulting in a reduction in tissue concentrations. Conversely, fat depletion during spring concentrates chemical residues within limited fat reserves, causing elevated internal tissue residue concentrations. For female animals > 2 years (age of maturity), tissue concentrations decline sharply during spring, corresponding to periodic elimination via lactation throughout the specified nursing period. The model reasonably predicts (i) the statistically significant increase, by 7 times, in PCB-153 tissue concentrations observed between male caribou sampled during the months of September and July and (ii) the relatively lower concentrations observed in female animals (compared to males) due to maternal contaminant transfer (Kelly and Gobas 2001).

The model was also used to predict bioaccumulation factors (BAFs) of organic chemicals in lichens vs. the K_{OA}. BAFs for lichens were represented by the ratio of the chemical concentration in the lichens (C_V, mol m^{-3} lipid) and gas-phase air concentrations (i.e., BAF = C_V/C_{AG}). BAFs for caribou and wolves are represented by the ratio of the chemical concentration in the animal's tissues (C_B, mol m^{-3} lipid) and gas-phase air concentrations (i.e., BAF = C_B/C_{AG}). BAFs were shown to increase from 10^5 and 10^{12} for lichens and from 10^5 and 10^{15} for caribou and wolves over a K_{OA} range of 10^5–10^{12} i.e., typical of many POPs.

Model results also showed that POPs with K_{OA}'s < 10^5 do not biomagnify in arctic terrestrial food chains, while substances that exhibit log K_{OA}'s > 5 and also exhibit a log K_{OW} > 2, show significant chemical bioaccumulation in arctic terrestrial food chains. Of course, if substantial degradation (e.g., photolysis) and biotransformation occurs, the extent of chemical biomagnification potential will be greatly diminished, regardless of the chemical's K_{OA} or K_{OW}. Nevertheless, the model predicted that persistent low K_{OW} and high K_{OA} substances such as β-HCH, 1,2,4,5 tetrachlorobenzene, and β-endosulfan can biomagnify in arctic terrestrial mammals such as caribou and wolves.

4.1.4.6. Assessment of food web bioaccumulation in terrestrial biota

- A biomagnification study of PFASs in the lichen-caribou-wolf food web showed that PFCAs with nine to eleven carbons as well as PFOS were significantly biomagnified in this food web.
- Modeling of POPs biomagnification in terrestrial food webs predicts successive cyclical fluctuations of tissue concentrations due to (i) seasonal changes in lipid content and body size and/or (ii) lactational excretion (females only).
- Modeling of POPs bioaccumulation in caribou suggests that increased body growth and lipid contents during the fall causes a dilution of chemical residues in the animal's tissues, resulting in a reduction in tissue concentrations. Conversely, fat depletion during spring concentrates chemical residues within limited fat reserves, causing elevated internal tissue residue concentration.
- Model results for PCBs in caribou were in good agreement with measurements made by Kelly and Gobas (2001). However, additional work with a wider range of chemicals is needed to evaluate the applicability of the model.
- Legacy POPs were also significantly biomagnified in the lichen-lemming-bunting food web but whether this is the case for new POPs such as the PFASs has not yet been investigated.
- A new route of contamination of lichen and plants at the base of the terrestrial food web was identified; breeding seabirds studied at Cape Vera (Devon Island) were responsible for transporting and depositing PCBs and OCPs to terrestrial vegetation at this location.

4.1.5. Marine biota

4.1.5.1. Introduction

Under the NCP "Blueprint" for monitoring from 2004 to 2011 (INAC 2004, 2012), the determination of POPs in marine biota has been the primary focus of the environmental measurements program. This work builds on previous measurements going back to the early 1970s. Early studies were summarized and reviewed by Muir et al. (1992b). With the start of the NCP in 1991, a substantial amount of data on POPs in marine biota (mainly marine mammals and seabirds) was generated during NCP funded studies (Fisk et al. 2003). Reviews by Muir et al. (1999) and Braune et al. (2005) summarize the body of knowledge on POPs in marine biota to late 2002. In this section, concentrations of POPs in major species of marine biota, including new chemicals not reported in previous assessments, are discussed and spatial trends are assessed. Temporal trends in marine species are discussed in section 4.2.

4.1.5.1.1 Invertebrates and marine fish

Marine invertebrates provide a link between phytoplankton and fish, seabirds and mammals in arctic marine food webs. These invertebrates are important not only in the transfer of carbon and nutrients, but also in the transfer of POPs and other contaminants to organisms at upper trophic levels. Marine and anadromous fish occupy a range of trophic levels in arctic marine ecosystems and hence concentrations of contaminants in their tissues can be quite variable. The arctic cod is a key link in marine food webs, between invertebrates, seabirds and marine mammals. It is a major diet item of many important arctic marine mammals, including the ringed seal and beluga. An understanding of the trends and dynamics of POPs in marine invertebrates and fish is important for understanding the trends of contaminants in arctic marine ecosystems. A number of fish species are also important components of the traditional human diet, e.g., arctic char, and some have become important commercial species, e.g., Greenland halibut (turbot). In addition, mussels are commonly harvested in arctic communities.

Over the period 2003–2011 and since the previous CACAR assessment report (Fisk et al. 2003), a significant amount of new data has been published on PBDEs and PFASs in marine invertebrates and fishes, and a limited amount on legacy POPs. A food chain study in the East Hudson Bay region determined legacy and new POPs (Kelly et al. 2007,

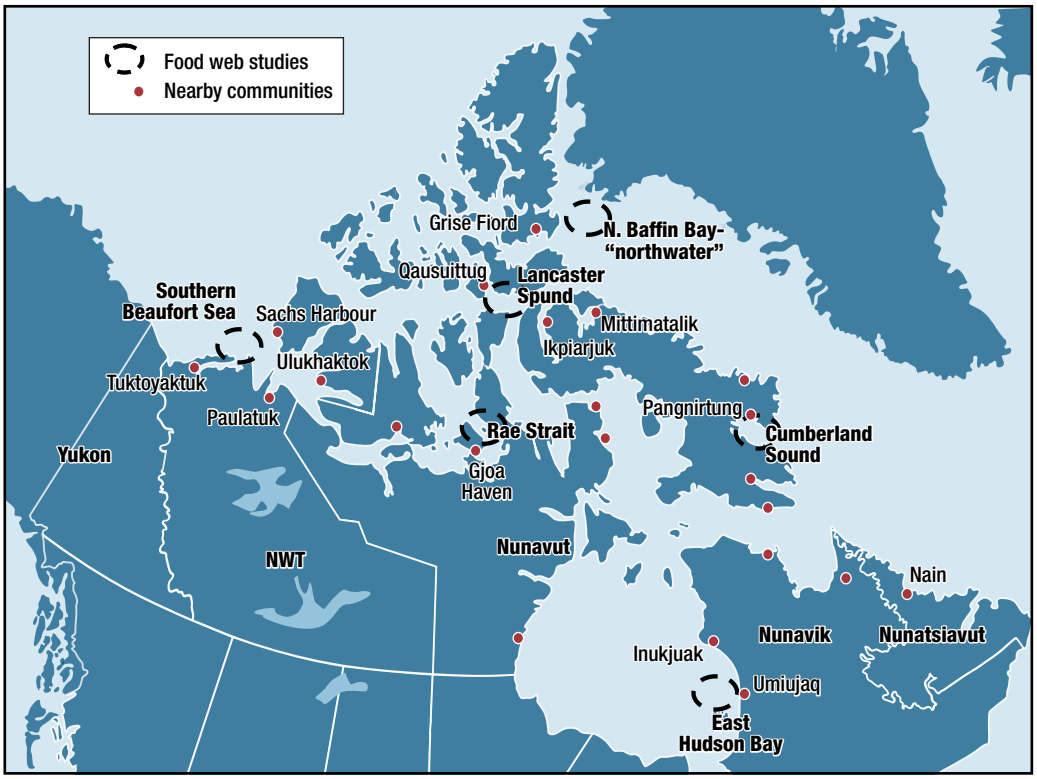

FIGURE 4.26

Sampling sites for invertebrates and marine fish collected in marine food web studies published during the period 2003–2011.

2008a, 2008b). Field sampling was conducted during the months of May to September between 1999 and 2003. Sediment and biota samples were collected along the eastern Hudson Bay coastline in close proximity to the Inuit village Umiujaq (64° 15' N, 113° 07' W). Samples included macroalgae (*Fucus gardneri*), bivalves (*Mytilis edulis*), arctic cod, capelin (*Mallotus villosus*) and sculpin (*Myoxocephalus scorpioides*). Other food chain studies have examined new POPs such as PBDEs, other BFRs, and PFASs in the arctic marine food webs in northern Baffin Island and southern Beaufort Sea (Tomy et al. 2004, Tomy et al. 2009b) as well as in Lancaster Sound and Rae Strait (Morris et al. 2010a). The study locations are shown in Figure 4.26. Further information on the food chain studies is given in section 4.1.6 which discusses marine food web biomagnification.

4.1.5.1.1.1. Legacy POPs in invertebrates and marine fishes

Kelly et al. (2007) reported that chlorobenzenes (1,2,4 TriCBz, PeCBz, HCBz), HCH isomers, *trans*-nonachlor, *p,p'*-DDT and *p,p'*-DDE were the dominant OCPs detected in East Hudson Bay sediment and nearshore biota (See Annex Table A4-6). Primary metabolites of heptachlor (heptachlor epoxide), chlordane (oxychlordane) and endosulfan (endosulfan sulfate) were also present in fish, seaducks and marine mammals. Lipid equivalent OCP concentrations in lichens and macro-algae were low, in the 0.1 ng g^{-1} to 1 ng g^{-1} range, with a rank order of ΣHCHs > ΣCBz > ΣDDT > ΣCHL. For fish, seaducks and marine mammals, OCP levels were in the 10 ng g^{-1} lw to 1,000 ng g^{-1} lw range, with a rank order of ΣDDT > ΣCHL > ΣCBz > ΣHCH, and are comparable to other studies of POPs in arctic fish, seabirds and marine mammals (Muir et al. 1988, Borgå et al. 2001, Norstrom and Muir 1994). Other cyclodiene pesticides, including β-endosulfan, aldrin, dieldrin and mirex, were pre-sent in biota samples in the range of 1–50 ng g^{-1} lw.

Borgå et al. (2005c) measured PCBs and OCP concentrations in invertebrates collected in 1998 from the North Water Polyna in northern Baffin Bay. The rank order of POPs concentrations in *Calanus* spp. were ΣHCH > ΣPCBs > ΣCHL > ΣDDT ≈ HCB. The concentration profile in *Themisto libelluia* was different to that of *Calanus* spp. where concentrations of ΣPCB (2.9 ± 1.3 ng g^{-1} ww) were greater than the other POPs. ΣCHL concentrations (2.6 ± 1.7 ng g^{-1} ww) were ca. 1.4 and 1.7 times greater than ΣDDT and ΣHCH, respectively. In the same study Borgå et al. (2005c) reported PCBs and OCPs in arctic cod. ΣPCB was the most prominent POP in arctic cod with concentrations that were ca. 2 times greater than that of ΣCHL (2.7 ± 0.7 ng g^{-1} ww) and ΣDDT (2.6 ± 0.5 ng g^{-1} ww). ΣHCH (0.9 ± 0.4 ng g^{-1} ww) and ΣHCB (0.8 ± 0.2 ng g^{-1} ww) were present at lower concentrations.

ΣPCB concentrations were also the dominant POPs in all three species of fish analyzed in a study by Kelly et al. (2007). The highest PCBs were found in salmon (129 ng g^{-1} lw). In arctic cod, ΣPCB concentrations (60 ng g^{-1} lw) were ca. 1.2 times and 6 times greater than ΣDDT and ΣHCH, respectively. ΣCBz and ΣCHL were ca. 2 times smaller than those of ΣPCBs (Annex Table A4-6). In sculpin, the rank order of concentrations was ΣPCBs (46 ng g^{-1} lw) > ΣCHL (20 ng g^{-1} lw) > ΣCBz (23 ng g^{-1} lw) > ΣDDTs (17 ng g^{-1} lw) > ΣHCH (13 ng g^{-1} lw).

Bidleman et al. (2013) determined concentrations of achiral and chiral OCPs in deep ocean scavenging amphipods (*Eurythenes gryllus*) collected from 2000–4000 m in the Arctic Ocean between 1993–1998. The order of abundance of legacy POPs was toxaphene > ΣPCBs ≈ ΣDDTs > ΣCHL > Σmirex compounds > Σchlorobenzenes ≈ octachlorostyrene ≈ α-HCH. Pentachloranisole, a degradation product of pentachlorophenol, was also detected. No correlations were found with $\delta^{13}C$ or with $\delta^{15}N$, except for toxaphene (individual chlorobornanes). Concentrations of organochlorines were generally, but not always, higher in *E. gryllus* than those reported in smaller marine benthic scavenging amphipods. Mean concentrations of ΣPCBs and sum of *p,p'*-DDT-related compounds in *E. gryllus* were similar to those reported by Svendsen et al. (2007) who had analyzed *E. gryllus* collected from 100 m depth at a station northeast of Svalbard in 2002. The Svalbard amphipods had higher levels of *trans*-nonachlor and HCB, and lower α-HCH and oxychlordane, than the deep water ampipods studied by Bidleman et al. (2013).

4.1.5.1.1.2. New POPs in invertebrates and marine fishes

The major new POPs reported in marine invertebrates and fishes are the PBDEs and PFASs. Elevated concentrations of ΣPBDEs were reported in macroalgae (324 ng g^{-1} lw) from eastern Hudson Bay (Kelly et al. 2008a) and in the same study, mean ΣPBDE concentrations in fish were 5.4 ng·g^{-1} lw in bivalves, 9.8 ng·g^{-1} in arctic cod and 72.8 ng·g^{-1} in sculpin. BDE-47 was the major BDE congener representing 30–40% of ΣPBDE (sum of di-hepta BDEs). Results for ΣPBDEs are presented in Annex Table A4-6. BDE-209 was not determined. Kelly et al. (2008b) reported ΣMeO-PBDEs but OH-PBDEs were also detectable in bivalves (14 ng g^{-1} lw), arctic cod

(9.9 ng g^{-1} lw), sculpin (3 ng g^{-1} lw) and salmon (42 ng g^{-1} lw). The MeO-PBDEs are likely natural products (Teuten and Reddy 2004, Teuten et al. 2005).

Tomy et al. (2008b; 2009b) reported PBDEs and HBCDD in both eastern and western Canadian Arctic marine food webs. In Frobisher Bay (Baffin Island), concentrations of ΣPBDEs in mixed zooplankton (73 ng g^{-1} lw), consisting predominantly of copepods with fifth stage *Calanus hyperboreus* removed was ca. 3 times greater than that measured in clams (21 ng g^{-1} lw) (Tomy et al. 2008b). Two zooplankton species were collected from Amundsen Gulf and the Mackenzie Delta within the eastern Beaufort Sea in 2004 (Tomy et al. 2009b). Measured concentrations of ΣPBDEs in zooplankton in this study were about 5 times smaller than what was measured in the eastern Canadian Arctic (72.9 ± 10.1 ng g^{-1}) but similar to what was measured by Morris et al. (2010a) in a food web from Barrow Strait (Nunavut, Canada) (ΣPBDEs: 18.6 ng g^{-1} lw in zooplankton and 16.6 ng g^{-1} lw in amphipods) (Morris et al. 2007). The BDE profile in zooplankton from the western Arctic was dominated by BDE-99 and BDE-47 and strikingly different to that observed in species from the eastern Canadian Arctic where the profile was dominated by BDE-153 and BDE-209 (Figure 4.27).

ΣPBDEs concentrations of 23 ± 13 ng g^{-1} lw were reported by Tomy et al. (2008b) in arctic cod and was similar to the ΣPBDEs concentration measured in arctic cod by Morris et al. (2007) of 23 ng g^{-1} lw and 9.8 ng g^{-1} lw by Kelly et al. (2008a) but much smaller than that measured in cod from the Beaufort Sea collected in 2004 and 2005 (205 ng g^{-1} lw) (Tomy et al. 2009b). ΣPBDE concentrations in herring and cisco from the Beaufort Sea collected in 2005 were 15 ng g^{-1} lw and 99 ng g^{-1} lw, respectively (Tomy et al. 2009b).

Tomy et al. (2008b) also determined isomers of HBCDD in two Canadian arctic marine food webs (Tomy et al. 2009b, Tomy et al. 2008b). The overall rank order of ΣHBCDD (sum of α- and γ-isomers) in invertebrates was redfish ≈ clams > shrimp and the α-isomer accounting for greater than ca. 75% in cod, redfish and shrimp. In clams, the γ-isomer contributed about 20% of the ΣHBCDD in zooplankton

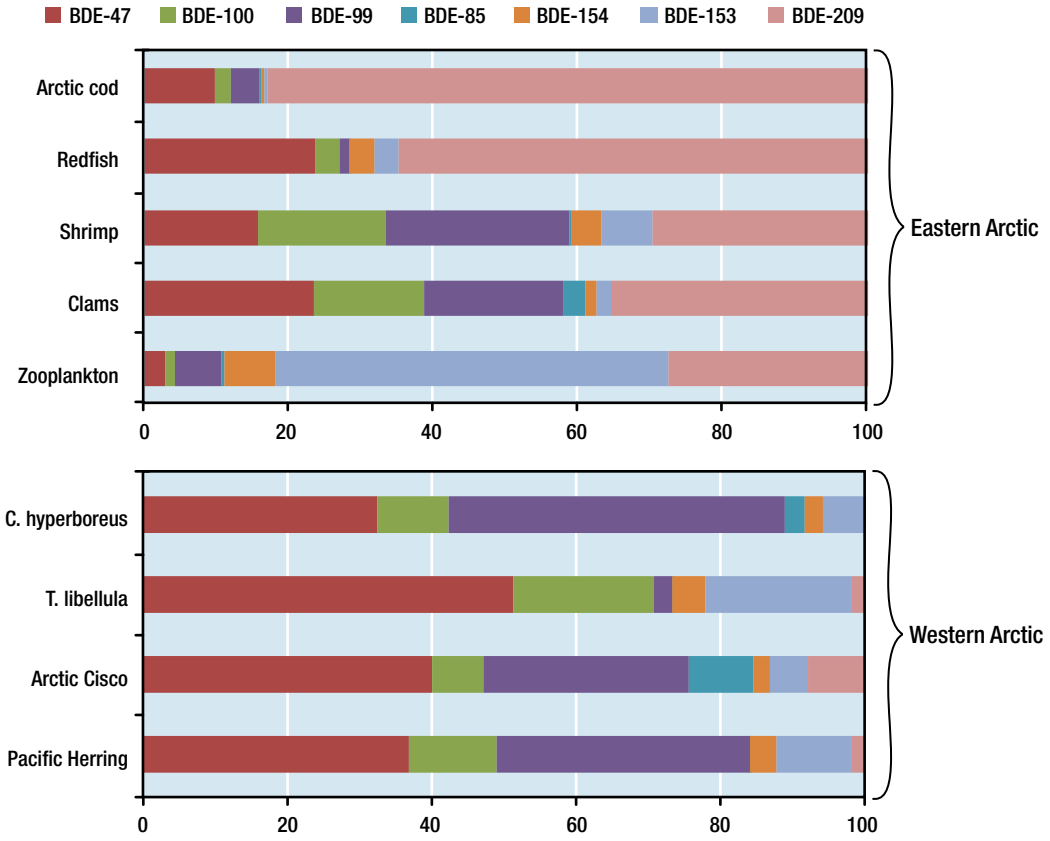

FIGURE 4.27

Proportions of various BDE congeners in marine invertebrates and fish from Frobisher Bay (eastern Arctic) and the southeastern Beaufort Sea (western Arctic). Results from Tomy et al. (2009b; 2008b).

and shrimp; the α-isomer predominated. Higher ΣHBCDD concentrations were found in samples from the eastern Arctic compared to those from the western Arctic.

In a study of PFASs of an eastern arctic marine food web based on samples collected from the Davis Strait in 2000 and 2001, and from Frobisher Bay in 2002, Tomy et al. (2004) showed the presence of PFOS related compounds. In shrimp, liver based N-EtPFOSA concentrations (10.4 ng g^{-1} ww) were ca. 30 times and 60 times greater than that of PFOS and PFOA. In clams, the rank order of concentrations was N-EtPFOSA > PFOS and PFOA was undetectable in the samples. No other investigators have reported N-EtPFOSA, which is a likely precurser of PFOS in biota.

Powley et al. (2008) reported on PFCA and PFSA concentrations in three different species of zooplankton (*C. hyperboreus, T. libellula* and *Chaetognatha*) obtained in 2004 near Sachs Harbor (NT). In zooplankton, PFOS concentrations ranged from non-detectable to 0.2 ng g^{-1} ww and from 0.3–0.5 ng g^{-1} ww in cod. PFDS and PFDoS were at undetectable concentrations in both samples. PFDA and PFDoA were the only PFCAs detectable in zooplankton, with concentrations ranging from 0.5–1.1 ng g^{-1} ww and 0.4–0.9 ng g^{-1} ww, respectively.

Tomy et al. (2009b) reported ΣPFCAs in zooplankton and in amphipod (*T. libellula*) were 5.7 ng g^{-1} ww and 2.0 ng g^{-1} ww, respectively in a Beaufort Sea food web. PFOS was also in zooplankton (0.3 ng g^{-1} ww) and *T. libellula* (2.6 ng g^{-1} ww). PFOSA was measurable at a concentration of 0.55 ng g^{-1} ww in zooplankton. PFOA concentrations in zooplankton (2.6 ng g^{-1} ww) were ca. 1.5 times greater than PFOS (1.8 ng g^{-1} ww) and ca. 7 times greater than N-EtPFOSA (Tomy et al. 2009b). Tomy et al. (2009b) also determined PFASs in the liver of Pacific herring and arctic cod. PFOS was undetectable in herring and cod but PFOSA was a prominent PFAS in both species. This contrasts with results for arctic cod muscle from Kelly et al. (2009) for eastern Hudson Bay and an earlier study by Tomy et al. (2004) that included arctic cod from northern Baffin Bay where PFOS was a major PFAS. Tomy et al. (2004) also reported the PFOS precursor, N-EtPFOSA, in arctic cod and redfish (*Sebastes mentella*) from northern Baffin Bay. This compound was present at about 70-fold higher concentrations than PFOS in arctic cod muscle but was not detectable in redfish muscle.

Kelly et al. (2009) measured PFASs, including C_7–C_{14} PFCAs, PFOS and PFOSA, in east Hudson Bay sediments, invertebrates and fishes collected from 1999–2003. PFOA, PFNA, PFDA and PFUnA were commonly detected in sediments and macroalgae while PFOS and C_7–C_{14} PFCAs were routinely detected in fish. PFCAs and PFOSA comprised > 90% of ΣPFASs in sediments, macroalgae and fish (Figure 4.28).

Endosulfan isomers and endosulfan sulfate were determined in cod, sculpin and salmon in eastern Hudson Strait using GC-high resolution MS and reported in supporting information published by Kelly et al. (2007). The Σendosulfan, consisting mainly of α-endosulfan, was detectable in arctic cod muscle and in salmon muscle but was below detection limits in sculpin.

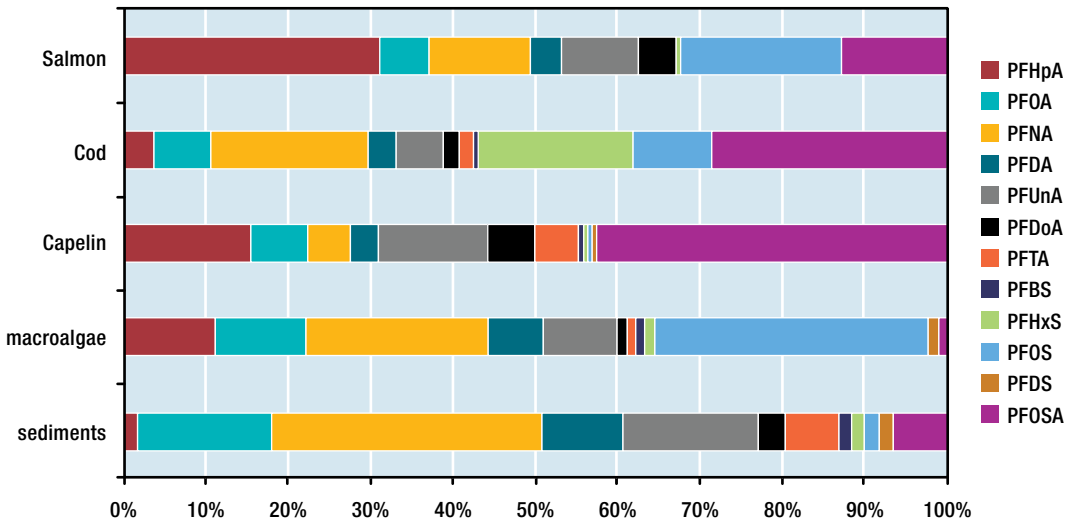

FIGURE 4.28

Proportions of PFASs in sediment, macroalgae and fish from the east Hudson Bay area near Umiujaq (Kelly et al. 2009).

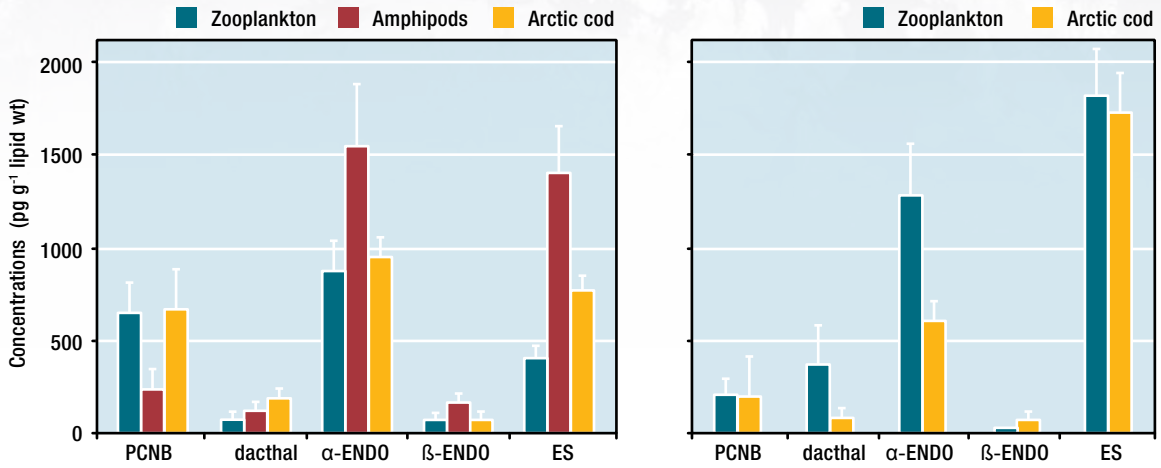

FIGURE 4.29

Concentrations of current use pesticides pentachloronitrobenzene (PCNB) and dacthal as well as endosulfan isomers and endosulfan sulfate (ES) in invertebrates and arctic cod from Barrow Strait and Rae Strait (Morris et al. 2010a).

Morris et al. (2010a) determined endosulfan and two other CUPs, PCNB and dacthal, in marine invertebrates and fish from Barrow Strait and Rae Strait (Figure 4.29). Alpha (α)-endosulfan and endosulfan sulfate were the most prominent CUPs (1550 ± 327 pg g^{-1} lw and 1400 ± 253 ng g^{-1} lw, respectively) with the highest concentrations in amphipods. Other CUPs including trifluralin, chlorpyrifos, chlorthalonil, tefluthrin, metribuzin, myclobutanil which have been reported in arctic air (see Chapter 3, section 3.1.4.4) were not detected in biota at detection limits of approximately 10 pg g^{-1} ww (Morris et al. 2010a).

4.1.5.2. Levels and spatial trends of legacy and new POPs in seabirds

There are approximately 50 species of arctic seabirds (de March et al. 1998) that have a variety of feeding and migration habits, and subsequently, POPs concentrations can vary considerably among species. Species such as the glaucous gull, great skua and great black-backed gull, that may migrate to more contaminated regions and/or that scavenge particularly on dead marine mammals, have the highest POP concentrations (de Wit et al. 2004; de March et al. 1998). Biological effects related to POP exposure have been seen in highly contaminated glaucous gulls at Svalbard (de Wit et al. 2004) and concerns about the effects of exposure to POPs remain for some other species of arctic seabirds. Seabirds also have the potential to act as a biovector (see Chapter 3, section 3.6) on the transport of POPs from one region to another (e.g., marine to the freshwater ecosystems) through the production and release of guano.

There has been a considerable amount of work on POPs in arctic seabirds since the first CACAR assessment report, encompassing a wide range of species. Sampling locations over the period 2003–2010 are shown in Figure 4.30 and detailed data are provided in Annex Tables A4-8 – 4A-12. Studies published after the CACAR II assessment based on samples collected earlier are also included. Differences in concentrations in liver and muscle for species are reviewed below and spatial trends in concentrations in eggs are considered separately.

4.1.5.2.1. Legacy POPs in seabird tissues

PCBs remain the predominant POPs measured in arctic seabirds, although the relative amount is related to the trophic position of the seabird (Borgå et al. 2001). Higher trophic level seabirds generally have a larger proportion of PCBs as a percentage of the total legacy organochlorines. This is due to the greater biomagnification potential of PCBs and the ability of seabirds to metabolize other POPs, such as α-HCH (Moisey et al. 2001) and chlordane-related compounds (Fisk et al. 2001a).

POPs were measured in the liver and fat of seven arctic seabird species collected in northern Baffin Bay in 1998 (Buckman et al. 2004). Concentrations of ΣPCB were the highest among the OC groups observed in all seabird species, and attained the highest concentrations in the gulls (glaucous gulls, ivory gull and black-legged kittiwake) and the procellariid (northern fulmar). ΣDDT and ΣCHL were the OC groups with the next highest concentrations followed by ΣCBz and ΣHCH. The exception to this ranking

FIGURE 4.30

Locations for seabird sampling in the Canadian Arctic 2003–2011.

is for thick-billed murres where the ΣCHL was found at much lower concentrations than in other seabirds. Thick-billed murres have been shown to have an exceptional ability to biotransform chlordane components (Fisk et al. 2001a). Glaucous gulls, ivory gulls and northern fulmars scavenge, and glaucous gulls prey on other seabirds, which accounts for high OC concentrations. Migration to more contaminated southern locations may also account for levels in the glaucous gull and black-legged kittiwake. Black-legged kittiwakes, a nonscavenging species, had higher concentrations than the alcids (guillemot, thick-billed murre and dovekie), because of their migration to southern habitats. The kittiwakes were found to be feeding at a lower trophic level than black guillemot in northern Baffin Bay (Hobson et al. 2002), and since the black guillemot does not undergo a major migration, this difference between the species highlights the impact of exposure to POPs in non-Arctic habitats by migrating seabirds.

The relative proportions of OC groups varied between liver and fat as well as between species. Significant differences in concentrations between fat and liver, however, were found for ΣCBz, ΣHCH, and ΣPCB but not for ΣCHL and ΣDDT. This is difficult to explain because OC groups are generally correlated, especially for biomagnifying compounds such as DDT and PCB. The differences are likely due to a combination of migration, diet shifts and reproduction. Lipid-corrected concentrations of OC components did not significantly vary between sex for any of the species, except ΣDDT in liver tissue where concentrations in females were found to be lower than in males. This is likely due to recent changes in diet but it is curious that this difference was not observed for other OC groups. ΣDDT, which was 86–97% *p,p'*-DDE in the liver and fat of all 7 seabird species, had the highest concentrations of any individual OC compound, followed by PCBs 138 and 153 and oxychlordane. Oxychlordane was 15–20% of ΣCHL in dovekie and black guillemot but 40–49% in the gulls and thick-billed murre and 71–77% in northern fulmar. The remainder was largely *trans*-nonachlor and heptachlor epoxide. ΣCBz was 62–93% HCB, 5–21% pentachlorobenzene and 3–12% tetrachlorobenzenes. HCH was 1–29% α-HCH and 63–99 β–HCH, but for most species was > 85% β-HCH (Buckman et al. 2004). Lipid based concentration of ΣPCBs in liver samples from black-legged kittiwake in this study (approximately 1,752 ng g^{-1} lw) was comparable to that in the liver of the same species (2,383 ng g^{-1} lw) sampled from Barents Sea in 1999 (Borgå et al. 2005b). However, hepatic

concentrations of ΣPCBs in black-legged kittiwake (approximately 3,575 ng g^{-1} lw) were lower compared to hepatic concentrations (7,981 ng g^{-1} lw) in samples collected from the Barents Sea in 1999 (Borgå et al. 2005b).

Breast muscle from 18 adult birds collected in Saglek Bay and Nain had ΣPCB concentrations ranging from 320 ng g^{-1} ww (near Nain) to 52,000 ng g^{-1} ww in Saglek Bay, where a military radar station, operated from the 1950s, released PCBs into the adjacent marine environment (Kuzyk et al. 2005). For more background on the Saglek Bay site and studies made there (see Chapter 3, section 3.4.2.2 and Chapter 5, section 5.2.1). There was little variation in the lipid fraction of the breast muscle (3.8 ± 0.9 %). In spite of the high maximum concentrations at Saglek Bay, mean ΣPCB concentrations in adult breast muscle did not differ significantly between the two locations (3,230 and 1,610 ng g^{-1} ww for Saglek Bay and Nain, respectively). It is difficult to determine whether both the high variability at Saglek Bay and the high maximum concentration reflect the influence from the local PCB contamination or other factors. Great black-backed gulls are not a species typically included in contaminants (or other) monitoring in northern Canada so comparatively little is known about their ecology and the influence of ecological factors on contaminant burdens. However, in their northern Labrador and Quebec breeding areas, the gulls are largely resident, moving only a limited distance south along the coast in the winter (Good 1998). Therefore, a difference in PCB exposure in over wintering areas does not appear to explain the variable and high maximum PCB concentrations at Saglek Bay. Another possible explanation is diet and/or trophic position. The diet of the great black-backed gull is similar to the generalist diets of glaucous and herring gulls (invertebrates, fish, rodents, eggs of other birds, and scavenging) but their large size also enables them to prey on adult birds and other large organisms (Good 1998).

Black guillemot nestling livers from Saglek Bay were also analyzed for PCBs. In 38 guillemot nestling livers, ΣPCB concentrations ranged from 9.0 ng g^{-1} ww in zone four (distant from the contamination) to 6,300 ng g^{-1} ww in zone one (close to the contaminated site; see Chapter 3, section 3.4.2.2) (Kuzyk et al. 2005). Geometric mean ΣPCB concentrations differed significantly among the four Saglek Bay zones ($p < 0.0001$). The mean concentration from zone one was over 140 times greater than the mean concentration from zone four. Guillemot livers from zone two and three had mean concentrations that were 24 times and 3 times greater than the mean concentration from zone four (Kuzyk et al. 2005).

Breast muscle from 18 adult black guillemots collected in Saglek Bay (zones one to three) and in Nain had ΣPCB concentrations ranging from 51 ng g^{-1} ww in Nain to 7,500 ng g^{-1} ww in Saglek Bay (Kuzyk et al. 2005). The geometric mean ΣPCB concentration in adult breast muscle from Saglek Bay was 16 times higher than the mean concentration from the Nain area. The lipid fraction of the breast muscle was consistent, averaging 1.9 ± 0.28%. The presence of high concentrations of PCBs in the black guillemots of Saglek Bay can be explained by their feeding strategy and foraging range. Consumption of fish and invertebrates associated with the seabed would tend to promote PCB uptake in a contaminated environment like Saglek Bay. The significance of fish in the diet would place guillemots at a relatively high trophic level, which may explain the apparent 20–40 fold biomagnification between sculpin and guillemot eggs in Saglek Bay.

Kelly et al. (2008a) reported concentrations of PCBs in tissue samples of common eider ducks and white winged scoters from eastern Hudson Bay as part of a marine food chain biomagnification study. Concentration of ΣPCBs in eider ducks liver samples ranged between 78 ng g^{-1} lw and 1,056 ng g^{-1} lw with an arithmetic mean of 287 ng g^{-1} lw while the mean ΣPCBs concentration was 2,500 ng g^{-1} lw (range of 440–14,100 ng g^{-1} lw) in white winged scoters. Mean concentrations of ΣDDTs, ΣHCHs, ΣCBz and ΣCyclodienes detected in common eider duck liver samples in this study were 179, 15, 48 and 192 ng g^{-1} lw, respectively in eider duck whereas these values were 565, 8.6, 71 and 119 ng g^{-1} lw, respectively in the white winged scoter.

ΣPCB and OCP concentrations are reported for the liver of northern fulmars collected from Cape Vera (NU) in 2003 (Mallory et al. 2006a). The level of contaminants found in fulmars collected at the Cape Vera colony in northern Canada varied with both breeding status and sex. This is the first study reporting on contaminants with sex-related differences in fulmars in the Canadian Arctic. Mean concentrations of ΣPCBs in breeding male fulmars was 2,943 ± 450 ng g^{-1} lw while it was 3,265 ± 810 ng g^{-1} lw for non-breeding male fulmars. The average concentrations of ΣPCBs were 1,383 ± 175 ng g^{-1} lw and 3,687±1505 ng g^{-1} lw for breeding and non-breeding female fulmars, respectively. Total OCP concentrations were higher compared to ΣPCBs and measured concentrations for this chemical class were 8,195 ± 846 ng g^{-1} lw and 10,332 ± 2,697 ng g^{-1} lw for breeding males and non-breeding males respectively, and 6,834 ± 1,814 ng g^{-1} lw and 13,910 ± 5,330 ng g^{-1} lw for breeding female and non-breeding female northern fulmars.

Mallory et al. (2005) reported a suite of legacy POPs (ΣPCBs, ΣDDT, ΣCHLs, dieldrin, ΣMirex, ΣCBz and ΣHCHs) in black guillemots, common eiders, glaucous gulls and northern fulmars, collected 100 km southeast of Qikiqtarjuaq (NU) in 2001. Considering only muscle and liver tissues, the glaucous gull had the highest concentration of all POPs examined, except for dieldrin (highest in fulmar tissues) and ΣHCH (highest in guillemot livers). Concentrations of ΣPCB, ΣDDT, ΣCHLs and ΣMirex increased following this pattern: eider < guillemot < fulmar < gull. Fulmars, however, had higher dieldrin and lower ΣHCH levels than the glaucous gull. When comparing lipid-normalized values of POPs, the glaucous gull had the highest contaminant burdens for all residues except dieldrin (which was highest in fulmars) and ΣHCH (which was highest in guillemots).

4.1.5.2.2. New POPs in seabird tissue

Significant differences were found for hepatic concentrations of ΣPBDE and BDE-47 among male thick-billed murres sampled from four colonies (Akpatok, Digges, Minarets, Prince Leopold) in 2008 (Figure 4.31). The birds from the Minarets had the highest levels, and those from Prince Leopold Island had the lowest levels of both ΣPBDE and BDE-47 (Figure 4.31). It is not clear what is driving these inter-colony differences.

Kelly et al. (2008a) reported concentrations of PBDEs in tissue samples of common eider ducks and white winged scoters from eastern Hudson Bay as part of a marine food chain biomagnification study. ΣPBDEs concentrations ranged between 4.9 ng g^{-1} lw and 78 ng g^{-1} lw (average concentration was 20 ng g^{-1} lw) in either ducks and ranged between 29 ng g^{-1} lw and 177 ng g^{-1} lw (average concentration was 71 ng g^{-1} lw) in white winged scoter liver samples. Hydroxylated-PBDEs were not at detectable levels in either species. ΣMeO-PBDEs ranged from 0.3 ng g^{-1} lw to 5.1 ng g^{-1} lw with an average concentration of 1.3 ng g^{-1} lw in eider duck and ranged between 0.34 ng g^{-1} lw to 13 ng g^{-1} lw with a mean value of 2.1 ng g^{-1} lw in white winged scoter.

Mean BDE-47 concentrations measured in liver of eider ducks (4 ng g^{-1} lw) and white-winged scoters (15 ng g^{-1} lw) from eastern Hudson Bay were 15 to 300 times lower than BDE-47 concentrations reported in eggs of double crested cormorant (*Phalacrocorax auritus*), and great blue herons (*Ardea herodias*) from the Georgia Basin-Puget Sound near Vancouver, Canada, measured at 250 ng g^{-1} lw and 1,365 ng g^{-1} lw, respectively (Elliott et al. 2005). Concentrations of individual MeO-PBDEs were generally equivalent or greater than concentrations of individual PBDE congeners. An evaluation of all halogenated organics (i.e, ΣOH-PBDEs, ΣMeO-PBDEs, ΣPBDEs, ΣPCBs, ΣDDTs, ΣHCHs, CBz, and ΣCyclodienes) monitored in seaducks revealed that the total brominated diphenyl ether burden (i.e., PBDEs and their OH- and MeO- analogues) was a relatively small percentage of the total organohalogen burden (< 10%) in those organisms.

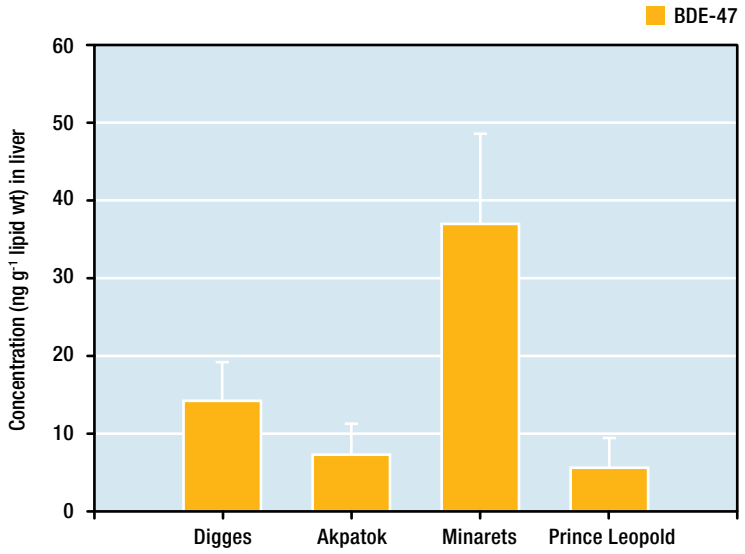

FIGURE 4.31

Concentrations (and standard deviations) of BDE-47 in livers of adult male thick-billed murres collected from four colonies in 2008 (n = 5 for each of the four colonies).

Polychlorinated naphthalenes (PCNs), which are bioaccumulative and exhibit dioxin-like toxicity, were measured in archived eastern Canadian arctic seabird livers collected as part of the Northwater (NOW) Polynya expedition in 1998. Livers from five species which included the glaucous gull, black-legged kittiwake, thick-billed murre (also known as Brünnich's guillemot), black guillemot and the northern fulmar were analyzed. Lipid weight concentrations of ΣPCN (sum of the triCNs to hexaCNs) ranged from a low of 1.7 ng g^{-1} lw in thick-billed murre to a high of 48 ng g^{-1} lw in the northern fulmar. Only a limited number of PCN congeners contributed to ΣPCN, characterized mainly by those that commonly bioaccumulate (tetraCN-42, pentaCNs-52/60, and hexaCNs-66/67). For comparison, glaucous gulls from the Norwegian arctic were found to contain 1.8-162 ng g^{-1} lw in eggs and 1.3–126 ng g^{-1} lw in plasma (Verreault et al. 2005b). Lipid-adjusted concentrations in seabird livers from the NOW were 100-fold greater than those reported in beluga whale blubber (0.04–0.38 ng g^{-1} lw) from near southern Baffin Island (Helm et al. 2002).

PFASs were also analyzed in liver tissues of glaucous gulls and black-legged kittiwake collected from Northwater Polynya in eastern Canadian Arctic in 1998 (Tomy et al. 2004). PFOS levels were 10.0 ± 4.6 ng g^{-1} ww (mean ± standard error) and 20.2 ± 3.9 ng g^{-1} ww in the black-legged kittiwake and glaucous gull, respectively. By comparison, PFOA levels were much lower. PFOA was not detected in the black-legged kittiwake but was 0.14 ± 0.05 ng g^{-1} ww in the glaucous gull. Concentrations of PFOS reported in this study were slightly higher or in the range of concentrations reported for this compound in other Canadian Arctic biota. Martin et al. (2004a) reported low nanogram per gram concentrations of PFOS in livers of northern fulmar from Prince Leopold Island that were 8–20 times lower than those of the glaucous gulls and black-legged kittiwakes reported by Tomy et al. (2004). As well, inter-species differences in PFOS concentrations exist in seabirds and this may, along with spatial differences, explain the differences observed between this study and Martin et al. (2004a). For example, PFOS concentrations in cormorant livers (61 ng g^{-1} ww) from the Mediterranean Sea were 3 times higher than those of glaucous gulls (Kannan et al. 2002). These differences are likely related to their diet choices, migration habitats, exposure, and differences in metabolic capabilities, all of which have been shown to influence concentrations of organochlorines in seabirds (Borgå et al. 2001, Buckman et al. 2004, Fisk et al. 2001a, Fisk et al. 2001b).

Martin et al. (2004a) reported PFASs in black guillemot and northern fulmar liver samples collected from Prince Leopold Island (NU), Canada in 1993. Concentrations of PFOS, PFOSA and C_8–C_{15} PFCAs were either below method detection limits or not detected in all samples with the exception of PFOS in northern fulmars (mean = 1.3 ng g^{-1} ww).

PFASs were determined in liver samples from two seabird species, thick-billed murres and northern fulmars, from Prince Leopold Island in the Canadian Arctic (Butt et al. 2007a) (see temporal trends section 4.2.3.). Thick-billed murre samples were from 1975, 1987, 1993 and 2004, whereas northern fulmars were from 1975, 1987, 1993 and 2003. In the most recent samples (2004 thick-billed murres, 2003 northern fulmars), PFAS profiles were dominated by the C_{11}–C_{15} PFCAs. Mean concentrations in murres and fulmars, respectively, were 4.6 and 1.4 ng g^{-1} ww for PFUnA, 3.7 and 0.9 ng g^{-1} ww for PFDoA, 7.1 and 3.8 ng g^{-1} ww for PFTrA, 4.5 and 2.9 ng g^{-1} ww for PFTA, and 2.0 and 2.3 ng g^{-1} ww for perfluoro-pentadecanoate (PFPA). Comparatively lower concentrations of PFHpA, PFOA, PFNA and PFDA were measured in the murre and fulmar samples. PFOS levels were 0.76 ng g^{-1} ww and 0.41 ng g^{-1} ww in thick-billed murre and northern fulmar, respectively. PFOSA levels were below the method detection limit (2.3 ng g^{-1} ww). Compared with other seabird species from arctic regions, PFOS concentrations were approximately 20-fold lower than those measured in glaucous gulls from the eastern Canadian Arctic presumably due to the higher trophic position of the glaucous gulls (Tomy et al. 2004). However, PFOS levels in the black-legged kittiwake from the eastern Canadian Arctic were approximately 10-fold lower than those in murres and fulmars at Prince Leopold Island, although all three species occupy similar trophic levels (Hobson 1993, Hobson and Welch 1992). Most likely, the observed trends can be attributed to species differences in PFAS elimination. Within the PFCAs, seabird contaminant profiles were dominated by the C_{11}–C_{15} carboxylates with PFTrA (C_{13}) being the predominant compound.

4.1.5.2.3. Seabird eggs

Eggs of thick-billed murres, northern fulmars, black-legged kittiwakes, black guillemots and glaucous gulls from Prince Leopold Island in Lancaster Sound in the Canadian High Arctic (Figure 4.32) were sampled in 2003–2004 and again in 2008, and analyzed for both the legacy and new POPs. While this ongoing work provides important temporal trend

information (section 4.2.3) it is also an opportunity to compare results among species and sampling locations (Figure 4.32).

4.1.5.2.3.1. Legacy POPs in seabird eggs

Concentrations of the major organochlorines in seabird eggs, total chlordanes (ΣCHL), total hexachlorocyclohexanes (ΣHCH), dieldrin, total DDT related compounds (ΣDDT), and total PCBs (ΣPCB) all varied significantly among the five seabird species sampled at Prince Leopold Island, both in 2003–2004 and in 2008, with glaucous gull eggs showing the highest concentrations (Figure 4.32). Buckman et al. (2004) found that glaucous gulls and ivory gulls had high organochlorine levels relative to the other seabird species collected from the Northwater Polynya in 1998. Concentrations of most of the major organochlorine groups and compounds, except dieldrin, found in ivory gull eggs collected from Seymour Island in 2004 (Braune et al. 2007) were also relatively high compared with eggs from Prince Leopold Island, although not as high as for the glaucous gulls (Figure 4.32). Unlike the fulmars from Prince Leopold Island, the fulmars from the Northwater Polynya (not shown in Figure 4.32) also had relatively high levels of most of the organochlorine groups (Buckman et al. 2004). Those authors attributed the inter-species differences to birds feeding at different trophic levels, although they acknowledge that the fulmars had higher organochlorine concentrations than expected based on their trophic position.

The previous spatial survey of contaminants in Canadian arctic seabird eggs was carried out in 1993 and included only the legacy POPs (see Braune et al. 2002). That survey included eggs of thick-billed murres from four arctic locations (Prince Leopold Island and Coburg Island in the High Arctic, Digges Island and Coats Island in northern Hudson Bay). The results of that survey showed that concentrations of all of the major groups of the legacy POPs except ΣHCH, were significantly different in the murres from Prince Leopold Island compared with other arctic murre colonies. There were no significant differences found for the major groups of legacy POPs in eggs from the two low arctic colonies at Coats Island and Digges Island (See map Figure 4.30). By 1998, significant differences between these two colonies remained only for ΣPCB, ΣDDT, and dieldrin (Braune et al. 2002). In 2003, significant differences between the two murre colonies remained only for dieldrin, but in 2008, significant differences re-appeared for ΣCBz and ΣHCH in addition to dieldrin. It is unclear if the changes for ΣCBz and ΣHCH reflect a real change,

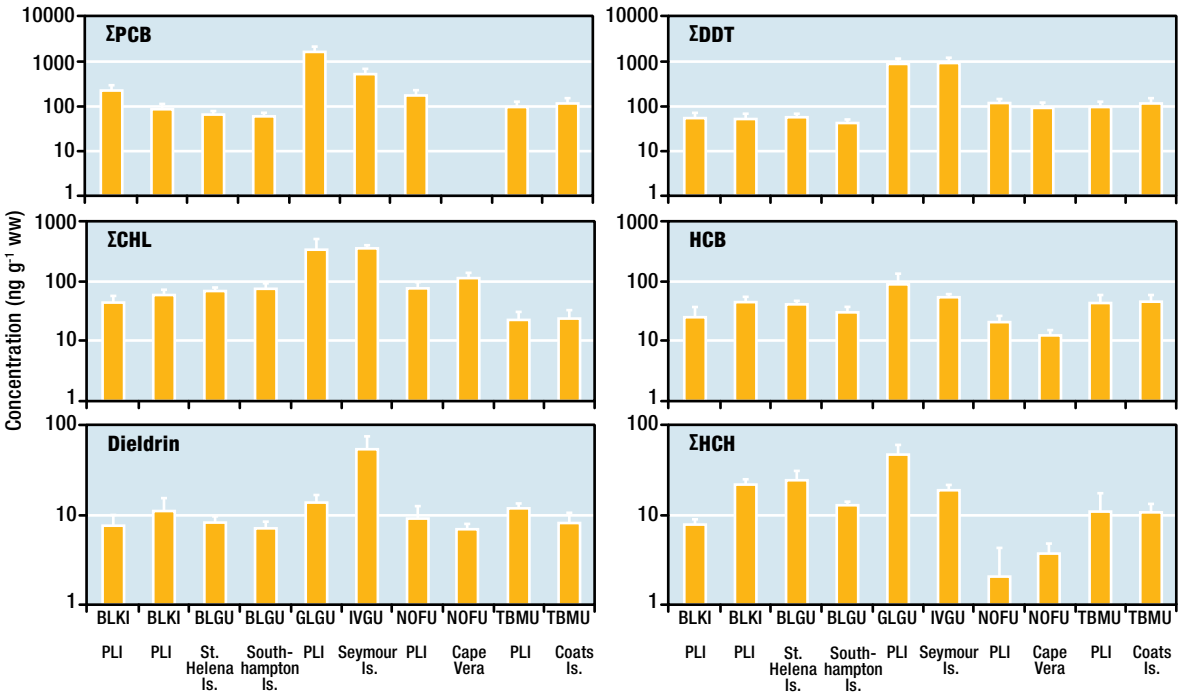

FIGURE 4.32

Mean concentrations (and standard deviations) of major legacy POPs (ng g^{-1} ww) in eggs of black-legged kittiwakes (BLKI), black guillemots (BLGU), glaucous gulls (GLGU), ivory gull (IVGU), northern fulmars (NOFU), and thick-billed murres (TBMU) from the Canadian arctic (means of collections between 2003 and 2008). PLI = Prince Leopold Island.

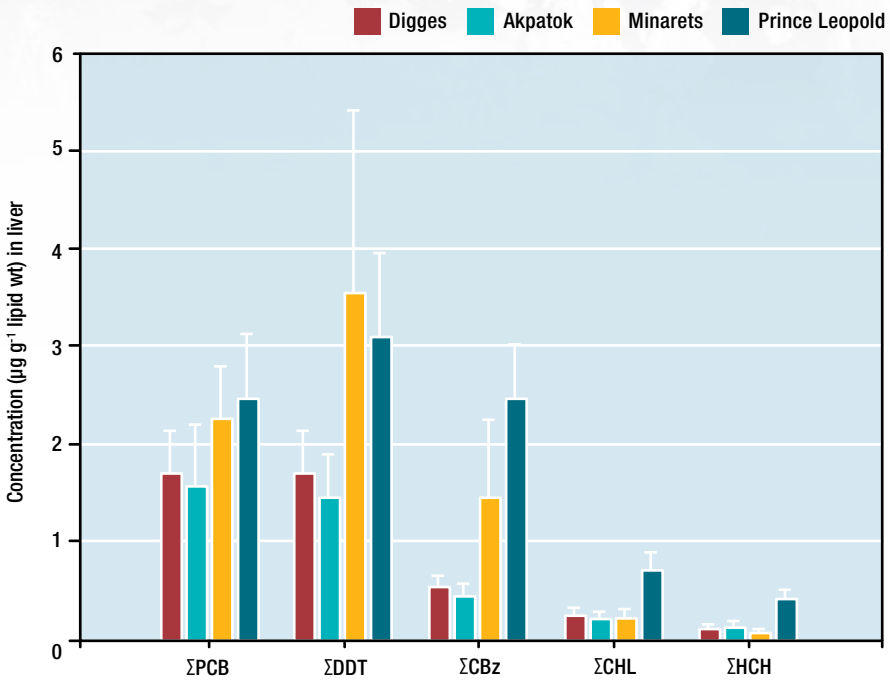

FIGURE 4.33

Concentrations (and standard deviations) of major organochlorine groups in livers of adult male thick-billed murres collected from four colonies in 2008 (n = 5 for each of the four colonies).

or simply variations in data from year to year. A comparison of liver concentrations from female thick-billed murres collected in 2007–2008 from Prince Leopold and Coats Islands showed significant differences for dieldrin, ΣCHL and ΣHCH but no significant difference was found for ΣCBz.

Significant differences were found for generally higher hepatic concentrations of ΣCBz, ΣHCH and ΣCHL among male thick-billed murres sampled from four colonies (Akpatok, Digges, Minarets, Prince Leopold; see Figure 4.30) in 2008 with birds from Prince Leopold Island and, for some organochlorine groups, the Minarets (Figure 4.33.). No significant differences were found among the colonies for ΣPCB or ΣDDT.

Northern fulmar eggs sampled at Prince Leopold Island and Cape Vera on Devon Island in 2003 showed no significant differences for any of the major legacy organochlorine groups except for ΣHCH (Mallory et al. 2006b). However, liver residue levels for adult fulmars sampled from those same two colonies in 2003 indicated that the males generally had higher residue levels than the females, and that the males from Cape Vera had the highest concentrations of most of the major organochlorine groups (Braune et al. 2010). The lower contaminant concentrations found in the post-laying females may be attributed to the female's ability to eliminate some of the contaminant burden into the egg (Mallory et al. 2006a). Hepatic organochlorine concentrations in two fulmars sampled from the Qikiqtarjuaq area in 2001 (Mallory et al. 2005) were lower than those found in the fulmars from Cape Vera and Prince Leopold Island. Except for α-HCH and oxychlordane, hepatic concentrations in the northern fulmars from Cape Vera and Prince Leopold Island were generally lower than levels found in fulmars sampled from the Northwater Polynya in Baffin Bay in 1998 (see Braune et al. 2010).

4.1.5.2.3.2. New POPs in seabird eggs

Archived arctic seabird samples have been screened for newer compounds such as the PFASs (Martin et al. 2004a), PCNs (Muir et al. 2004) and brominated flame retardants such as the PBDEs (Braune and Muir 2005).

Brominated flame retardants: Egg concentrations of one of the major BDE congeners, BDE-47, as well as ΣPBDEs, both varied significantly among the five seabird species sampled at Prince Leopold Island in 2008 (Figure 4.34). Glaucous gull eggs had the highest concentrations of both ΣPBDE (141 ng g^{-1} lw) and BDE-47 (55 ng g^{-1} lw) and northern fulmar eggs, the lowest (ΣPBDE: 4.9 ng g^{-1} lw; BDE-47:

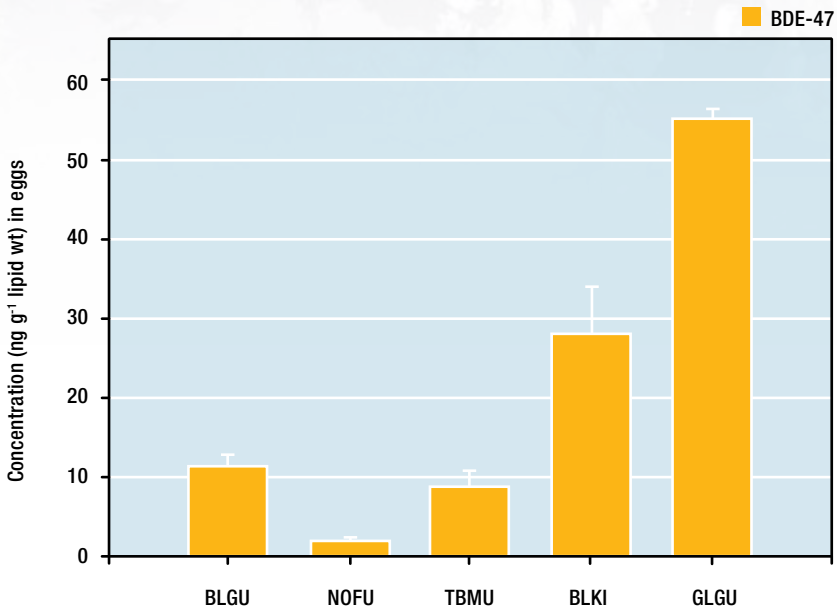

FIGURE 4.34

Mean concentrations (and standard errors) of BDE-47 (ng g^{-1} lw) in eggs of black guillemots (BLGU), northern fulmars (NOFU), thick-billed murres (TBMU), black-legged kittiwakes (BLKI) and glaucous gulls (GLGU) collected from Prince Leopold Island in 2008.

2.4 ng g^{-1} lw). HBCDD was detected only in eggs of the black-legged kittiwakes (16 ng g^{-1} lw) and glaucous gulls (28 ng g^{-1} lw), likely related to the trophic position in the case of the gulls, and the over-wintering area for the black-legged kittiwakes. Concentrations of ΣPBDE (45 ng g^{-1} lw) and BDE-47 (27 ng g^{-1} lw) in ivory gull eggs from Seymour Island in 2004 (Braune et al. 2007) were comparable to those in the black-legged kittiwake eggs from Prince Leopold, but the mean HBCDD level (2.1 ng g^{-1} lw) was considerably lower. Deca-BDE (BDE-209) was not detected (< 1 ng g^{-1} ww) in any of the egg samples analyzed from Prince Leopold, nor was it found in ivory gull eggs (Braune et al. 2007).

There were no significant differences found for ΣPBDE and BDE-47 levels in thick-billed murre eggs from Prince Leopold Island (ΣPBDE: 15 ng g^{-1} lw; BDE-47: 9.3 ng g^{-1} lw) and Coats Island (ΣPBDE: 27 ng g^{-1} lw; BDE-47: 11 ng g^{-1} lw), and HBCDD was not detected (< 1 ng g^{-1} ww) in the murre eggs at either colony.

Perfluoroalkyl substances: C_{11} (PFUA) and C_{13} (PFTriA) were the predominant PFCAs in eggs of both northern fulmars and thick-billed murres sampled from Prince Leopold Island between 1975 and 2009. PFOS was the major perfluorosulfonic acid (PFSA) measured, and PFOSA was detected at very low concentrations in only a few samples. No fluoro telomer alcohols (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) were detected in any of the samples, and fluorotelomer unsaturated acids (6:2 FTUA, 8:2 FTUA, 10:2 FTUA) were detected in only a few samples but could not be quantified.

Egg concentrations of ΣPFCAs and PFOS both varied significantly among the five seabird species sampled at Prince Leopold Island in 2008 (Figure 4.35). Black guillemots, which had the highest PFOS levels, also had the lowest ΣPFCA levels, whereas northern fulmars, which had the highest ΣPFCA levels, and similar PFOS levels.

The black-legged kittiwakes and glaucous gulls also had similar ΣPFCA and PFOS levels in their eggs. There were no significant differences found for hepatic concentrations of ΣPFCA or PFOS among male thick-billed murres sampled from four colonies (Akpatok, Digges, Minarets, Prince Leopold; see map Figure 4.30) in 2008. However, Braune et al. (2010) found that hepatic concentrations of PFCAs in 2003 were higher in northern fulmars from Cape Vera on Devon Island than in fulmars from Prince Leopold Island, although there were no significant differences in PFOS levels.

Compared with eggs of glaucous gulls from the Norwegian Arctic (Verreault et al. 2005a) and eggs of guillemots (common murre) from the Baltic Sea (Holmström et al. 2005), the PFOS concentrations

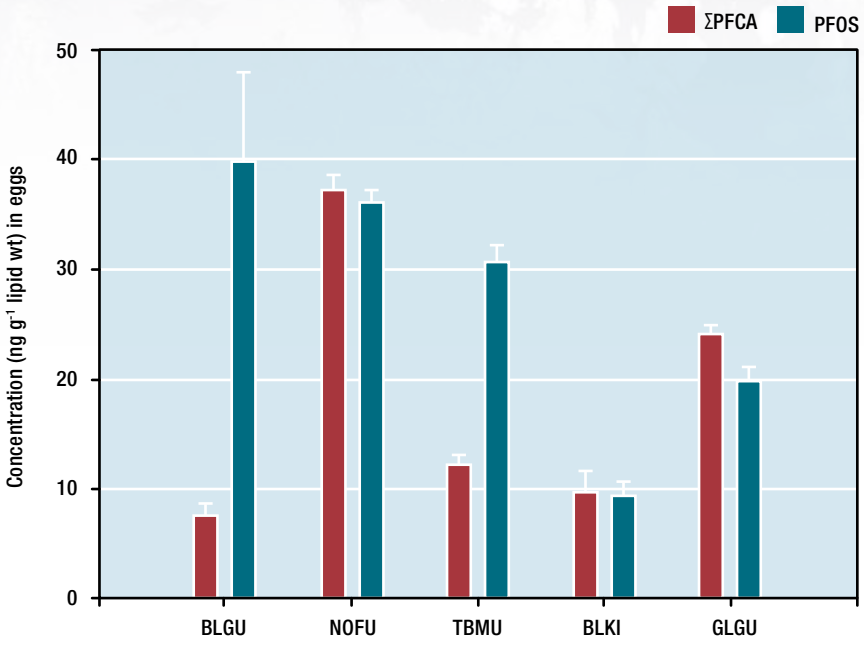

FIGURE 4.35

Mean concentrations (and standard errors) of ΣPFCAs and PFOS (ng g^{-1} ww) in eggs of black guillemots (BLGU), northern fulmars (NOFU), thick-billed murres (TBMU), black-legged kittiwakes (BLKI) and glaucous gulls (GLGU) collected from Prince Leopold Island in 2008.

in the eggs of Canadian Arctic seabirds are relatively low. Fluorotelomer unsaturated acids were also not detected in glaucous gull eggs from the Norwegian Arctic (Butt et al. 2007a, Verreault et al. 2005a), however, the 8:2 and 10:2 FTUAs was detected in livers of northern fulmars and thick-billed murres from Prince Leopold Island.

Polychlorinated naphthalenes (PCNs): At Prince Leopold Island, the total PCN concentrations in thick-billed murre eggs averaged 177 pg g^{-1} ww over the period 2003–2006, and in northern fulmar eggs, concentrations averaged 185 pg g^{-1} ww. Although the total PCN concentrations in seabird eggs were about 50–65 times higher than concentrations found in ringed seal samples collected from Resolute Bay in 2005 (Muir et al. 2006b), PCNs contributed < 0.25% to the total toxic equivalents (TEQ) resulting from PCDD/Fs, non-ortho PCBs and PCNs in eggs of both the thick-billed murres and the fulmars (Braune et al. 2007).

Chlorinated paraffins: Northern fulmar collected in 2003 from Prince Leopold Island and Cape Vera on Devon Island were analyzed for short and medium chain chlorinated paraffins (SCCP/MCCPs) and both the SCCPs (< 1 ng g^{-1} lw) and MCCPs (< 10 ng g^{-1} lw) were undetectable in the fulmar eggs (Muir et al. 2004).

4.1.5.3. Levels and spatial trends in marine mammals

A much greater number of studies have been conducted on marine mammals compared to terrestrial animals and seabirds in the Canadian Arctic, both recently and historically. The focus on marine mammals stems from their importance in the culture and diet of the Inuit, but also because levels of POPs in general are elevated in marine mammal tissues due to their trophic positions. Therefore, more than for any other group of arctic biota, there are concerns about POPs in marine mammals both with respect to the effects on the animals themselves and the transfer to humans.

Sampling sites for marine mammals over the period 2003–2011 are shown in Figure 4.36.

Over this time period, the priorities under the NCP "Blueprint" for environmental monitoring (INAC 2004) included beluga, narwhal, ringed seal, walrus and polar bear. The emphasis was mainly on temporal trends on contaminants and thus broad spatial surveys were curtailed in favour of annual sampling at a limited number of sites (INAC 2004; Macdonald 2004).

Samples are obtained with the help of local hunters in participating communities. The availability of samples is thus quite good in some communities but can also be challenging due to the lack of suitable animals and the costs associated with hunting, which

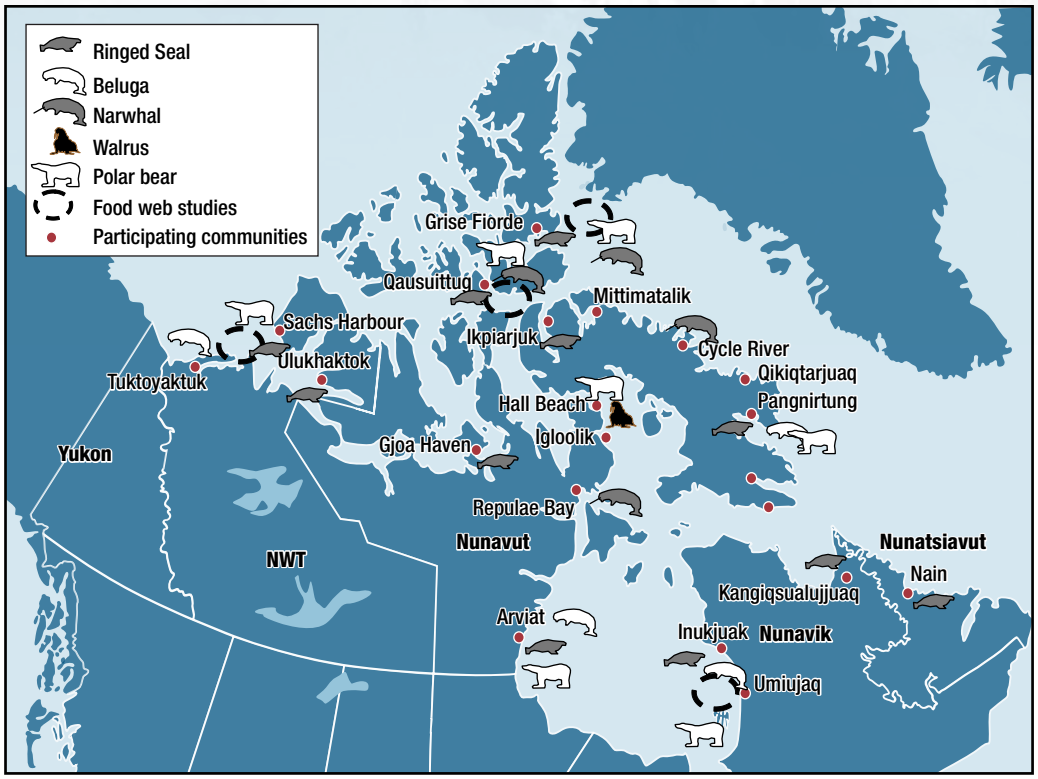

FIGURE 4.36

Locations of marine mammal sampling in the Canadian Arctic, 2003–2011.

deters hunters. Furthermore, there are numerous factors affecting the availability of animals: (i) practical (weather and ice conditions), (ii) ecological and anthropogenic factors, e.g., climate change in relation to introduction of new species and pathogens to the Arctic, and (iii) changes in the foodweb and prey–predator interactions, These issues may also influence and/or confound the exposure to POPs (Letcher et al. 2010b).

While contaminants in arctic marine mammals are largely attributed to delivery via long range transport of atmospheric pollutants or to long distance movement in ocean currents (see Chapter 2, section 2.3.5), some localized sources can be important. Past and present military radar stations have released PCBs into local environments. For example, a radar station operated at Saglek Bay from the 1950s to the present, released PCBs into the adjacent marine environment (see Chapter 3, section 3.4.2.2). A gradient of PCB concentrations was observed in sediments, shorthorn sculpins, and black guillemot eggs away from the main area of contamination. While age, trophic level and variable habitat use masked a clear contribution to ringed seals, one relatively contaminated individual out of six sampled may have reflected some contribution from the radar station PCBs. Further research has shed more light on the consequences of the Saglek Bay PCB source and delivery to upper trophic level ringed seals (Brown et al. 2013).

All relevant data on legacy and new POPs in marine mammals that have become available since the last CACAR are reviewed herein. Over the period 2003–2011 there has been new data on POPs (including isomers, precursors, and metabolites and other degradation products) in apex mammalian species in the arctic marine food web. Table 1.1, in Chapter 1, summarizes the chemicals that have been included in surveys of sample extracts. As noted for fish and invertebrates, the PFASs and PBDEs are the most commonly reported and have become routinely analyzed since the early 2000s.

Some of this work (to 2008) has been examined in several review papers (Bidleman et al. 2010, Butt et al. 2010, de Wit et al. 2010, Hoferkamp et al. 2010, Letcher et al. 2010b, Rigét et al. 2010, Weber et al. 2010) etc.). These reviews summarized new information on POPs that had been published from 2002 to 2008 in key, targeted arctic wildlife populations, including marine mammals. As noted in the introduction (4.1.1), the spatial trends of POPs discussed in this section are often qualitative because they are based on evaluations of means and ranges of

concentrations from different studies. In the case of the sums of groups of compounds, such as PCBs and chlordanes (CHL), some laboratories have included more congeners or components than others in the ΣPCB and ΣCHL results. Rigorous comparisons between locations also require information on age, sex, blubber thickness, nutritional status, collection season, and reproductive status of the animals, all of which can have an important influence on contaminant concentrations. Adjustment for these factors was beyond the scope of this assessment.

4.1.5.3.1. Ringed seals

As a key component of the diet of polar bears and Inuit of Canada and Greenland, ringed seals are the most abundant and widely distributed pinnipeds in the Arctic. Fish, mainly arctic cod, and crustaceans (amphipods, mysids, and euphausids) are the main constituents of the ringed seals' diet. Studies of the ringed seal blubber fatty acid profiles suggest that arctic cod are important for seals particularly in the eastern Arctic while capelin and sandlance may be more important in Hudson Bay animals (Thiemann et al. 2007). Fatty acid studies suggest that ringed seals forage within limited areas (Thiemann et al. 2007), and confirmed other observations that they are relatively sedentary with males possibly occupying the same under ice habitat for up to 9 months (Reeves 1998, Smith 1987). Some regional movements, e.g., from the western Canadian Arctic islands to the East Cape of Siberia (Smith 1987), and between Greenland and Canadian waters have been documented (Teilmann et al. 1999).

4.1.5.3.1.1. Legacy POPs in ringed seals

Spatial trends of legacy POPs in the Canadian Arctic were previously reported in Fisk et al. (2003) based on results from samples collected at 8 communities between 1998 and 2002. For most POPs the lowest levels were observed in seals from the western and central Canadian Arctic Archipelago with higher levels in Hudson Bay. The exception was ΣHCH, which was higher in the samples from Ulukhaktok (Holman) in the western Canadian Arctic.

Spatial trends of six major legacy POPs, based on samples collected from 12 locations in the Canadian Arctic between 2003 and 2010, are shown in Figure 4.37. The spatial comparison is based only on samples from females and juvenile males. Females and juveniles were selected because their concentrations of halogenated organics are not strongly affected by age (Muir et al. 2000b). PCBs remain the major POP in ringed seal blubber with mean concentrations ranging from 250–980 ng g^{-1} lw. There are few clear geographic trends for ΣPCBs, ΣDDT, and ΣCHL with the exception of higher mean concentrations at Nain for ΣPCBs and ΣDDT (Figure 4.37). The ΣPCBs concentrations at Nain (2005) are higher than those reported for female seals (511 ± 328 ng g^{-1} lw; n=16) sampled along the Labrador coast in 2009 (Reimer and Ross 2011). However, the sample size from Nain in 2005 (n=8) was small and more recent work by Reimer and Ross (2011) with much larger sample sizes is likely more representative of prevailing levels.

Average concentrations of ΣHCH, ΣCBz and toxaphene are higher in the western and central Archipelago locations than Hudson Bay and the eastern Arctic (Pangnirtung). This geographic trend has been previously observed for ΣHCH and ΣCBz although previous data for the western Arctic were only from Holman (Fisk et al. 2003). ΣHCH consisted mainly of α-HCH, which usually represented approximately 90% of the total HCH isomers in the blubber lipid of ringed seals (Addison et al. 2009). Kelly et al. (2007) reported legacy POPs in the blubber of female ringed seals from Nunavik and Labrador communities (Inukjuaq, Makkovik) with geometric mean concentrations of ΣPCBs (493, 87.9–2,760 ng g^{-1} lw), ΣDDTs (483, 44.0–5,290 ng g^{-1} lw), ΣHCHs (204, 53.2–785 ng g^{-1} lw), and ΣCBz (40.6, 14.8–112 ng g^{-1} lw). These samples were collected in 1998–1999 and thus pre-date results presented in Figure 4.37. Further discussion of temporal trends of legacy POPs is provided in section 4.2.4.1.

4.1.5.3.1.2. New POPs in ringed seals

The period 2003–2011 has seen the measurement of many new organic contaminants in ringed seals in the Canadian Arctic. Table 1.3, in Chapter 1, summarizes the chemicals that have been included in surveys of sample extracts. The PFASs and PBDEs are the most commonly reported and have become routinely analyzed since the mid-2000s. These are therefore the main focus of the overview of spatial trends of new POPs.

Perfluoroalkyl substances: Following the first report of PFOS in Canadian Arctic ringed seals (plasma–location not identified) by Geisy and Kannan (2001), Martin et al. (2004a) assessed PFASs in various arctic species, including ringed seals, collected in 2001 from Ulukhaktok (NT) and from Ausuittuq/Grise Fjord (NU). PFOS was the major contaminant detected in most samples. The dominant PFCA detected was PFNA, and concentrations generally decreased for all other PFCA homologues with increasing perfluoroalkyl chain length. In general,

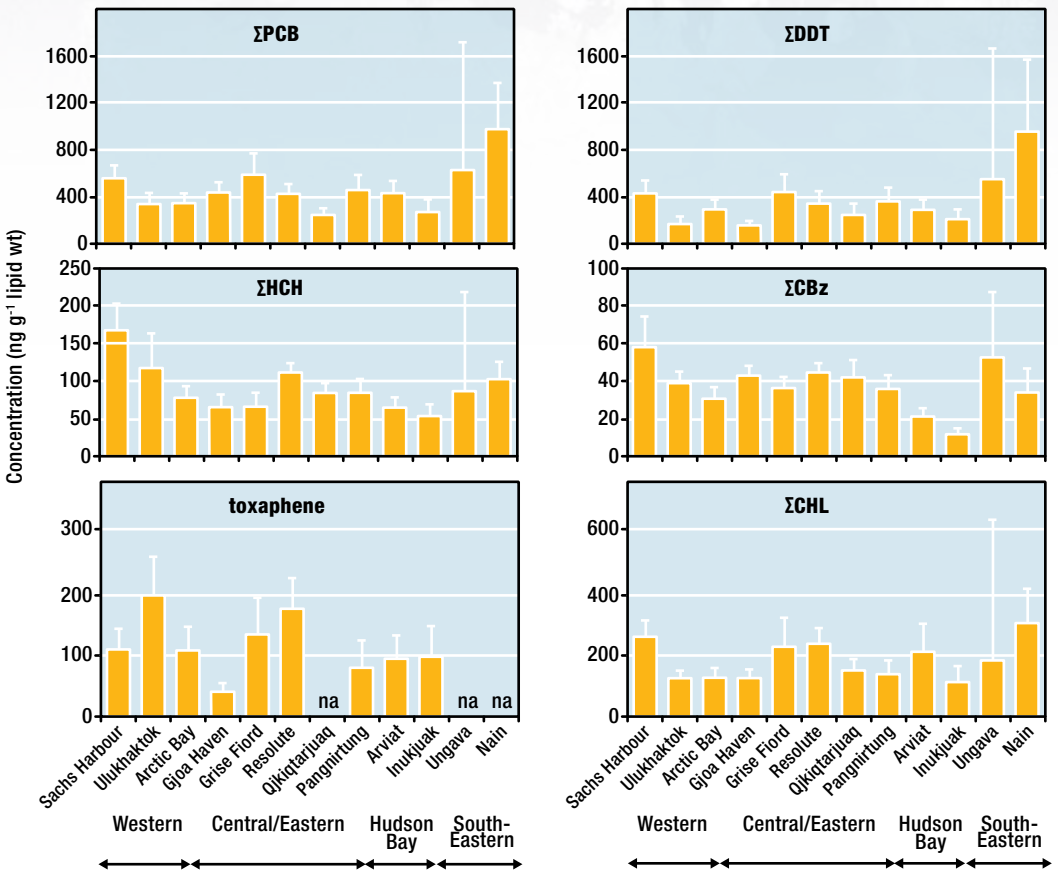

FIGURE 4.37

Arithmetic mean concentrations (and 95% confidence limits) for major legacy POPs in blubber of ringed seals for the period 2003-2010. Sampling locations are arranged from west to east. Sample numbers at each site vary from 3 (Ungava; Kangiqsualujjuaq) to 64 (Arviat). Further details are provided in Annex Table A4-1.

odd-length PFCAs exceeded the concentration of even-length PFCAs, and concentrations decreased with increasing chain length.

Butt et al. (2008) carried out a comprehensive assessment of the spatial trends of perfluoroalkyl compounds in liver samples from 11 populations of ringed seals from the Canadian Arctic collected between 2002 and 2005. Perfluorooctane sulfonate was the dominant PFAS measured, with concentrations ranging from 6.5 ng g^{-1} ww to 89 ng g^{-1} ww, contributing between 29% and 56% of the total PFAS concentration (Figure 4.38). Geometric mean concentrations of total C_9–C_{15} PFCAs ranged from 8.8 ng g^{-1} ww to 84 ng g^{-1} ww, and C_9–C_{11} PFCAs predominated. Geographic differences were observed including elevated levels in the Gjoa Haven (Rae Strait, central Canadian Arctic Archipelago) and Inukjuak populations (eastern Hudson Bay), to lower concentrations at Pangnirtung (Cumberland Sound, Baffin Island) (Figure 4.38). Specifically, geometric mean concentrations of PFNA, PFDA, and PFOS at Gjoa Haven were 8.1-, 4.2-, and 2.6-fold higher than the geometric means of the other 10 ringed seal populations. Authors concluded that the elevated PFAS concentrations measured at Gjoa Haven and Inukjuak were likely not the result of the direct contamination from nearby local sources, like the use of aqueous film–forming foams which is generally associated with high levels of PFSAs (PFHxS and PFOS) (Moody et al. 2003, Stock et al. 2007), but rather were due to long range atmospheric and ocean transport (See Chapter 3, section 3.2.3). Geographic trends of PFASs were examined by grouping individual seal populations into four broad regions, excluding Gjoa Haven: (1) southeast Beaufort Sea, (2) Hudson Bay, (3) south Baffin Island and Labrador and (4) the High Arctic.

Concentrations of most PFASs tested (C_9–C_{15} PFCAs, PFOS, and PFOSA) were statistically similar across the regions, with the exception of PFUnA and PFTrA, which were highest in the Hudson Bay population. These results were consistent with PFAS spatial trends in polar bears in the same population, which showed elevated levels of PFOS and PFCAs

with chain lengths greater than 10 (Smithwick et al. 2005) (see section 4.1.5.3.5.2). Among the PFCAs, odd-number chain length PFCAs were generally greater than their corresponding PFCAs with even number chain lengths (PFNA, PFOA, PFUnA PFDA, and PFTrA PFDoA). These odd–even PFCA trends have been observed in other arctic wildlife populations, including ringed seals (Martin et al. 2003b, Martin et al. 2004a) and polar bears (Smithwick et al. 2005), and are consistent with FTOH degradation as the source of PFCAs. Perfluorinated carboxylate profiles were dominated by either PFNA or PFUnA. PFNA contributed between 18% and 58% to the ΣPFCA profile and PFUnA contributed between 16% and 45%. The predominance of PFCAs with ≥ 9 carbons and the observation that the odd carbon number homologue is in greater concentration than the adjacent lower, even carbon number homologue, e.g., $C_{11} > C_{10}$, $C_9 > C_8$, has been consistently reported for arctic ringed seals (Bossi et al. 2005, Martin et al. 2004a, Smithwick et al. 2005, Tomy et al. 2009b, Powley et al. 2008).

Several other studies have reported PFASs in seals. Tomy et al. (2009b) reported PFASs in ringed seal liver from Ulukhaktok collected in 2004. The concentrations were very similar to those reported by Butt et al. (2008) for nearby Sachs Harbour (Figure 4.38) and also to Powley et al. (2008) who reported PFOS concentrations of 18–34 ng g^{-1} ww in liver of ringed seals from Ulukhaktok. Powley et al. (2008) found low concentrations of PFOS in blubber (0.4–0.9 ng g^{-1}) and blood (2.5–8.6 ng g^{-1}). In addition to the usual list of PFCAs, Powley et al. (2008) also reported 2H,2H,3H,3H-pentadecafluorodecanoic acid (7-3 acid) a metabolite of fluorotelomer alcohols via rat metabolism (Fasano et al. 2006). The 7-3 acid was found in the range of 0.5–2.5 ng g^{-1}, which was about 50% of the concentrations of PFNA in ringed seal liver.

Powley et al. (2009) also investigated the presence of branched vs. linear isomers of PFOS and PFCAs in ringed seal liver as a means of assessing sources (see further discussion of PFAS isomers in Chapter 2, section 2.3.5.2). Powley et al. (2009) did not detect PFCA branched isomers while the branched isomer content of PFOS was approximately 4%, much lower than the technical product (approximately 30%). De Silva et al. (2009) investigated PFCA isomers in ringed seals from Resolute Bay and found that branched isomers were undetectable. This implies

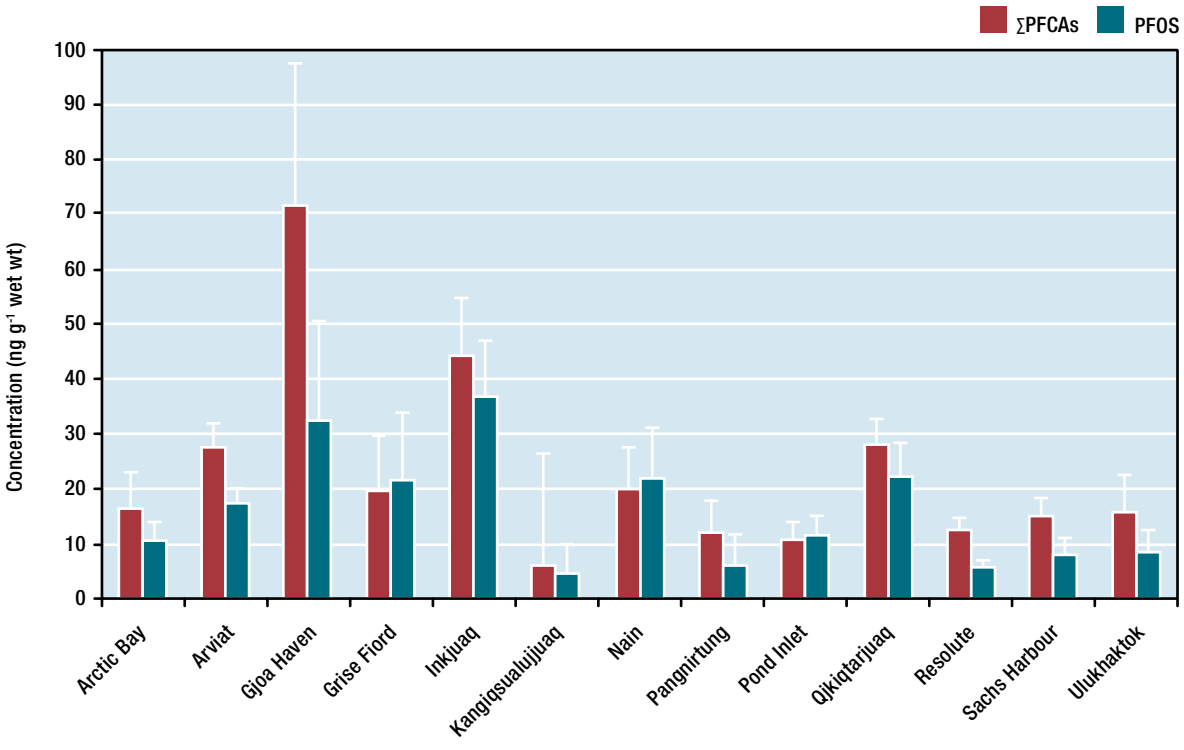

FIGURE 4.38

Geometric mean concentration (and 95% confidence limits) of perfluorooctane sulfonate (PFOS) and perfluorocarboxylates (sum PFOA, PFNA, PFDA, PFUnA) in liver of ringed seals from individual locations in the Canadian Arctic over the period 2003 to 2010. Data from Muir et al.(2011) and Butt et al. (2008).

a fluorotelomer source of PFCAs, however, it may also reflect different pharmacokinetics of branched vs. linear isomers, i.e., more rapid elimination of branched isomers.

Ostertag et al. (2009) estimated the human dietary exposure to PFASs in ringed seal tissues. Total PFAS concentrations (sum of PFOS and C_8–C_{11} PFCAs) in ringed seal ranged from 1.0 ng g^{-1} ww to 10.2 ng g^{-1} ww in liver, blood and meat, both boiled and raw. The range in ΣPFA concentrations in narwhal (0.4–1.6 ng g^{-1} ww), bearded seals (0.2–2.2 ng g^{-1} ww) and walrus (non-detectable–0.8 ng g^{-1} ww) was smaller than in the other animals studied.

PCDD/Fs: Addison et al. (2005) reported PCDD/Fs in the blubber of ringed seals from Ulukhaktok. PCDD and PCDF concentrations were low in all seals (typically < 10 pg g^{-1} and < 5 pg g^{-1}, respectively), did not change between 1981 and 2000, and had no sex or age-related differences. While the study concluded that this is consistent with an important role of atmospheric transport of these compounds, the importance of the metabolism of planar compounds including PCDDs and PCDFs relative to many of the globular PCBs is evident.

Brominated flame retardants: Ikonomou et al. (2002) were the first to report PBDEs in ringed seals in the Canadian Arctic at Ulukhaktok. In a follow-up paper, they compared PBDE patterns in two southern Canadian seal species—harbour seals from British Columbia (BC) and grey seals from Nova Scotia (NS) (Ikonomou and Addison 2008)—with ringed seals at Ulukhaktok and noted that the latter had a higher proportion of lower brominated congeners, and a lower proportion of higher bromine congeners, than did the NS and BC seal samples. This is consistent with selection in favour of more volatile compounds during atmospheric transport to the Arctic. The authors attribute this to the important role that atmospheric transport plays in delivering PBDEs to the Canadian Arctic, although species-specific differences and differences in feeding ecology cannot be ruled out.

Spatial trends of ΣPBDEs and BDE-47 in blubber of female ringed seals from 14 locations are presented in Figure 4.39. These results are based on samples collected from 2002 to 2010 (as described in Muir et al. 2009b) and represent the sum of BDE-17, -28/33, -49, -47, -66, -100, -99, -85, -154, -153, -138, -183, -190, and -209. BDE-47 was the major congener, representing 55% to 80% of ΣPBDEs. Sample sizes varied from n=3 (Quaqtaq, Kangiqsujuaq, Kangiqsualujjuaq) to n=70 (Arviat) (Annex Table A4-1). A distinct trend of increasing PBDEs from west to east is evident, with the highest concentrations in samples from Inukjuak and Nain. Reimer and Ross (2010) reported mean ΣPBDEs (combined males and females from Nunatsiavut Fiords collected in 2006–2008), ranging from 23 ng g^{-1} lw to 49 ng g^{-1} lw, which appears to confirm the higher PBDEs along the Labrador coast compared to those determined further north and west.

Kelly et al. (2008a, b) reported on PBDE concentrations in ringed seal (n=11) collected in 1998–1999 from Nunavik/Labrador (Inukjuaq, Makkovik). Mean ΣPBDE concentrations were 11 ng g^{-1}, lw and 14 ng g^{-1} lw in female (n=6) and male (n=5) ringed seals, respectively. These results are similar to those from Nunavik locations sampled in 2002 and 2007 (Figure 4.37; Annex Table A4-1).

HBCDD was determined in blubber of ringed seals from 10 locations sampled as of 2006 (Figure 4.39). Concentrations were about 10-fold lower than the ΣPBDEs and less than method detection limits in several locations. The results in Figure 4.39 are based on analysis by gas chromatography-negative ion mass spectrometry which provides a result for ΣHBCDD because α- and γ-isomers of HBCDD in the samples were most likely thermally isomerized to the α-isomer in the GC injection port (Gebbink et al. 2008). Although site-to-site variation is high, there are indications that HBCDD is higher in seals in Hudson Bay compared to other locations in the central and western Arctic. Tomy et al. (2009b) reported mean concentrations of ΣHBCDD of 0.66 ± 0.30 ng g^{-1} in ringed seal blubber from Ulukhaktok (2004 collection), which is very similar to the results observed for samples collected over the period 2007–2010 (Figure 4.39). They used liquid chromatography tandem mass spectrometry, which permitted determination of individual HBCDD isomers. The α- and γ-isomers were present in ratios of approximately 3:2.

Other BFRs determined in ringed seal blubber samples are listed in Chapter 1, Table 1.3. Of the 16 individual compounds surveyed, BTBPE was detected in approximately 20% of samples (> 0.02 ng g^{-1}). HBB, BB-101, and BEHTBP were detected (> 0.02 ng g^{-1}) in approximately 5% of samples.

Natural brominated compounds: Kelly et al. (2008b) reported the presence of methoxylated PBDE (ΣMeO-PBDEs) concentrations in male ringed seal blubber from Nunavik. Concentrations ranged from 1.7 ng g^{-1} lw to 26 ng g^{-1} lw (n=9) and thus were higher than PBDEs. However, ΣOH-PBDE was not at detectable levels in any of the samples. Previous studies have attributed the occurrence of

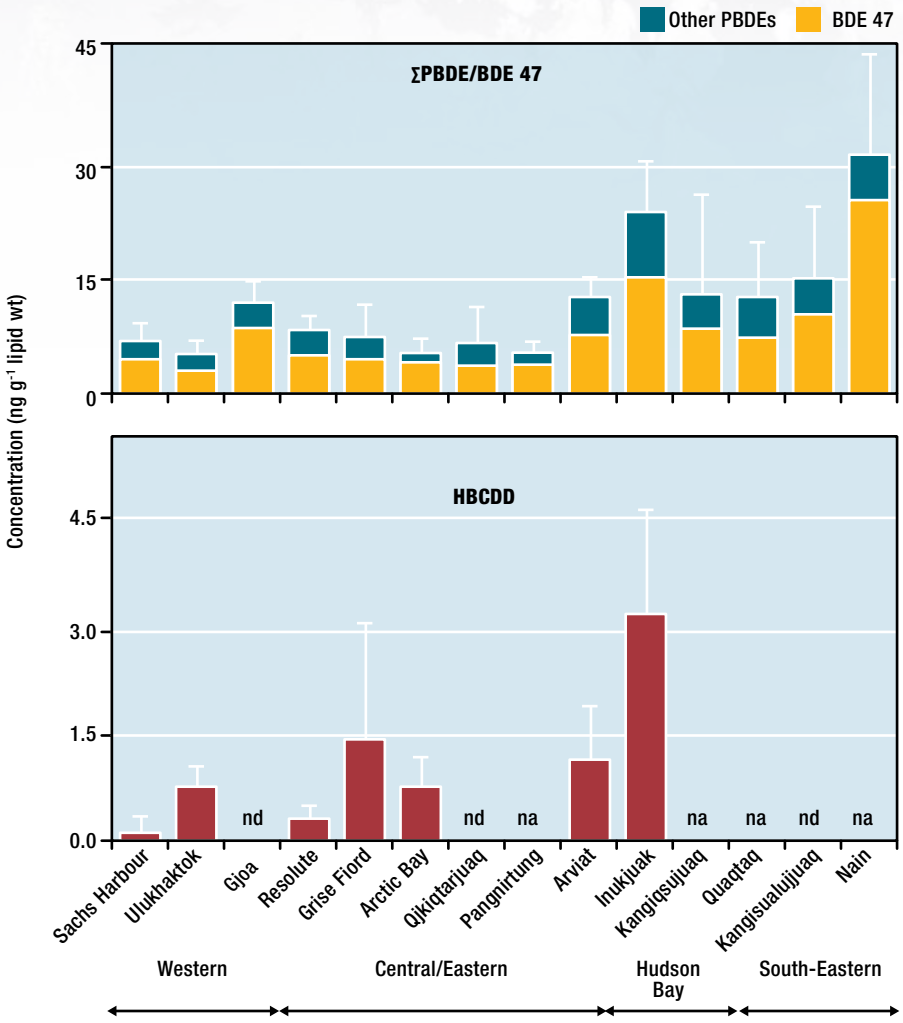

FIGURE 4.39

Mean concentrations (and 95% confidence limits) of ΣPBDEs and HBCDD in blubber of female ringed seals from 14 locations across the Canadian Arctic. BDE-47 concentrations are shown as part of the ΣPBDE results. HBCDD was not determined at all locations ("na") and was not detectable at others ("nd"). Results are from Muir et al. (2009b).

MeO-PBDEs residues in wildlife and humans to accumulation of natural products rather than PBDE metabolism (Teuten and Reddy 2004, Teuten et al. 2005). However, Kelly et al. (2008b) were unable to detect MeO-PBDEs in other environmental media (i.e., sediments) or macroalgae from the region (see section 4.1.6.3).

Tittlemier et al. (2002) reported on concentrations of four halogenated dimethyl bipyrroles (ΣHDBPs) in marine mammal blubber from various locations worldwide (Tittlemier et al. 2002). Mean concentrations of ΣHDBP in ringed seals from Pangnirtung (n=9, 1999), western Greenland (n=9, 1999), Eureka (n=6, 1994) and the southern Beaufort Sea (n=35, 1997–1998) were 0.4, 0.8, 1.2 and 0.6 ng g^{-1} lw. Thus HDBPs were present at similar concentrations to several PBDE congeners in the early 1990s. Current levels in ringed seals in the Canadian Arctic are unknown.

Polychlorinated naphthalenes: Arithmetic mean concentrations of PCNs in blubber of female ringed seals from 9 communities across the Canadian arctic ranged from 27 ng g^{-1} lw to 77 ng g^{-1} lw (Figure 4.40). Tetra- (CN-32,-35, 36, 33/34/37, 38, 42, 28/43, 46, 47), penta (CN-50, 52/60, 53, 57, 58, 59, 61, 62 and hexa (CN 64/68, 66/67) congeners predominated. No clear geographic trends are evident although the mean concentrations in seals from the western and central Arctic locations are higher than at Nain or Qikiqtarjuaq. The concentrations found in ringed seals were generally similar to the mean of 48 ng g^{-1} lw (range of 35–71 ng g^{-1}) found in ringed seals from Pangnirtung sampled in 1993 (Helm et al. 2002).

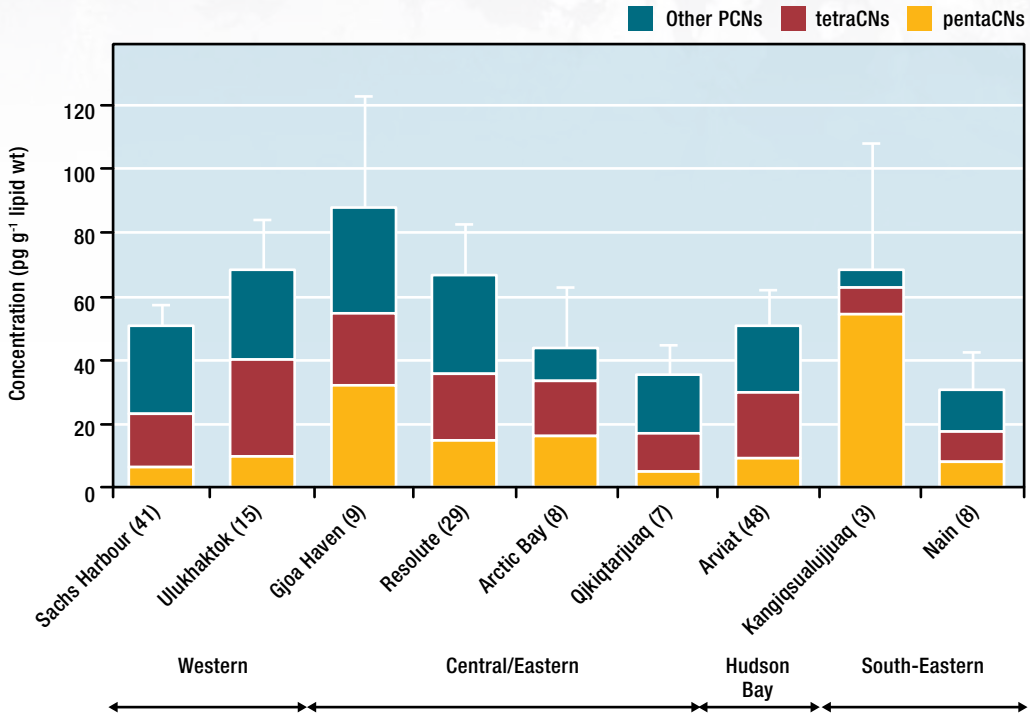

FIGURE 4.40

Mean concentrations (and standard deviations) of ΣPCNs in blubber of female ringed seals (vertical line = 95% confidence limit) from 9 locations across the Canadian Arctic. Results are based on samples from 2002–2010 and sample sizes (shown in parentheses) vary because some locations were sampled multiple times. The fractional amounts of tetra-, penta- and other PCNs are shown within the bars.

Chlorinated paraffins: Short and medium chain chlorinated paraffins (SCCP-MCCPs) were determined in ringed seal blubber by GC-high resolution mass spectrometry (HRMS) using negative ion (Tomy et al. 2000) or MAB-ionization mode (Moore et al. 2004). Mean concentrations ranged from 46 ng g^{-1} lw to 138 ng g^{-1} lw in female ringed seals (Figure 4.41). Male ringed seals sampled at Pangnirtung in 2002 had higher concentrations than females (248 ± 166 ng g^{-1} lw (n=6) and 79 ± 24 ng g^{-1} lw (n=12) respectively). Undecanes (C_{11}) and dodecanes (C_{12}) were the predominant chain lengths in seals. Within these chains, hexachloro-alkanes predominated (Muir et al. 2004). MCCPs were not detected in ringed seals (< 10 ng g^{-1} lw) (Muir et al. 2004). Analytical challenges with SCCPs have prevented analysis of samples from a wider range of locations.

Chlordecone: Extracts of ringed seal blubber were screened for chlordecone using GC-high resolution mass spectrometry (Muir et al. 2009a). A peak with correct retention time and mass fragment ratios (m/z 238.884 and 236.8314) was observed in samples from Arviat and Resolute Bay at a signal to noise of about 20:1. However, low recoveries of chlordecone were observed in the extraction and isolation steps and no further work was done. Dallaire et al. (2006) reported preliminary results suggesting chlordecone was detectable in human blood plasma with a geometric mean concentration of 38 ng L^{-1}.

Endosulfan: Arithmetic mean concentrations of total endosulfan (ΣEndosulfan; sum of α-endosulfan, β-endosulfan and endosulfan sulfate) in blubber of female ringed seals from 9 communities across the Canadian Arctic ranged from 0.14–1.4 ng g^{-1} lw (Figure 4.42).

The β-isomer predominated at most locations, representing 25% to 82% of ΣEndosulfan. Endosulfan sulfate (ES) was detectable in almost all samples at concentrations ranging from 2% to 64% of ΣEndosulfan. The results in Figure 4.42 represent analyses by GC-low resolution mass negative ion spectrometry (NIMS) and are updated from results reported by Muir et al. (2009b) and Weber et al. (2010). Kelly et al. (2007) determined the three endosulfan species in blubber of ringed seals from Nunavik by GC-high resolution mass spectrometry (HRMS) using the method of Rayne and Ikonomou (2003). Weber et al. (2010) concluded that α-endosulfan, β-endosulfan and endosulfan sulfate were best analyzed by GC-NIMS and HRMS rather than by GC-ECD, which had been employed in a number of earlier studies.

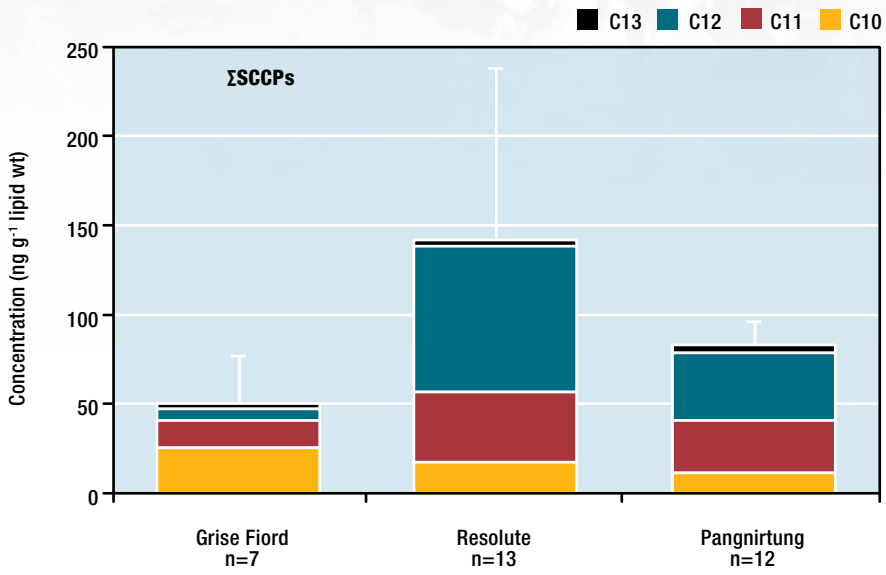

FIGURE 4.41

Mean concentrations (ng g^{-1} lw) of ΣSCCPs in blubber of female ringed seals (vertical line = 95% confidence limit) from 3 locations in the Canadian Arctic. Results are based on samples collected from 1998–2004.

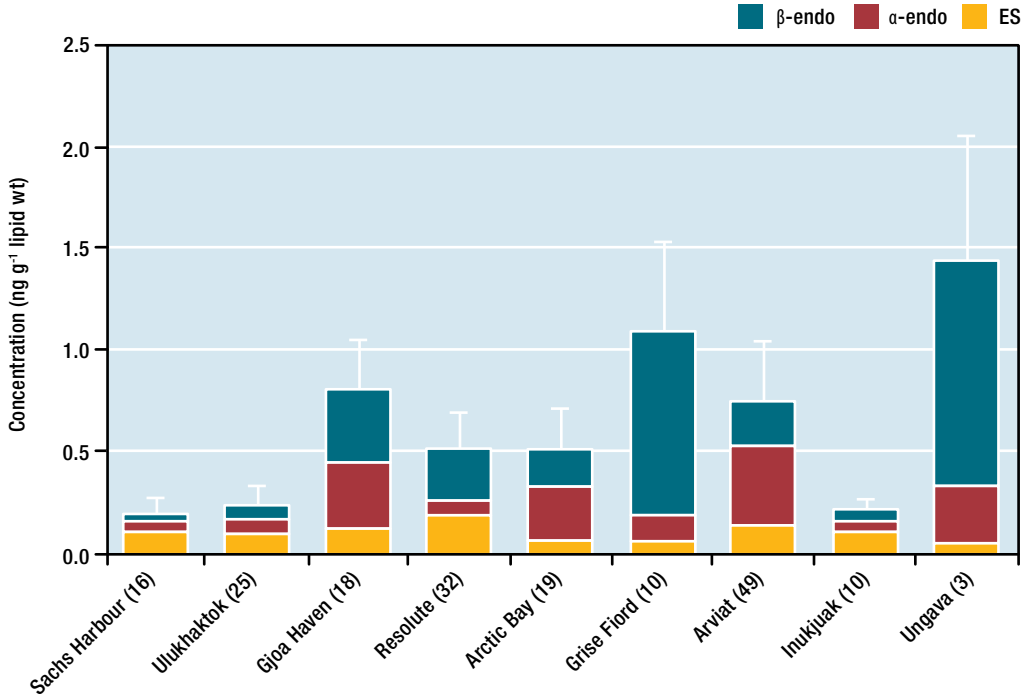

FIGURE 4.42

Mean concentrations (and 95% confidence limits) (ng g^{-1} lw) of ΣEndosulfan in blubber of female ringed seals from 9 locations based on samples collected from 2003–2010. The fractional amounts of α- endosulfan, β-endosulfan and endosulfan sulfate (ES) are shown within the bars.

ΣEndosulfan concentrations were significantly lower in the two western Arctic locations compared to sites further east and south, with the exception of Inukjuak (Figure 4.42). The generally higher concentrations may be related to the fact that major use areas of endosulfan in North America were in the east, in Ontario, New Brunswick and PEI as well as in the US mid-west (see Chapter 2, section 2.2.3.2).

4.1.5.3.2. Walrus

Walrus are long-lived benthic feeders and important indicator species for bioaccumulating contaminants in benthic marine food webs. They play an important role in native traditional hunting of Inuit in eastern Canadian Arctic communities. Levels of POPs in this species are less well studied compared to seals and beluga in Canadian waters. This species has had a low priority for contaminant investigations because studies of walrus in the other regions (Born et al. 1981, Taylor et al. 1989) showed low levels of PCBs and ΣDDT. These levels were about 5 to 10 times lower than in ringed seals from the same areas. However, some individual walrus are believed to be including ringed seals in their diet, and therefore feed at higher trophic levels than others, resulting in much higher contaminant burdens (Muir et al. 1995). Since CACAR II, only a few studies have reported concentrations of legacy POPs and certain new chemicals such as PFASs in walrus, when they were sampled as part of marine food chain studies.

4.1.5.3.2.1. Legacy POPs in walrus

Legacy POPs continued to be determined in walrus from Hall Beach and Igloolik (NU) (Stern et al. 2009). Major POPs in blubber were PCBs (arithmetic means; 370 ng g^{-1} lw males; 133 ng g^{-1} lw females), ΣCHL (203 ng g^{-1} lw males; 159 ng g^{-1} lw females) and toxaphene (370 ng g^{-1} lw males; 306 ng g^{-1} lw females) (See Annex Table A4-1). Two samples from males collected at Grise Fiord (NU) had much higher concentrations of PCBs (1,307 ng g^{-1} lw) indicating that there could be large variations among walrus depending on their diets, as discussed above.

4.1.5.3.2.2. New POPs in walrus

Ostertag et al. (2009) estimated the dietary exposure of PFASs from traditional foods among Inuit in Nunavut, Canada (Ostertag et al. 2009). Local foods were sampled in Nunavut between 1997 and 1998. Because of the small sample size, comparing concentrations of PFASs in different tissues was not possible. The range of ΣPFAS concentrations in walrus liver (non detectable–0.8 ng g^{-1} ww) was smaller than in the other animals studied.

Tomy et al. (2004) reported on PFASs in walrus from Cape Dorset (NU) collected in 1998 (n=5). Only PFOS and PFOA were detectable in walrus liver at concentrations of 2.4 ng g^{-1} ww and 3.4 ng g^{-1} ww, respectively. For the BFRs, the ΣPBDE concentrations in walrus were ca. 45 times smaller than in narwhal (0.4 ng g^{-1} lw and 18 ng g^{-1} lw, respectively). ΣHBCDD concentrations in walrus were reported to be 0.7 ng g^{-1} lw by Tomy et al. (2008b) in the same sample set collected in their earlier study in 2004. Walrus contained > 60% of the γ-diastereoisomer of HBCDD. ΣPBDE concentrations were 0.4 ng g^{-1} lw in walrus.

4.1.5.3.3. Beluga whales

Beluga or white whales are small (up to 4.5 m long) toothed cetacean (odontocete) with a circumpolar distribution in the Arctic. Beluga whales are relatively long-lived (> 35 years) and feed near the top of the marine food web on a variety of fish, as well as on invertebrates such as cephalopods and shrimp (Banfield 1974). They are present from Alaska, across the Canadian Arctic to western Greenland, with large populations in Hudson Bay and among the islands in the eastern Canadian Arctic. Beluga movements are extensive, seasonal and are generally predictable. They come into coastal waters and estuaries in mid-summer, and winter offshore in pack ice and polynyas (Brodie 1989). Like ringed seals, belugas are an important and common item in the diet of the Inuit.

The CACAR II assessment included results (to 2002) of belugas from Hudson Bay, Hudson Strait, Cumberland Sound and Mackenzie Bay. Since then, additional samples have been analyzed from the southern Beaufort Sea population (Husky Lakes, Hendricksen island), the southeast Baffin Island stock (Cumberland Sound, Pangnirtung (NU)) and in southern Hudson Bay (Sanikiluaq (NU)) (Stern et al. 2009, Stern et al. 2011).

4.1.5.3.3.1 Legacy POPs in beluga whales

Stern et al. (2005) presented an extensive study of beluga collected from community hunts and stock assessment programs at 15 locations across the Canadian Arctic between 1993 and 2001. Similar concentrations and proportions of POPs were found over large spatial areas (i.e., eastern vs. western sites). However, some geographic differences were apparent, with higher levels of HCB, β-HCH, γ-HCH and more highly chlorinated PCBs at western sites, and higher levels of many other contaminants, including *p,p'*-DDE and toxaphene in the eastern Arctic, notably at south Baffin Island. Males had higher levels of POPs than females, reflecting reproductive loss by adult females. Growth dilution was also evident, with some younger whales more contaminated than expected. Principal Components Analysis (PCA) of whales from the 15 sites revealed that beluga could be separated into five geographic groupings on the basis of contaminant signatures.

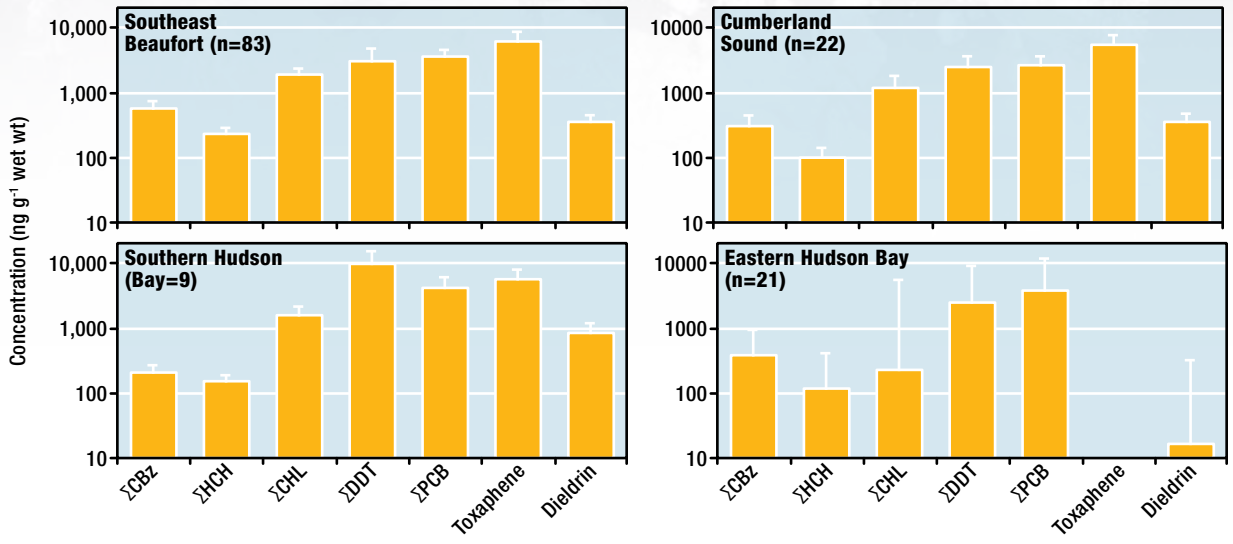

FIGURE 4.43

Concentrations (arthmetic means and upper 95% confidence limits, ng g^{-1} ww) of major POPs in blubber of male belugas from the southeast Beaufort Sea area (Hendrickson Island) (2003–2010), Cumberland Sound (Pangnirtung) (2002–2010), southern Hudson Bay (Sanikiluaq) (2009) and eastern Hudson Bay (Umiujaq) (1999–2003). Results are from Stern et al. (2009, 2011) except for eastern Hudson Bay which are from Kelly et al. (2007) which are geometric means (+upper 95% CI). Toxaphene was not determined in the eastern Hudson Bay animals.

Concentrations of major POPs in male belugas collected over the period 1999–2010 are presented in Figure 4.43. Addditional data by year is provided in Annex Table 4A-1.

Male beluga are compared because they have higher levels than females and, generally, the concentrations of POPs are significantly related to age while females show a more complex relationship of POPs to age due to losses via fetal development and lactation. For large comparsions among locations, results have been adjusted for age using analysis of covariance models (Stern et al. 2005). However, this was not done for the comparisons shown in Figure 4.43.

In general, concentrations of major legacy POPs (ΣCHL, ΣDDT, ΣPCB, toxaphene, dieldrin) were similar in the male beluga from Cumberland Sound and Hendrickson Island. ΣCBz and ΣHCH were higher in the Hendrickson Island samples. The western Arctic beluga were generally older (mean ages 24–27 y; 2003–2009) compared to the Cumberland Sound animals (mean ages 6–17 y; 2002–2009). Thus if adjusted for age, it is likely that most POPs would be higher in the eastern Arctic samples. Toxaphene (determined by GC-ECD in all these samples) was the most prominent contaminant in samples from Cumberland Sound and Hendrickson Island (means of 6,030 ± 2,010 ng g^{-1} ww and 5,480 ± 2,320 ng g^{-1} ww, respectively). The highest concentrations of ΣDDT were observed in samples from Sanikiluaq (9,300 ± 6,160 ng g^{-1} ww). Beluga from the eastern Hudson Bay animals may be a separate stock from those hunted at Sanikiluaq, based on multivariate analyses using the PCB "fingerprint" in beluga (Innes et al. 2002, Stern et al. 2005). These animals had similar ΣDDT and ΣPCB concentrations as the Cumberland Sound animals and much lower dieldrin and ΣCHL as beluga sampled at other locations (Figure 4.43). Kelly et al. (2007) noted that primary metabolites of OCPs were often detectable at equivalent or greater concentrations than that of the parent compound. For example, levels of oxychlordane (732 ng g^{-1}) and heptachlor epoxide (201 ng g^{-1}) were 3 the technical chlordane constituents (*cis*- and *trans*-chlordane and heptachlor, at approximately 1–170 ng g^{-1}). Concentrations of *p,p'*-DDE (1,700 ng g^{-1}) were approximately four times greater than *p,p'*-DDE (428 ng g^{-1}) (i.e., DDE/DDT ratio of approximately 4).

McKinney et al. (2006b) reported on PCBs and OCPs in the liver of beluga whales from two Canadian populations: the St. Lawrence Estuary (SLB), and western Hudson Bay in the Canadian Arctic (WHB) (McKinney et al. 2006b). The ΣPCB and ΣDDT concentrations were higher in SLB compared with the beluga from WHB. Of 18 detectable OH-PCBs in SLB (mainly 4-OH-CB107, 4-OH-CB112, and 4′-OH-CB120), only 4′-OH-CB120 was found in WHB. The ΣOH-PCB concentrations were less than 0.2% of the ΣPCBs in both populations but were higher in SLB (65 ± 22 ng g^{-1} lw) than in WHB (3.1 ± 0.5 ng g^{-1} lw). The $\Sigma MeSO_2$-PCB concentrations were higher in SLB (3801 ± 1322 ng g^{-1} lw)

relative to WHB (77 ± 23 ng g^{-1} lw) and were 11% and 4%, respectively, of the ΣPCB concentrations. It was concluded that OH-PCBs and $MeSO_2$-PCBs are metabolites derived from accumulated PCBs.

4.1.5.3.3.2 New POPs in belugas

Perfluoroalkyl substances: Kelly et al. (2009) reported relatively high concentrations of PFOS and PFCAs in beluga liver from eastern Hudson Bay collected in 1999 and 2003, whereas PFHxS and PFDS were lower and less frequently detected. Figure 4.44 shows concentrations of individual PFASs, PCBs, OCPs and PBDEs in eastern Hudson Bay beluga liver. In general, PFAS concentrations were equivalent to or higher than organochlorine concentrations, while PBDEs were comparatively low. Several PFASs (PFNA, PFDA, PFUnA, PFOS and PFOSA) exhibited concentrations comparable to or higher than legacy POPs such as PCB-153, HCBz and *p,p'*-DDE. Conversely, concentrations of Br_3-Br_8 PBDE congeners exhibited comparatively lower concentrations in beluga liver.

PFOS concentrations in eastern Hudson Bay beluga (mean 37.3, range 3.0–109 ng g^{-1} ww in male liver) were similar to those observed in beluga livers sampled from Baffin Island (12.6 ± 1.1 ng g^{-1} ww) (Tomy et al. 2004) and the southeastern Beaufort Sea (median 12.5, range 4.3–20 ng g^{-1} ww) (Tomy et al. 2009b). Reiner et al. (2011) reported PFOS concentrations in liver of Chukchi Sea beluga ranging from 1.8–38 ng g^{-1} ww, which was similar to the Hudson Bay and Baffin Island beluga.

Concentrations of PFOS were relatively high in a beluga calf liver (158 ng g^{-1} ww, n=1), but this result could not be fully validated due to limited sample size (Kelly et al. 2009). Other studies of PFASs have also shown higher PFOS and PFCA concentrations in liver of calves and fetus, compared to adult animals (Dorneles et al. 2008; Reiner et al. 2011). In beluga, PFOS and PFCA concentrations were higher ($p < 0.05$) in protein-rich compartments (liver and blood), compared to other tissues/fluids (milk, blubber, muscle and fetus) (Kelly et al. 2009).

Whereas similar profiles might be expected in both species of the same superfamily, a marked presence of PFOSA was detected in arctic belugas compared to bottlenose dolphins from the western Atlantic (Houde et al. 2006b). Tomy et al. (2004, 2009b) and Reiner et al. (2011) reported similar findings of relatively high concentrations of PFOSA in beluga whales in both eastern Arctic and Southern Beaufort/Chukchi populations. These high PFOSA burdens in beluga may be the result of differences in diet and/or biotransformation capacity relative to other arctic wildlife species although they could also reflect different source regions. Reiner et al. (2011) found higher proportions of PFOSA in Chukchi Sea animals compared to the Cook Inlet population that feeds in a more urban influenced area. High proportions of PFOSA are seen in some marine fishes (section 4.1.5.1.1.2). Arctic beluga whales generally have a lower biotransformation potential toward POPs such as PCBs and BFRs (McKinney et al. 2006a) since they are exposed at lower concentrations to environmental contaminants that are known to induce xenobiotic-metabolizing enzyme systems (McKinney et al. 2004). Hart et al. (2008) reported similar findings of relatively high PFOSA residue burdens in beluga whales as well as melon-headed whales (*Peponocephala electra*).

BFRs: PBDEs have been determined in blubber of male and female belugas from the southeastern

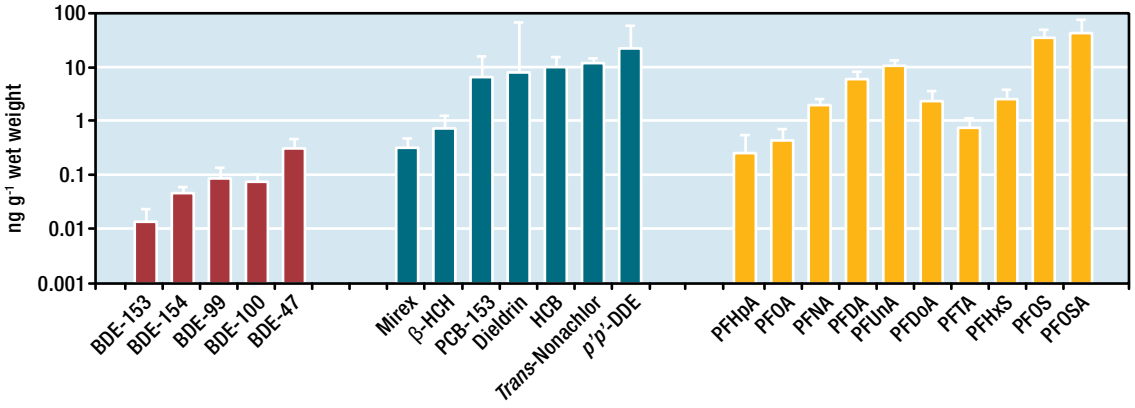

FIGURE 4.44

Concentrations (ng g^{-1} ww) of selected PBDEs, PCBs, OCPs and PFASs in beluga whale liver from eastern Hudson Bay. Data are geometric means and standard deviations (from Kelly et al. 2008a, Kelly et al. 2009).

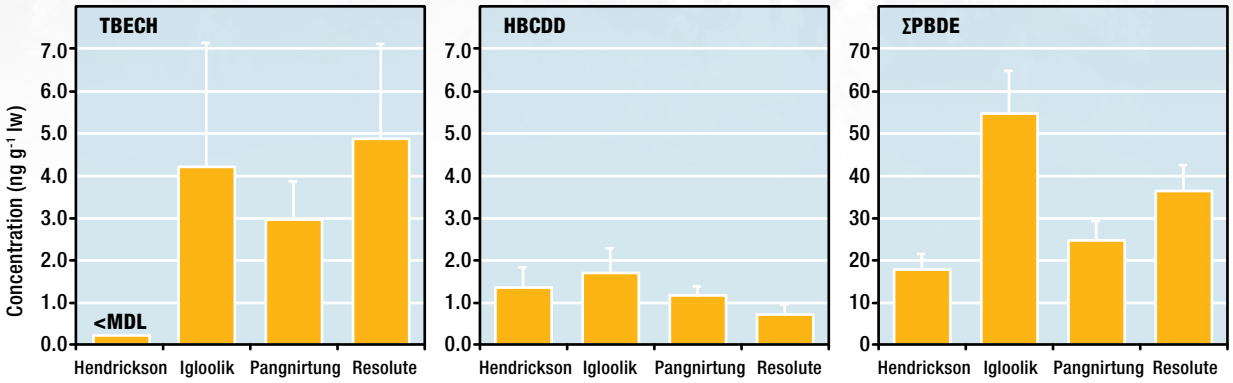

FIGURE 4.45

Concentrations (arithmetic means and upper 95% confidence limit, ng g^{-1} lw) of TBECH, HBCDD and ΣPBDEs in blubber of belugas (males and females) from Hendrickson Island (8), Igloolik (5), Pangnirtung (10) and Resolute (6) (Tomy et al. 2008a). Note that the vertical axis scale for PBDEs is 10 times the scale for TBECH and HBCDD. TBECH was reported in only one of eight samples from Hendrickson Island and therefore average levels appear to be <MDL of approximately 0.1 ng g^{-1} lw.

Beaufort Sea and southeastern Baffin Island populations (Cumberland Sound; Pangnirtung) over the period 2003–2010 (Tomy et al. 2011a, Tomy et al. 2009a; Annex Table A4-1). As part of food web studies, additional PBDE data were reported by Tomy et al. (2009b, 2008b) (see section 4.1.5.1.1.2). Geometric mean concentrations of ΣPBDE (sum of 6 Br_3–Br_7 congeners) ranged from 6 to 21 ng g^{-1} lw in the Cumberland Sound samples and from 4 to 18 ng g^{-1} lw in the Beaufort Sea animals. Tomy et al. (2008a) compared ΣPBDEs, HBCDD and TBECH concentrations in blubber of beluga from 4 locations (Figure 4.45). Mean ΣPBDEs ranged from 17 ng g^{-1} lw in Hendrickson Island beluga to 54 ng g^{-1} lw in animals from Igloolik.

Kelly et al. (2008a, b) reported geometric mean concentrations of ΣPBDEs 34 ng g^{-1} lw (95% confidence interval, 13–96 ng g^{-1} lw, n=21) in male beluga blubber collected between 1999 and 2003 from eastern Hudson Bay. Female beluga had much lower concentrations (16 ng g^{-1} (95% confidence interval, 4.4–59 ng g^{-1} lw, n=14). While spatial trends cannot be rigorously evaluated, and the PBDE concentrations could be changing rapidly over time (see section 4.2.4.4), it is likely that the eastern Hudson Bay animals had higher levels than those from Cumberland Sound (Pangnirtung) and the Southern Beaufort Sea (Hendrickson Island).

McKinney et al. (2006b) analyzed PBDEs in beluga liver from western Hudson Bay (collected in 2002 and 2003) as well as from the St. Lawrence River estuary population. ΣPBDE concentrations of 53 ng g^{-1} lw (n=11) in beluga liver from WHB were ca. 45 times lower than measured PBDE concentrations in St. Lawrence River beluga (2,210 ng g^{-1} lw) (McKinney et al. 2006b). Mean BDE-47 concentrations observed in eastern Hudson Bay male beluga blubber (15 ng g^{-1} lw) by Kelly et al. (2008a, b) were 15 to 140 times lower than mean BDE-47 in St. Lawrence River male beluga blubber (210 ng g^{-1} lw) (Lebeuf et al. 2004) and southern resident male killer whales from the Strait of Georgia (450 ng g^{-1} lw) (Rayne et al. 2004).

Kelly et al. (2008a, b) found ΣPBDE concentrations in whole blood and blubber of male belugas from eastern Hudson Bay (n=7 and n=21, respectively) were greater than those measured in females (n=7 and n=14, respectively). In male liver (n=17), ΣPBDE concentrations (18 ng g^{-1} lw) were ca. 2 times greater than that in milk of female belugas. Elevated ΣPBDE concentrations were also measured in calves (n=9, < 1 year) likely due to offloading of PBDEs from mother to calf. Muir et al. (2004) found ΣPBDE concentrations in male belugas from the Hudson Strait (30 ng g^{-1} lw, n=4) and east Hudson Bay (41 ng g^{-1} lw, n =3) that were similar to those reported by Kelly et al. (2008a).

ΣHBCDD (sum of α- and γ-isomers) has been determined in blubber of belugas from the southeastern Beaufort Sea and the southeastern Baffin Island (Cumberland Sound) stocks over the period 2003–2010 (Tomy et al. 2011a, Tomy et al. 2009a; Annex Table A4-1). Additional HBCDD data were reported by Tomy et al. (2009b, 2008b) as part of food web studies (see section 4.1.6.3) and in a comparison of PBDEs, HBCDD and TBECH among four sampling locations (Tomy et al. 2008a) (Figure 4.45).

Arithmetic mean concentrations of HBCDD ranged from 1.3 ng g^{-1} lw in Hendrickson Island, 0.73 ng g^{-1} lw at Resolute and 1.7 ng g^{-1} lw in animals from Igloolik, suggesting no major trends for this compound across the Canadian Arctic Archipelago.

Tomy et al. (2008a) reported on isomer-specific concentrations of a novel cycloaliphatic brominated flame retardant, β-tetrabromoethylcyclohexane (β-TBECH), in beluga from four locations: Hendrickson Island (NWT), 2006; Pangnirtung (Southeast Baffin Island), 2005; Igloolik (NU), 2005; and Resolute (NU), 2003. Mean β-TBECH in blubber of animals from Pangnirtung (n=8) were 2.7 ng g^{-1} lw ca. 2 times greater than animals from Igloolik (n=3, 6.1 ng g^{-1} lw) and Resolute (n=5, 5.2 ng g^{-1} lw). β-TBECH was detectable in one animal from Hendrickson Island at a concentration of 2.7 ng g^{-1} lw. Mean β-isomer concentrations (4.3 ng g^{-1} lw) were approximately 8 times smaller than Σ_{17}P BDEs (33.7 ng g^{-1} lw) but 4 times greater than ΣHBCDD (1.1 ng g^{-1} lw) (Figure 4.45).

Natural brominated compounds: McKinney et al. (2006b) reported on OH- and MeO-PBDEs in beluga liver from western Hudson Bay and the St. Lawrence estuary. Of the 15 OH-PBDEs analyzed, only two congeners were detectable, but not quantifiable (notably 2′ -OH-BDE68 and 6-OH-BDE-47), in animals from both populations. Of the 15 MeO-PBDEs, 4′-MeO-BDE17 and 6-MeO-BDE-47 in the St. Lawrence animals and 2′-MeO-BDE68 and 6-MeO-BDE-47 in the Hudson Bay had concentrations from 20 ng g^{-1} lw to 100 ng g^{-1} lw. It was concluded that the OH-PBDEs and MeO-PBDEs most likely are of natural origin and accumulated in beluga whales, whereas the OH-PCBs and $MeSO_2$-PCBs are metabolites derived from accumulated PCBs.

Kelly et al. (2008b) detected five OH-PBDEs at very low concentrations (0.01–0.1 ng g^{-1} lw) in beluga blubber and milk confirming negligible formation/retention of OH-PBDEs. However, appreciable levels of several MeO-PBDEs were observed in beluga tissues (blood, liver and blubber). Congeners 2′-MeO-BDE-68 and 6-MeO-BDE-47 exhibited the highest concentrations, 58 ng g^{-1} lw (95% confidence interval, 18–180 ng g^{-1}) and 240 ng g^{-1} lw (95% confidence interval, 72–800 ng g^{-1}), respectively.

Tittlemier et al. (2002) reported on concentrations of four halogenated dimethyl bipyrroles (ΣHDBPs) in marine mammal blubber from various locations worldwide (Tittlemier et al. 2002). Mean concentrations of ΣHDBP in belugas from Chesterfield Inlet (NU) (17.8 ng g^{-1} lw, n=3, 1997) were similar to those from Igloolik (16.6 ng g^{-1} lw, n=9, 1995). Thus HDBPs were present at similar concentrations to several PBDE congeners in the mid-1990s. Current levels in beluga blubber are unknown.

PCNs: Helm et al. (2002) reported that PCN concentrations in blubber of beluga whales from Kimmirut (NU) in southern Baffin Island sampled in 1994 were approximately six times more contaminated than ringed seals, but several times less contaminated than marine mammals from the Baltic Sea. PCN patterns in beluga were dominated by penta constituents (33–55% of total). When compared against planar PCBs, PCNs contributed 11% of TEQ despite being present at less than 1% of planar PCB concentrations. The small sample size precluded an evaluation of the effects of age and sex on PCN concentrations (Helm et al. 2002).

More recently, Tomy et al. (2011a) measured PCNs in southern Beaufort Sea animals collected from 2000 and 2008. There were no statistical differences (Student t-test, $p > 0.05$) in the concentrations of ΣPCNs (tri- to octa-chloronaphthalenes) in animals analyzed from the two time periods. Total PCN concentrations in whale blubber ranged from 118 pg g^{-1} ww to 430 pg g^{-1} ww and were in the same range as those reported in beluga blubber from Kimmirut, NT of 36–383 pg g^{-1} ww (Helm et al. 2002). As is typical of biotic samples that are higher in the food web, the dominant PCNs present are those that are most bioaccumulative. These include tetraCN-42, pentaCNs-52/60, and hexaCNs-66/67. Most other congeners were not detected in these samples. On average, the hexaCNs were the most dominant contributors to total PCNs (44% ± 16%) followed by the pentaCNs (31% ± 9%) and the tetraCNs (20% ± 12%) (see Figure 4.46). Using relative potencies for the PCN congeners based on enzyme induction assays, average dioxin toxic equivalents (TEQ) contributed by PCNs are estimated to be 0.290 pg g^{-1} blubber. This is also within the range of 0.028–0.43 pg g^{-1} TEQ reported previously (Helm et al. 2002).

Endosulfan: Kelly et al. (2007) determined α-endosulfan, β-endosulfan and endosulfan sulfate in beluga blubber samples by GC-HRMS using the method of Rayne and Ikonomou (2003). They found β-endosulfan was the primary endosulfan species (geometric mean in males, 12.6 ng g^{-1} lw, 95% confidence interval, 4.5–35 ng g^{-1}). In contrast, concentrations of endosulfan sulfate, the primary metabolite of endosulfan, was relatively low (0.86 ng g^{-1} lw, 95% confidence interval, 0.2–3.5 ng g^{-1}), compared to β-endosulfan while α-endosulfan was not detected (< 0.34 ng g^{-1} lw). The results suggest that β-endosulfan is the dominant endosulfan isomer (it is also observed in ringed seals;

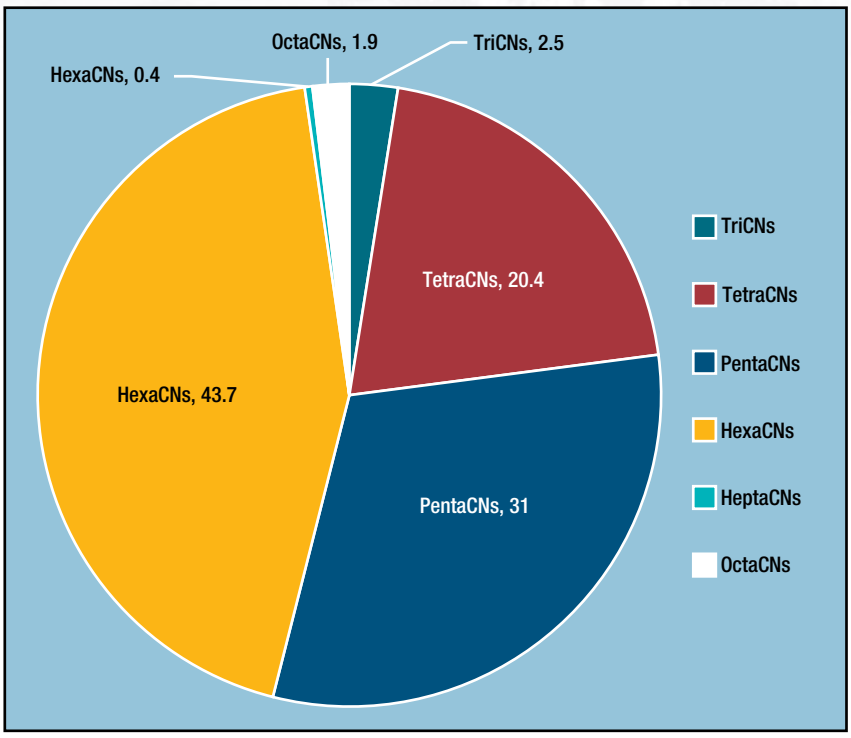

FIGURE 4.46

Relative distribution of PCN homologue groups in beluga whale blubber from Hendrickson Island. Animals from 2000 (n=10) and 2008 (n=10) were treated together as there was no statistical differences in concentrations in animals from either year (Tomy et al. 2011b).

section 4.1.5.3.1.2) and that beluga and other marine wildlife may efficiently metabolize/eliminate endosulfans, as well as the primary metabolite, endosulfan sulfate.

The results for endosulfan sulfate reported in blubber of male belugas sampled at the nearby eastern Hudson Bay community of Umiujaq, contrasted with those reported by Stern et al. (2005) for belugas from eastern Hudson Bay (Sanikiluaq; n=20) which ranged from 33 ng g^{-1} lw to 69 ng g^{-1} lw. Weber et al. (2010) noted poor agreement between the three detection techniques that have been used for endosulfan (GC-ECD, GC-NIMS, and GC-HRMS) and that the endosulfan sulfate results in beluga determined by GC-ECD are confounded by interferences. However, Weber et al. (2010) also noted that the GC-HRMS method may have overestimated the β-endosulfan due to interferences with the internal standard used to quantify this isomer. Endosulfan related compounds have not been reported for beluga sampled between 2003–2010 and thus no spatial trend for endosulfan can be assessed from the available data.

4.1.5.3.4. Narwhal

Narwhal are deep-water benthic feeders. In CACAR II, levels of PCBs, DDT and chlordanes in narwhal from Pont Inlet (northeast Baffin Island), Broughton Island (east Baffin Island), and Grise Fiord (south Ellesmere Island) were reported. Although narwhal are an important species in the diet of Inuit, they have received less attention in terms of contaminant studies than beluga.

4.1.5.3.4.1. Legacy POPs in narwhal

Stern et al. (2009, 2008) reported legacy POPs in narwhal collected in 2006 from Pond Inlet, Igloolik, Resolute, Repulse Bay and Clyde River. Concentrations of major legacy POPs in male narwhal are presented in Figure 4.47 and additional results (males and females) are provided in Annex Table A4-1. Toxaphene (determined by GC-ECD) was the most prominent POP in all samples. Highest toxaphene levels were found at Clyde River and Pond Inlet (14,880 ± 4,790 ng g^{-1} lw and 14,870 ± 4,258 ng g^{-1} lw, respectively). ΣCHL, ΣDDT and ΣPCB concentrations were also higher at Clyde River and Pond Inlet than at the other locations. Previous spatial trend comparisons (Fisk et al. 2003) also noted higher levels of most POPs in narwhal sampled at Pond Inlet, compared with those from Qikiqtarjuaq (eastern Baffin Island), or Grise Fiord (southern Ellesmere Island). The reason is unclear but similar to beluga, it may be related to differences in diets and food webs along the migration path of the

animals. Age differences between the sampled populations could also be an important factor (ages of narwhal cannot be determined accurately).

4.1.5.3.4.2. New POPs in narwhal

Ostertag et al. (2009) estimated the dietary exposure of PFASs from traditional foods sampled in Nunavut between 1997 and 1998. The range in ΣPFAS (sum PFOS and PFCAs) concentrations in narwhal blubber and muktuk (0.4–1.6 ng g^{-1} ww) were very low. Tissues such as liver, where higher concentrations would be expected, were not measured.

Tomy et al. (2004) reported on PFA concentrations in narwhal blubber (Qikiqtarjuaq, 2000, n=5, all males) from the eastern Canadian Arctic. PFOS and N-EtPFOSA concentrations in liver were similar (11 ng g^{-1} ww) and greater than that of PFOA (0.9 ng g^{-1} ww) and PFOSA (6.2 ng g^{-1} ww). In the same samples, ΣHBCDD concentrations were 3.9 ± 0.9 ng g^{-1} lw (geometric mean) which were greater than other sampled species (e.g., beluga and walrus) (Tomy et al. 2008b) but similar to ringed seal blubber (Figure 4.39). α-HBCDD contributed more than 70% of the total HBCDD burden in narwhal. Σ_7BDE concentrations in narwhal were ca. 45 times greater (18 ng g^{-1} lw) than in other marine mammals (i.e., walrus; 0.4 ng g^{-1} lw). BDE-209 accounted for less than 2% of the total BDE burden, whereas the BDE-47 accounted for over 40%.

4.1.5.3.5. Polar bears

Polar bears are widely distributed inhabitants of the Arctic and subarctic region and range over large areas in search of food. They move south with the ice in the fall and winter and then north as the pack ice melts in the spring and summer. These seasonal movements of the sea-ice also influence the distribution and concentration of their primary prey, ringed and bearded seals (Kingsley 1985, Stirling et al. 1982). As apex arctic predators, polar bears often eat only the blubber from a seal (Stirling and McEwan 1975) giving them relatively high continual exposure to organohalogens compared to any other arctic wildlife. Polar bears also have a superior biotransformation capacity and have the highest levels of metabolites of POPs, some of which are potent endocrine disruptors (Letcher et al. 2000). This explains why concerns about the effects of POPs in arctic wildlife are greatest for this species.

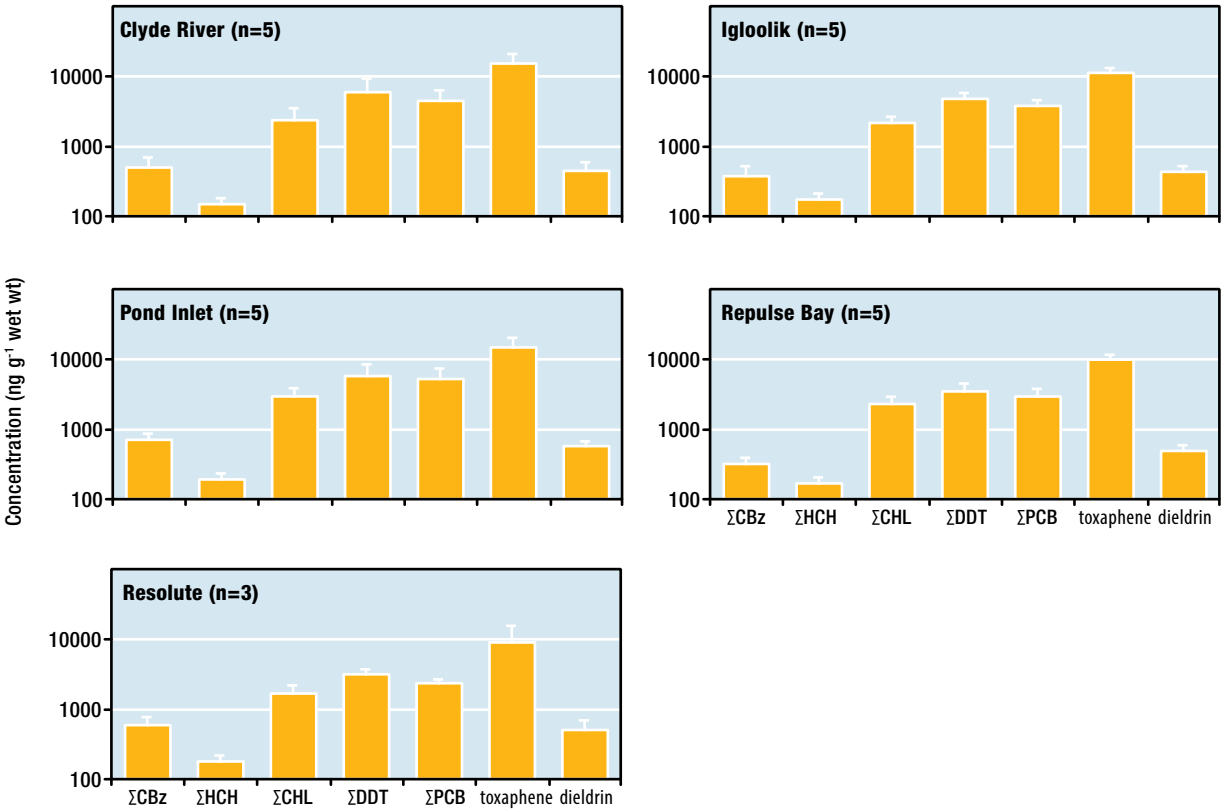

FIGURE 4.47

Concentrations (Arithmetic mean and upper 95% confidence limit) of major POPs in blubber of male narwhal from 5 locations.

Previous research on polar bears in the Canadian and European Arctic found evidence that the immune system and potentially the endocrine systems of polar bears were compromised by POPs exposure, in particular PCBs (Andersen et al. 2001). Although consumed by the Inuit, the polar bear makes up a small percentage of their diet. However, through the process of biomagnification, the polar bear, including subpopulations in Canada, achieves some of the highest POPs concentrations of any arctic species or any species on the planet (Letcher et al. 2009, Letcher et al. 2010b, Smithwick et al. 2005, Verreault et al. 2005c, Muir et al. 2006a, Letcher et al. 2010a). Letcher et al. (2010b) reviewed the available data for contaminants in polar bears (to 2008) and noted that most data was from the "hotspot" Arctic areas of East Greenland, Svalbard and Hudson Bay in Canada. The highest levels of POPs in polar bears are generally seen in these areas. Here we assess and summarize studies on legacy and new POPs in polar bears for the period 2002–2010.

Previous assessments of spatial trends of POPs in polar bears have not determined the influence of diet due to difficulties in quantifying the diets of individual bears. However, the relative contribution of regional contamination compared with differences in diet and the geographic variation in levels of POPs in bears from various subpopulations, including those in Canada, were recently reported in McKinney et al. (2011a). Diet variation between Alaska, Canada, East Greenland and Svalbard subpopulations was assessed using muscle $\delta^{15}N$ and $\delta^{13}C$ and fatty acid composition signatures relative to their main prey (ringed seals). Western and southern Hudson Bay signatures were characterized by depleted SIs, lower proportions of C_{20} and C_{22} monounsaturated FAs and higher proportions of C_{18} and longer chain polyunsaturated fatty acids. East Greenland and Svalbard tracer signatures were reversed relative to Hudson Bay. Alaskan and other Canadian Arctic signatures were intermediate. It was postulated that regional diet differences might predominate over inter-annual, seasonal or demographic variation. Among various POPs, McKinney et al. (2011a) showed that diet signatures significantly explained the variation in the overall adipose levels of PCBs (18–21%). However, diet influence was shown to be contaminant class-specific, since diet only explained lower amounts of variation in OCP (e.g., CHL) levels. Hudson Bay diet signatures were associated with lower PCB concentrations. It was demonstrated that understanding diet and food web factors is important in the interpretation of trends of POPs, particularly in a changing Arctic.

4.1.5.3.5.1. Legacy POPs in polar bears

Verreault et al. (2005c) reported on a suite of POPs including OCPs and by-products, PCBs, $MeSO_2$-PCB and *p,p'*-DDE metabolites in adipose tissue of adult and sub-adult polar bears, almost exclusively females, sampled between 1996 and 2002 from populations spanning Arctic and subarctic regions of Alaska, Canada, East Greenland, and Svalbard (Figure 4.48). The polar bears of East Greenland and Svalbard populations were distinguished by higher proportions of DDT-related compounds, nonachlors, oxychlordane, and higher-chlorinated and persistent PCB congeners (hepta- to nona-chlorinated). Conversely, results in Alaska, the westernmost population of the North American Arctic, were characterized by higher proportions of relatively volatile compounds such as HCHs, pentachlorobenzene (PnCBz), and lower-chlorinated PCB congeners (tri- to penta-chlorinated), and lower proportions of oxychlordane. ΣHCH concentrations showed the steepest negative west–east gradient across the populations studied and were significantly highest in Alaska bears compared to those in the western Hudson Bay and to populations east of Lancaster Sound/Jones Sound. It was noted that this may indicate an ongoing contribution of HCHs from China, southeastern Asia, and North America. In Canadian bears, the spatial distribution of ΣCBz, dieldrin and Σmirex was fairly uniform across the study areas. This may suggest that ΣCBz, dieldrin, and mirex are relatively well equilibrated in surface waters throughout the Canadian Arctic and subarctic. Conversely, ΣDDT concentrations increased gradually from west to east. ΣPCB dominated the composition pattern across the investigated Canadian subpopulations, except for Foxe Basin/Gulf of Boothia and Lancaster Sound/Jones Sound, where ΣCHL concentrations were the highest. ΣPCB concentrations increased most steeply with longitude, and also increased with latitude. The CB99 to CB180 ratios for samples across the (Canadian) Arctic reflected the regional signatures and atmospheric input originating from different types of technical PCB formulations.

McKinney et al. (2011b) reported on legacy POPs in adipose tissue collected in 2006–2008 from the same eleven polar bear subpopulations spanning from Alaska east to Svalbard, that were assessed earlier by Verreault et al. (2005c). Levels of major legacy POPs in polar bear adipose tissue from the 8 Canadian subpopulations are presented in Figure 4.49 and detailed data are listed in Annex Table A4-13. It was found that ΣPCB levels were high relative to other legacy POPs and lowest in the Lancaster/Jones Sound and

FIGURE 4.48

Map of Arctic and subarctic regions showing the 8 sampling locations (circled areas) for polar bears in the Canadian Arctic: southern Beaufort Sea, northern Beaufort Sea, Lancaster/Jones Sounds, Gulf of Boothia, Baffin Bay, Davis Strait, western Hudson Bay, and southern Hudson Bay, as well as Bering-Chukchi Sea (Alaska), Scoresbysund (East Greenland) and Svalbard (Norway) area.

Gulf of Boothia samples. ΣCHL levels were highest among legacy OCPs and relatively spatially uniform. ΣDDT levels were relatively low and spatially variable. Dieldrin had distinctly higher concentrations in the eastern Arctic and Hudson Bay.

McKinney et al. (2011b) found that measured PCB concentrations in Hudson Bay bears were lower than in bears from East Greenland and Svalbard areas as has been reported previously (Verreault et al. 2005c). However, after adjusting results for diet using a dietary index based on muscle nitrogen and carbon stable isotope ($\delta^{15}N$, $\delta^{13}C$) and adipose fatty acid signatures relative to their main prey (ringed seals), ΣPCB levels were 137% and 91% higher in WHB and SHB populations reflecting different diets in these areas compared to other locations.

4.1.5.3.5.2. New POPs in polar bears

Perfluoroalkyl substances: Following the first reports of PFOS in polar bears from Alaska in 2001 (Giesy and Kannan 2001, Kannan et al. 2001), Martin et al. (2004a) determined PFASs, including PFCAs, in polar bears collected at Sanikiluaq. PFOS was the major contaminant detected in most samples and, in polar bear liver, was the most prominent organohalogen (mean PFOS = 3100 ng g^{-1} ww) compared to individual PCB congeners, chlordane, or HCH-related chemicals in fat. As high trophic level mammals, polar bears showed lower concentrations of ΣPFCAs than total PFOS equivalents (ΣPFOS). In general, odd-length PFCAs exceeded the concentration of even-length PFCAs, and concentrations decreased with increasing chain length. PFOS and PFCA concentrations were much lower for animals of the Canadian Arctic than for the same species living in mid-latitude regions of the United States.

Bioaccumulative PFCAs and PFSAs were reported in the liver collected in 2001–2002 for polar bears from 4 subpopulations in the Canadian Arctic (Smithwick et al. 2005) along with Alaskan, East Greenland and Svalbard samples. PFOS concentrations were higher in southern Hudson Bay bears than from all other sampling locations. Male bears showed a significant increase in concentration up to age six for PFCAs with C_{10} to C_{14} carbon chains. Significant correlations were found between adjacent chain length PFCAs, (e.g., PFNA to PFDA).

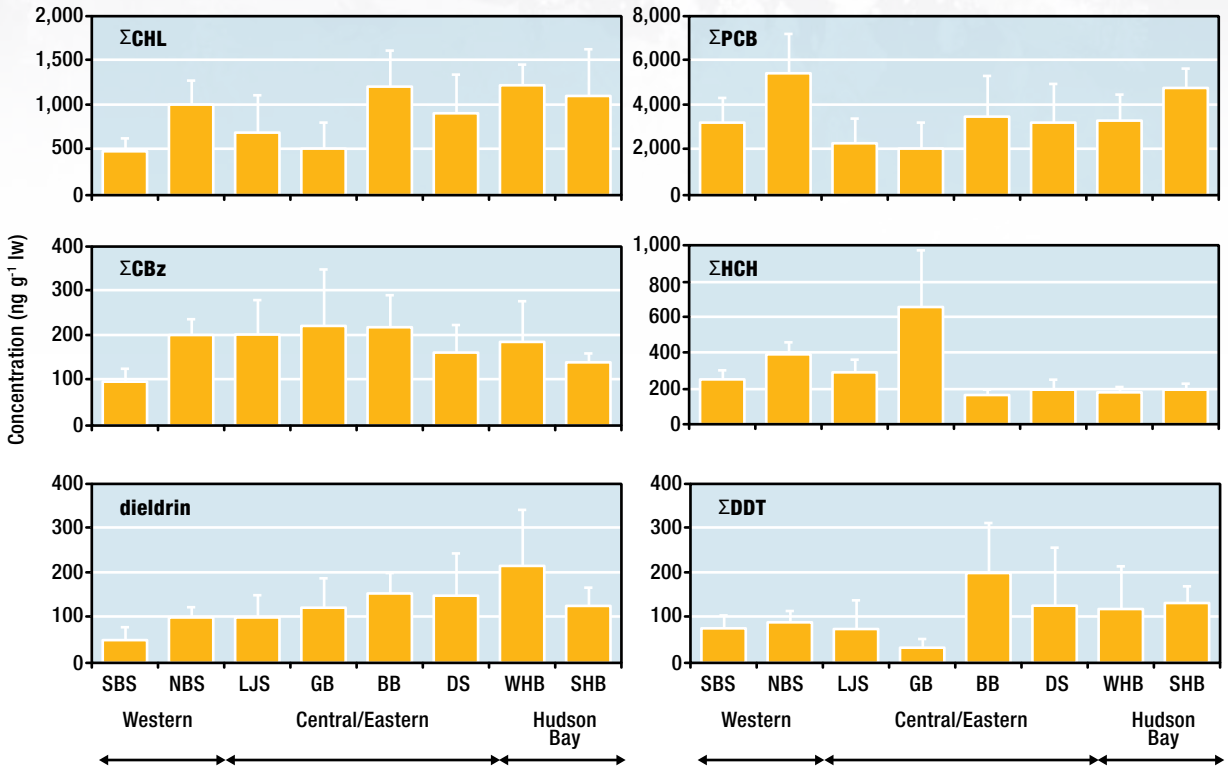

FIGURE 4.49

Unadjusted concentrations (arithmetic means ± 95% confidence interval) of legacy POPs (ng g^{-1} lw) in adipose tissue of polar bears collected in 2007-2008 from southern Beaufort Sea (SBS), northern Beaufort Sea (NBS), Lancaster/Jones Sounds (LJS), Gulf of Boothia (GB), Baffin Bay (BB), Davis Strait (DS), western Hudson Bay (WHB), and southern Hudson Bay (SHB) (McKinney et al. 2011a).

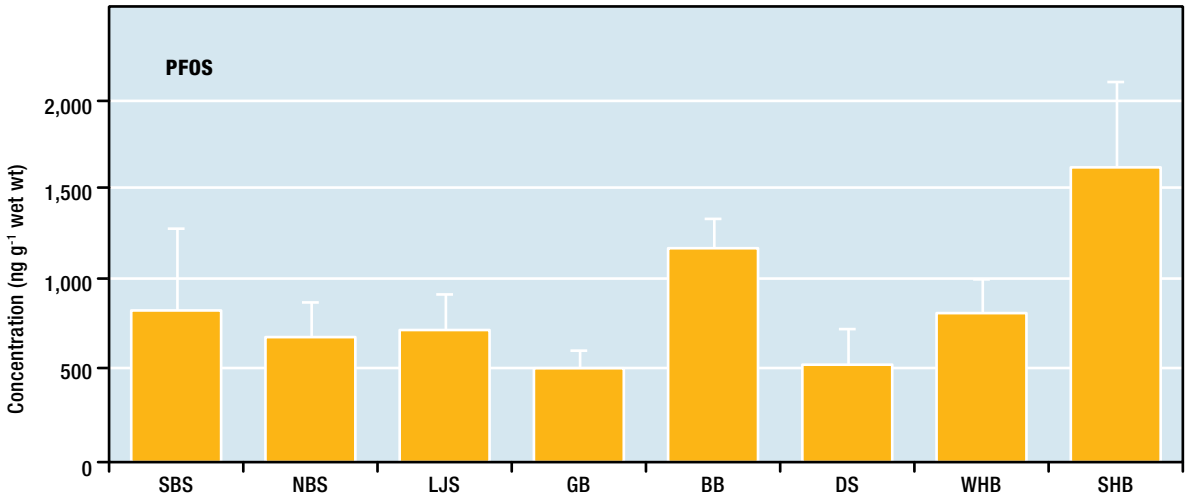

FIGURE 4.50

Concentrations (arithmetic means ± 95% confidence interval) of PFOS in liver of polar bears collected in 2007-2008 from 8 management zones in the Canadian Arctic (Letcher et al. 2010a). Full names of sampling areas are provided in the caption to Figure 4.49.

PFCAs, PFSAs and PFOSA in 2007–2008 liver samples of bears from all 8 Canadian management zones were recently reported (Houde et al. 2011, Letcher et al. 2010a, Letcher et al. 2009). Consistent with 2001–2002 collected samples (Smithwick et al. 2005), ΣPFSA concentrations were reported to be comprised of > 99% PFOS. Concentrations of PFOS are presented in Figure 4.50 and additional information is given in Annex Table A4-13. The ΣPFCA concentrations were comprised largely of C_9

(PFNA), C_{10} (PFDA) and C_{11} (PFUnA), with much lesser amounts of C_8 (PFOA), C_{12} (PFDoA) and C_{13} (PFTrA), and very low or non-detectable C_6 (PFHxA), C_7 (PFHpA), C_{14} (PFTeDA) and C_{15} (PFPA). Of all the Nunavut and NWT samples, the 10:2 FTUCA was barely quantifiable in all but one NWT bear. FTOHs were not detectable in any bear sample, and levels of PFOSA were in the low ng g^{-1} ww range but quantifiable with very high frequency in samples.

Spatial trends for the 2007–2008 samples indicated that PFOS, ΣPFCA and PFOSA levels are highest in bears from southern Hudson Bay, and lower but comparable among collected samples of the Beaufort Sea, Gulf of Boothia, Lancaster/Jones Sound, Davis Strait and Baffin Bay.

Ostertag et al. (2009) estimated the dietary exposure of PFAs from traditional foods among Inuit in Nunavut. Comparing concentrations of PFASs in different tissues was not possible because of the small sample size. The measured ΣPFAS concentration in one polar bear sample (7 ng g^{-1} ww) was in the same range as that measured in ringed seal and beluga (1.2 ng g^{-1} ww to 6.9 ng g^{-1} ww).

PFCA and PFOS isomers: Based on various configurations of the C_8 hydrocarbon chain, eighty-nine structural isomers of PFOS are theoretically possible. Analysis of PFOS isomers in Canadian, East Greenland and Svalbard subpopulations showed that linear PFOS was highly enriched (approximately 99% of the total PFOS concentration) in polar bear liver relative to technical PFOS products, where linear PFOS has been shown to constitute approximately 65% of the total PFOS concentration (Chu and Letcher 2009). Furthermore, the six mono(trifluoromethyl)-branched PFOS isomers were < 1% of the total PFOS concentration, and none of the four bis(trifluoromethyl)-branched isomers were detectable. The branched isomers were thus depleted as it has been reported that in the PFOS technical mixture, mono(trifluoromethyl)-branched and bis(trifluoromethyl)-branched PFOS isomers constituted 33% and approximately 2%, respectively, of the total PFOS concentration (Chu and Letcher 2009).

Brominated flame retardants: Muir et al. (2006a) reported PBDEs (penta-BDE-derived) and HBCDD concentrations in Canadian polar bears as part of a larger study that included subpopulations in Alaska, East Greenland and Svalbard (sites shown in Figure 4.48). The major penta-BDE-derived PBDE congeners (e.g., BDE-47, -99, -100, -138 and -183) were determined in adipose tissue of adult and subadult female polar bears sampled between 1999 and 2002 from subpopulations in Arctic Canada. Only 4 congeners (BDE-47, -99, -100 and -153) were consistently identified in all samples. BDE-47 was the major PBDE congener representing from 65% to 82% of the ΣPBDEs. Age was not a significant covariate for individual PBDEs or ΣPBDE. Higher proportions of BDE-99, -100, and -153 were generally found in samples from the Canadian Arctic than from Svalbard or Alaska. ΣPBDE concentrations in female bears from Svalbard (49.8 ng g^{-1} lw) were very comparable to those previously reported by Wolkers et al. (2004) in this region (45.6 ng g^{-1} lw). Muir et al. (2006a) detected more congeners in the Svalbard bears, with BDE-47 comprising 82 ± 9% of the ΣPBDE, whereas Wolkers et al. (2004) found that BDE-47 comprised 100% of the ΣPBDE in female bears. Relative to Svalbard and East Greenland, significantly lower ΣPBDE concentrations were found in the fat of bears from Canada and Alaska. No samples were available at the time for Canadian bears, but higher total-α-HBCDD concentrations were found in the fat of bears from Greenland and Svalbard than in those from Alaska. The spatial trends for PBDEs and HBCDD parallel those for PCBs implying similar source regions for long range transport to the Arctic and bioaccumulation pathways in the arctic marine food web. HBCDD was detected in bears from all three locations, however mean HBCDD concentrations in Svalbard (44.4 ng g^{-1} lw) and East Greenland (44.5 ng g^{-1} lw) bears were much greater than in those from Bering-Chukchi (0.40 ng g^{-1} lw). These data indicate that HBCDD was bioaccumulating in bears to concentrations comparable to, or exceeding those, of PBDE (Muir et al. 2006a).

McKinney et al. (2011a, 2011b) reported on various BFRs in adipose tissue from the eleven polar bear subpopulations spanning Alaska east to Svalbard in samples collected from 2005–2008. PBDE, 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) and total-(α)-HBCDD levels found in bears from Canadian subpopulations during the period 2007–2008 are presented in Figure 4.51 and are listed in Annex Table A4-13. PBDEs, total-(α-)HBCDD and BB-153 were consistently detected. Highest mean ΣPBDE, BB-153 and HBCDD levels were found in bears from southern Hudson Bay (65.9 ng g^{-1} ww, 79.2 ng g^{-1} ww and 4.54 ng g^{-1} ww, respectively) while the lowest concentrations were found in southern Beaufort Sea and Lancaster/Jones Sound populations, although HBCDD was undetectable in the animals sampled from the Gulf of Boothia. Adjusting for diet using a dietary index, McKinney

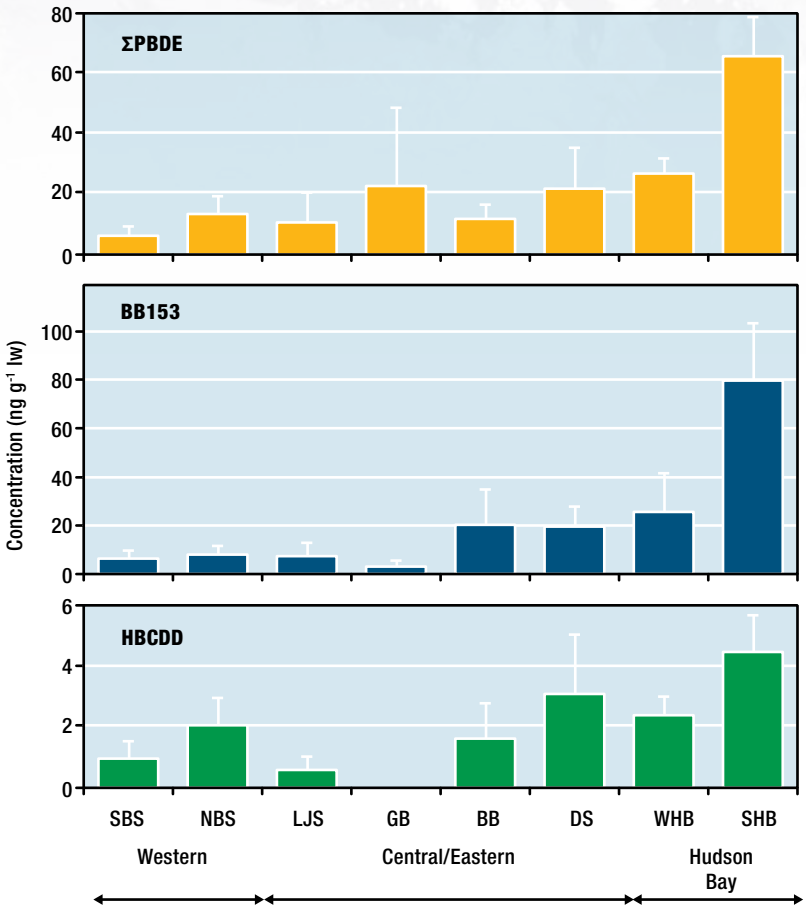

FIGURE 4.51

Concentrations (arithmetic means and upper 95% confidence llimit, ng g^{-1} ww) of ΣPBDEs, BB-153 and HBCDD in polar bear adipose tissue collected in 2007-2008 from 8 Canadian subpopulations (McKinney et al. 2011a, 2011b). HBCDD values were <MDL at GB. Full names of sampling areas are provided in the caption to Figure 4.49.

et al. (2011a) found that ΣPBDEs from both Hudson Bay populations (WHB and SHB) were higher than those in Svalbard and East Greenland bears. Unadjusted concentrations of ΣPBDE of the SHB animals were also higher than in East Greenland or Svalbard (McKinney et al. 2011a). HBCDD levels were much lower than ΣPBDE levels in all Canadian subpopulations, however, they were higher in Svalbard bears, consistent with greater European HBCDD use vs. North American penta-BDE product use (see Chapter 2, section 2.2.3).

McKinney et al. (2011b) also screened polar bear adipose samples for a large suite of less studied BFRs including BB-101, PBT, PBEB, HBB, BTBPE and DBDPE (See Chapter 1, Table 1.3 for full names). The frequency of detection of these BFRs is shown in Figure 4.52. PBEB, HBB, BB-101 were detected at frequencies of about 30–50% in southern Hudson Bay Bears and at lower frequency in other Canadian Arctic locations. BTBPE and DBDPE differed from the pattern seen with other BFRs. They had highest detection frequency in bears from the Canadian Archipelago (Figure 4.52).

4.1.5.3.6. Arctic fox

The arctic fox is one of the few species that constitutes an important component of both the terrestrial and marine ecosystems (Hiruki and Stirling 1989). Arctic foxes are opportunistic predators and scavengers that rely heavily on small mammals throughout most of their range (Audet et al. 2002). However, other foods such as birds and their eggs can be critical components of arctic fox diets in some years and in some parts of the Arctic (Bantle and Alisauskas 1998, Hersteinsson and MacDonald 1996). On land, arctic foxes feed mainly on lemmings, birds, and their eggs, as well as scavenge on caribou remains (Kapel 1999, Kennedy 1980, Stickney 1991) whereas coastal foxes will also eat marine invertebrates (Fay and Stephenson 1989,

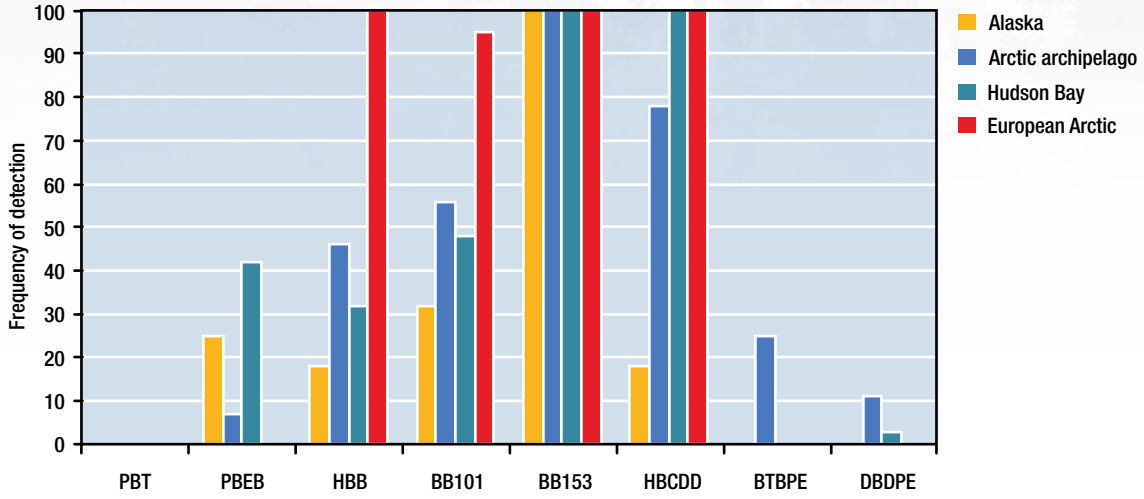

FIGURE 4.52

Frequency of detection of non-PBDE BFRs in polar bear adipose sampled from 4 regions over the period 2005–2008 (adapted from McKinney et al. 2011b).

Kapel 1999) and fish (Banfield 1987) in summer. In winter and spring on the sea-ice, arctic foxes scavenge the remains of ringed seals and bearded seals killed by polar bears (Andriashek et al. 1985, Fay and Stephenson 1989, Hiruki and Stirling 1989, Kapel 1999, Stirling and Archibald 1977), and they will also actively prey on newborn seal pups and eat placental remnants (Andriashek et al. 1985, Lydersen and Gjertz 1986, Smith 1976).

4.1.5.3.6.1. Legacy POPs in arctic fox

No additional new data for legacy POPs in arctic fox from the Canadian Arctic could be found for the observed timeframe for this review (2002–mid 2012). The last published POPs data in arctic fox was produced by Hoekstra et al. (2003a) and summarized in CACAR II. However, we think it is worth presenting the results as the peer reviewed publication on this data was available in 2003. Arctic fox muscle and liver were collected in 1999–2001 at Barrow (AK) USA, Ulukhaktok (NT) Canada and Arviat (NU) Canada, to investigate body residue patterns of POPs (Hoekstra et al. 2003a). At all sites, the rank order for POPs in muscle was ΣPCB > ΣCHL > ΣHCH > toxaphene > ΣCBz > ΣDDT. In liver, ΣCHL was the most abundant POP, followed by ΣPCB > toxaphene > ΣHCH > ΣCBz > ΣDDT. The most abundant POP analytes detected in arctic fox muscle and liver were oxychlordane, PCB-153, and PCB-180. The mean lipid-adjusted concentrations of ΣPCBs in arctic fox liver from Ulukhaktok and Barrow (1,853 ± 430 ng g^{-1} lw and 1,516 ± 370 ng g^{-1} lw, respectively) were significantly lower than ΣPCBs in arctic fox liver from coastal Iceland (5,400 ± 2,000 ng g^{-1} lw) and Svalbard (9,700 ± 1,900 ng g^{-1} lw) (Klobes et al. 1998, Wang-Andersen et al. 1993). This is consistent with the west–east gradient of ΣPCB concentrations in ringed seals (Muir et al. 2000b). The relative profile of organochlorines in liver found in this study is in good agreement with the overall profile of chlorinated contaminants in arctic fox from Iceland (Klobes et al. 1998) and PCB concentrations in populations from Svalbard (Wang-Andersen et al. 1993). Oxychlordane and heptachlor epoxide were the most predominant forms of chlordane-related compounds quantified in arctic fox muscle and liver tissues. HCB, DDE and ΣPCB concentrations were four- five- and eight-fold lower than detected in Svalbard, respectively (Fuglei et al. 2007).

4.1.5.3.6.2. New POPs in arctic fox

Martin et al. (2004a) determined PFASs in arctic fox liver from western Hudson Bay (Arviat) as part of an assessment of PFOS and PFCAs in Canadian Arctic wildlife. PFOS was the major PFSA detected in most samples. Mean PFOS concentrations (250 ng g^{-1} ww) were ca. 6 times greater than PFOSA (19 ng g^{-1} ww). ΣPFCA concentrations were lower and in general, odd-length PFCAs exceeded the concentration of even-length PFCAs, and concentrations decreased with increasing chain length. PFNA was also the dominant PFCA in arctic fox with a mean concentration of 22 ng g^{-1} ww. The rank order of the other PFCAs was PFDA ≈ PFUnA > PFTrA > PFDoA. Despite their remote habitat, arctic fox had unexpectedly high concentrations of PFOS in liver, with concentrations about 10 times higher than those found in ringed seals (Figure 4.38)

and about 100 times higher than in wolf liver (Müller et al. 2011). This may be explained by their opportunistic and scavenging dietary pattern that includes small terrestrial mammals and marine mammal carcasses.

4.1.5.4. Chiral chemicals in marine species

Chiral analysis is an area of study that offers enhanced insight into biological processes affecting chemical pollutants (see also Chapter 2, section 2.3.6). A chiral compound exists as pairs of nonsuperimposable mirror images called enantiomers. Enantiomers have identical physico-chemical proper-ties and abiotic degradation rates, but can have different rates of biotransformation (Buser and Müller 1992). The chemical manufacturing process results in a mixture containing approximately 50% of each chiral compound, termed racemic. Selective biotransformation of one chiral component over another can occur and results in an enantiomeric enrichment (Buser and Müller 1992). This resulting selective accumulation of a single enantiomer can provide information on the fate and dynamics of the chemical and may have significant toxicological ramifications. It has been proposed that the comparison of enantiomeric ratios (ERs; ratio of one enatiomer to another) or enantiomeric fractions (EFs; ratio of one enantiomer to the sum of both enantiomers) may provide information on the biotransformation capacity of a species and the trophic transfer of contaminants in a food web (Wiberg et al. 2000). However, in literature, enantiomer fraction is suggested as a superior descriptor over ER as EF values are limited to between 0–1 and provide an advantage for the purposes of calculation and graphic plotting (De Geus et al. 2000, Harner et al. 2000, Ulrich et al. 2003). A racemic EF = 0.5, whereas the preferential degradation of the (+) or (-) enantiomer yields EFs < 0.5 and > 0.5, respectively. Enantiomers have identical abiotic degradation rates but they can have different rates of biotransformation, providing information on the ability of species to biotranform chiral persistent compounds. Since CACAR II, few studies have examined the ratios/fractions of enantiomers or isomer ratios of chiral persistent pollutants.

Enantiomer fractions of chiral POPs (α-HCH, *o,p'*-DDT, *trans*-chlordane (TC) and *cis*-chlordane (CC), MC6, oxychlordane) were determined in deep sea amphipod (*E. gryllus*) (Bidleman et al. 2013) from the Arctic ocean. The EFs of *o,p'*-DDT in *E. gryllus* were > 0.5 in all samples, indicating depletion of (+) enantiomer and which shows the greater estrogenic activity (Hoekstra et al. 2001). Mean EFs of MC6 ranged from 0.43–0.47 on the different expeditions, while TC was 0.48–0.52 and CC was 0.48–0.51. By comparison, mean EFs in the benthic amphipod *Paramphithoe hystrix* from the eastern Arctic ocean were: TC 0.45, CC 0.62 and *o,p'*-DDT 0.79 (Borgå and Bidleman 2005). Borgå and Bidleman (2005) also found that ice amphipods (*Gammarus wilkietzkii*) contained nearly racemic α-HCH, chlordanes and *o,p'*-DDT, while greater deviation from racemic was found for these chemicals in epibenthic and benthic amphipods.

Enantiomer fractions of several chiral POPs including PCB atropisomers were determined in wolverine (from Kugluktuk NU in 1998 and 1999) and arctic fox (from Ulukhaktok (NT) in 2000) liver samples in the western Canadian Arctic (Hoekstra et al. 2003b). Several chiral OCPs and metabolites (α-HCH, *cis*- and *trans*-chlordane, oxychlordane, heptachlor exo-epoxide) and PCB atropisomers (PCB-91, -95, -136, -149) were non-racemic in arctic fox and wolverine liver samples. These results provided further support for the increased ability of these species to biotransform POPs. The EFs for *trans*-chlordane, oxychlordane, heptachlor epoxide, PCB-91, PCB-136 and PCB-149 were significantly different among species whereas the enantiomeric profiles for α-HCH and PCB-95 were not. Since it is not possible to determine if differences in EF patterns among the wolverines and arctic foxes were due to enantio-selective biotransformation or burdens of non-racemic proportions of chiral POPs via dietary sources, the enantiomeric profiles of these compounds suggested similarities in the stereochemical disposition of chiral POPs among the species. EFs of oxychlordane in arctic foxes (0.68 ± 0.02) and wolverines (0.71 ± 0.02) from this study were more (+) enantiomer enriched compared to arctic fox liver (0.59 ± 0.02) analyzed from Iceland (Klobes et al. 1998).

Chiral signatures of α-HCH and relative proportions of HCH isomers in the marine food web of the Northwater Polynya (NOW) in northern Baffin Bay in the Canadian Arctic were assessed in ringed seal blubber and muscle samples collected in 1998 (Moisey et al. 2001). EFs of α-HCH in ringed seal blubber were near racemic, suggesting either equal biotransformation of both enantiomers or no enantiospecific biotransformation in these seals. However, the α-HCH BMF in ringed seals was > 1, suggesting that they were not efficiently biotransforming α-HCH. Similar, near racemic EFs for ringed seal blubber have been reported (Wiberg et al. 2000). Comparable EFs of α-HCH were noted in blubber, liver, and lung tissue of neonatal northern

fur seals but with high EFs in the brain, which was attributed to selective crossing of the blood brain barrier (Mössner et al. 1992). Non-racemic EFs of chiral PCB congeners PCB-174, -176 and -183 were determined (Warner et al. 2005) in the same set of samples as in the study by Moisey et al. (2001). As the enantiomer fractions of chiral PCBs were racemic in prey of these animals, results suggested stereoselective and species-specific biotransformation of individual PCB steroisomers by ringed seals. Although seals have limited CYP2B-type biotransformation capacity compared to other mammals (Boon et al. 1989, Borgå et al. 2004), results from this study suggest that stereoselective biotransformation of chiral PCBs nevertheless may be occurring in ringed seals. However, stereoselective biological processes that alter EFs in ringed seals and other Arctic species appear to be species selective and regioselective.

More recently, Tomy et al. (2008b) reported enantiomer fractions of α- and β-HBCDD in the beluga, narwhal and walrus blubber from Frobisher Bay near Iqaluit (1996), Cape Dorset (1998) and Broughton Island (2000). Of special note for stereospecific analysis of HBCDD, EFs of racemic standard solutions of HBCDD can result in EF values that deviate from 0.5 (Dodder et al. 2006, Marvin et al. 2007). Mobile phase composition and column bleed are factors that can contribute to the variability of EF values for HBCDD (Marvin et al. 2007). Therefore, careful consideration must be given to interpretation of EF values for HBCDD. For the α-isomer, narwhal, beluga, and walrus all had EF values that were statistically greater than for an external standard, suggesting stereoselective enrichment of the (-) α-enantiomer relative to the (+) α-enantiomer in these animals. To examine whether trophic magnification of HBCDD may be enantioselective, the relationship between trophic levels (TL) and log-normalized concentrations of the individual enantiomers was investigated. Results suggested that only the (-) α-enantiomer showed a strong positive relationship between concentration and TL with a TMF value of 2.2. Consequently, it was hypothesized that there might be an overall change in EF throughout the entire food web. Relationships between EF values and TL revealed a small but statistically significant increase in the EF, suggesting that there may be enantiospecific accumulation of the (-) α-HBCDD. However, it is unclear whether this arises from a lower bioaccumulation potential of the (+) α-HBCDD relative to the (-) α-HBCDD and/or to the greater suspectibility of the (+) α-HBCDD to metabolism.

4.1.5.5. Assessment of spatial trends of POPs in marine species

- PCBs and toxaphene remain the most prominent POPs in marine mammals, followed by DDT and chlordane-related compounds, HCH isomers and chlorobenzenes. Information on toxaphene is limited to whales and seals.
- PCBs remain the most prominent POPs in seabird eggs and higher trophic level seabirds generally have a larger proportion of PCBs as a percentage of the total organohalogen compounds.
- Prominent new POPs are PBDEs and PFOS, which are detectable in all biota. With the exception of PFOS in polar bear livers, they are generally at much lower concentrations than PCBs or toxaphene.
- Other brominated compounds such as BB-153 and HBB have been detected at high frequency in polar bears but data is lacking for other species. Similarly, β-TBECH has been detected in beluga but not reported in other species.
- Accurate data for endosulfan and endosulfan sulfate are limited to ringed seals and beluga from eastern Hudson Bay. Further study in other species is warranted.
- PCNs remain important dioxin-like contaminants, especially in beluga and in seabird eggs. Spatial coverage in ringed seals has improved.
- Naturally occurring MeO-PBDEs were observed in beluga tissues (blood, liver and blubber) at concentrations similar or higher than PBDEs. No data are available for these compounds in other marine biota in the Canadian Arctic. Additional data would be useful to fully assess the exposure to brominated diphenyl ether related chemicals.
- Among the seabird eggs (black-legged kittiwakes, black guillemots, glaucous gulls, ivory gull, northern fulmars, and thick-billed murres) sampled in the Canadian Arctic, glaucous gulls had the highest concentrations of PCBs, other legacy POPs and PBDEs due to their high trophic position relative to most of the other species.
- In ringed seals, average concentrations of ΣHCH, ΣCBz and toxaphene are higher in the western and central Archipelago locations than in Hudson Bay and the eastern Arctic (Pangnirtung). Also, β-HCH level is higher in the western and central Arctic Archipelago. This suggests the influence of Pacific waters and Asian sources at these sites.
- PFASs, PBDEs and HBCDD are higher in ringed seals in Hudson Bay than in other locations reflecting the closer proximity to source regions in southern Canada and northern US.

- Hudson Bay beluga also had higher ΣDDT and ΣPBDEs than in other locations i.e., than southern Beaufort or eastern Baffin (Cumberland Sound) stocks. However, ΣPBDE concentrations in beluga liver from Hudson Bay is approximately 45 times lower than measured PBDE concentrations in St. Lawrence beluga illustrating the generally much lower concentrations of these contaminants in arctic resident species.
- Beluga and narwhal have the dubious distinction of having the highest concentrations of most POPs compared to other marine mammals (seals, polar bear, walrus).
- Polar bears have similar levels of PCBs (in subcutaneous fat) as beluga and narwhal blubber but much lower levels of other POPs.
- Spatial trends of POPs in polar bears are generally similar to those in ringed seals with higher ΣHCH in the western and central Archipelago and higher DDT, dieldrin and chlordane related compounds in animals from Hudson Bay and eastern Arctic.
- PFOS concentrations in polar bear liver are the highest of any arctic animals studied and those from the southern Hudson Bay have the highest levels.
- PBDEs, HBCDD and BB-153 are also higher in Hudson Bay polar bears than in bears from other regions in the Canadian Arctic, which may reflect the effect of proximity to source regions in eastern North America.
- Studies using a dietary index that included fatty acid and stable isotope measurements show that PCB and PBDE concentrations in polar bears are strongly influenced by diet. This may explain much of the spatial variation among POPs in Canadian Arctic polar bears.
- Spatial coverage data for POPs in seabirds, beluga and ringed seals is poor with important areas such as Hudson Bay, Nunavik and Nunatsiavut omitted entirely or not well represented.
- Limited or no data are available for POPs in seal species such as harbour seals, harp seals and bearded seals, which are increasing in importance in certain areas as annual ice cover declines.
- There are no data on POPs for cetaceans such as killer whales or on bowhead whales that have been recently harvested in the eastern Canadian Arctic.

4.1.6. Marine food web biomagnification

4.1.6.1. Bioaccumulation pathways/processes

The pathways and processes that result in elevated concentrations of POPs in arctic marine mammals and seabirds continue to be of interest. During the period 2003–2011, the number of substances being studied in the full marine food web expanded to include BFRs, PFASs and CUPs. This has widened the range of physical-chemical properties of chemicals studied in arctic marine food webs. Also, modeling studies have been carried out to examine the arctic accumulation properties of hypothetical chemicals with properties similar to non-ionic POPs (Czub et al. 2008, Kelly and Gobas 2001).

The terms biomagnification and bioaccumulation were defined earlier (section 4.1.4.1). Most legacy POPs such as DDT, chlordane, toxaphene, HCB and PCBs are characterized by their ability to biomagnify, resulting in higher lipid based concentrations in predators relative to their prey (Borgå et al. 2001, Muir et al. 1988, Norstrom et al. 1988, Kelly and Gobas 2001, Fisk et al. 2001a). For non-ionic POPs, food web biomagnification occurs when lipid weight concentrations increase with increasing trophic position. For the ionic perfluoroalkyl compounds, it occurs due to the accumulation in proteineous tissues such as liver and blood (Borgå et al. 2012). Substances with bioaccumulation potential are of great concern due to their possible toxicological effects on significant tissue and organs in high-trophic level species such as predatory fish, birds and mammals (Ross et al. 2000).

Characterizing the underlying processes and mechanisms—dietary absorption, various elimination processes, metabolic transformation, and growth dilution—controlling the biomagnification process is important to develop better and more proactive policies related to bioaccumulative substances. Although the factors controlling bioaccumulation of non-ionic organic contaminants in aquatic organisms are relatively well understood, empirical bioconcentration factors (BCFs) from laboratory studies and bioaccumulation factors (BAFs) from field samples can differ by several orders of magnitude (e.g., Arnot and Gobas 2006, Borgå et al. 2005a, Burkhard et al. 2012).

A number of studies have been carried out on the food web transfer of persistent organic chemicals in marine ecosystems since CACAR II. In addition to a broader range of chemicals, these studies incorporated a larger number of species and trophic levels in the arctic marine food web and incorporated stable nitrogen isotope ratios ($\delta^{15}N$) to discern trophic position. See Jardine et al. (2006) and Borgå et al. (2012) for further discussion of stable isotope methology and calculation of TMFs. Relative trophic positions of species within food webs have been estimated using $\delta^{15}N$, whereas $\delta^{13}C$ has differentiated

nearshore/offshore, benthic/pelagic, sympagic (ice-associated)/pelagic, freshwater/marine, terrestrial/freshwater and terrestrial/marine feeding strategies (Hebert et al. 2008, Hobson and Welch 1992, Post 2002, Smith et al. 1996). Results for various POPs in several of these marine food web studies are also presented in section 4.1.5.

4.1.6.2. Biomagnification studies of legacy POPs in the marine food web

Southern Beaufort Sea: BAFs of HCHs, PCBs, chlorobenzenes and members of the chlordane and DDT families were investigated in organisms from the lower food web (plankton to fish) of the southern Beaufort Sea to characterize their entry into the food web (Hickie et al. 2008). BAF values were calculated using temorally matched water and zooplankton (*C. hyperboreus*) samples collected at four times during the SHEBA (Surface Heat Budget of the Arctic Ocean) drift study between 1997 and 1998. Biomagnification through the food web was quantified by examining the relationship between lipid-normalized POPs concentrations and the trophic level of organisms as defined by $\delta^{15}N$ values. A positive correlation between PCB-180 concentrations (ng g^{-1} lw) and the trophic level of the organisms was observed; the higher the trophic level, the higher the concentration. Food web magnification factors for poikilothermic species in the Beaufort and Chukchi Seas ranged from 1 to 7.5 and correlated with octanol-water partition coefficients.

Cumberland Sound: McKinney et al. (2012) studied food web organochlorine transfer in the Cumberland Sound marine food web. A unique aspect of this study was the comparison of BMFs and TMFs with transient/subarctic species included relative to those that only included resident species. For contaminants that biomagnified in a transient-and-resident food web and a resident-only food web scenario, TMFs were higher in the former (2.3 to 10.1) compared to the latter (1.7 to 4.0) (Figure 4.53). Transient/subarctic species have higher tissue contaminant levels and greater BMFs likely due to higher energetic requirements associated with long-distance movements or the consumption of more contaminated prey in regions outside of Cumberland Sound (Figure 4.53). The authors noted that the increasing presence of migratory forage fish such as capelin and herring, as well as harp seals, in Cumberland Sound appears to be resulting in the introduction of POPs from lower latitudes into the marine food web via a biovector route and directly influences contaminant concentrations in forage-fish consuming marine mammals and seabirds.

Eastern Hudson Bay: Results of the eastern Hudson Bay marine food web study indicated strong positive relationships ($r^2 > 0.8$, $p < 0.001$) between trophic level and concentrations of legacy POPs such as PCBs, mirex, HCHs, HCBz, dieldrin and DDTs (Figure 4.54, Table 4.1 and Annex Table A4-14) (Kelly et al. 2008a). TMFs generally ranged between approximately 3 and 11 for legacy POPs (Annex Table A4-14). The data indicate that legacy POPs exhibit a high degree of biomagnification in the eastern Hudson Bay marine food web.

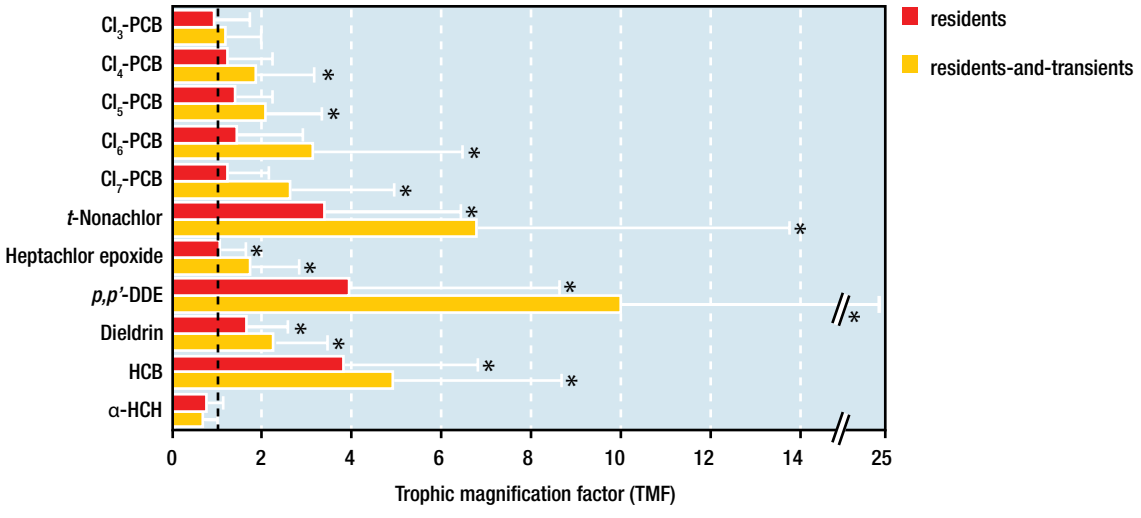

FIGURE 4.53

Calculated contaminant TMFs in a Cumberland Sound resident species-only compared to a resident-and-transient species marine food web (McKinney et al. 2012). TMFs (+ upper 95% confidence limit) are the antilog of the log(contaminant) vs. trophic level (TL) regression slope. Thick dashed line indicates TMF = 1. Asterisks indicate statistically significant biomagnification, i.e., TMF > 1.

4.1.6.3. Biomagnification studies on new POPs in the marine food web

PBDEs: These studies involved field collection and analysis of samples for PBDEs (Kelly et al. 2007, 2008a, 2008b, 2009). The results from the study are discussed in the marine biota section (4.1.5.1.1.2). See Figure 4.26 for study locations. Additional study details and results are provided in Annex Tables A4-6 and A4-14.

Concentrations of the majority of PBDEs did not show significant increases ($p > 0.05$) with trophic level (TL) in the eastern Hudson Bay marine food web (Figure 4.54, Annex Table A4-14) which used the same food web in identical samples used for PCB analyses discussed above. An exception was PBDE-47, which exhibited slight concentration increases with increasing trophic level ($p < 0.05$) with a TMF of 1.6 (95% CI = 1.2–2.0). TMF values of other PBDEs (BDE-28, -49, -66, -99, -100, -153 and -154) ranged between 0.96–1.2 and were not statistically different from 1. The data demonstrate that Br_3–Br_7 PBDEs exhibit a substantially lower degree of trophic magnification in this marine food web compared to recalcitrant Cl_5–Cl_7 PCBs with comparable K_{OW}'s. The reduced biomagnification of PBDE congeners in this food web is likely due to debromination and/or cytochrome P450 mediated metabolism of these compounds (Hakk and Letcher 2003).

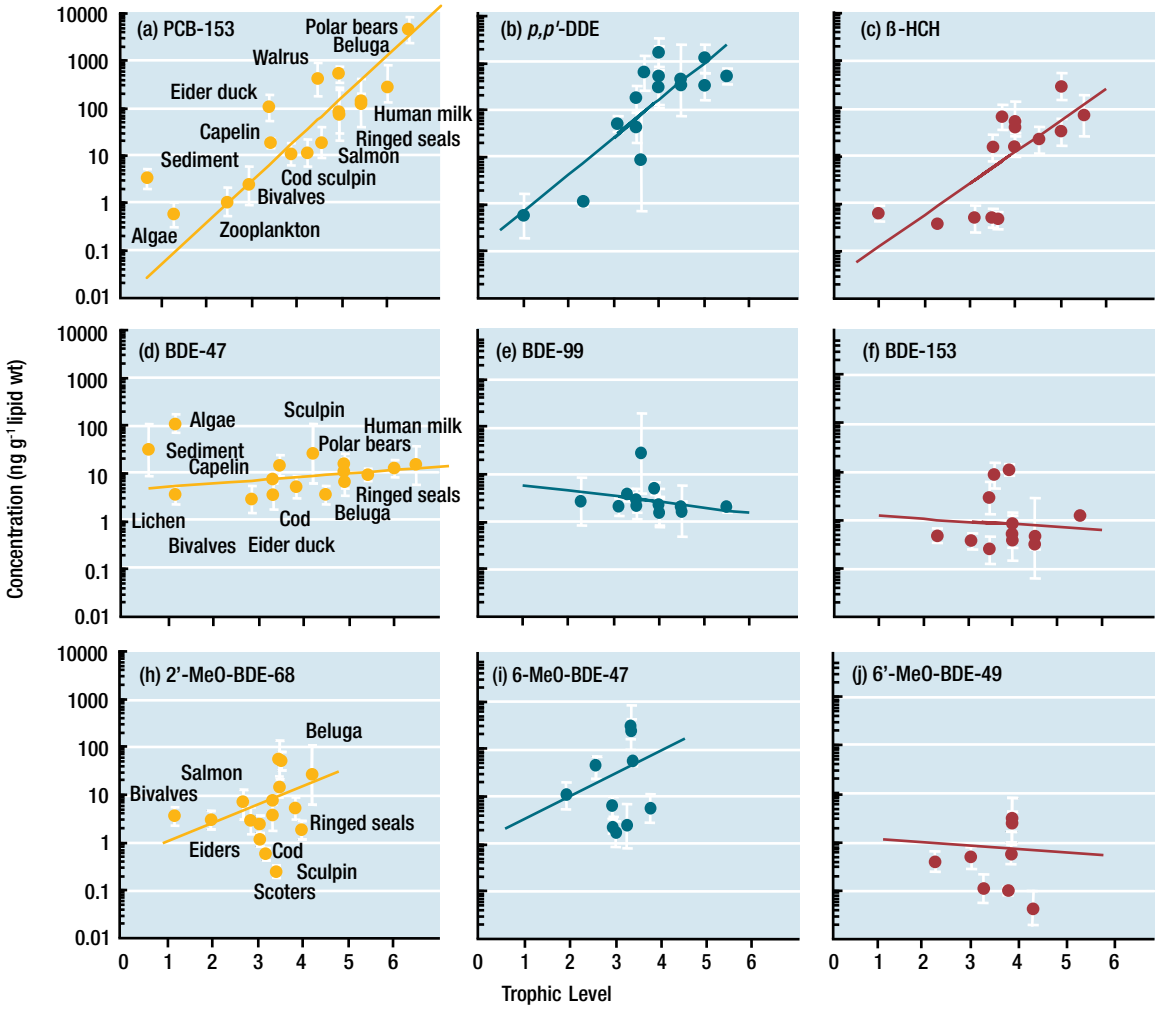

FIGURE 4.54

Chemical concentrations in organisms of the arctic marine food web (ng g^{-1} lipid equivalent) compared to trophic level for (a) PCB-153, (b) *p,p'*-DDE, (c) β-HCH, (d) BDE-47, (e) BDE-99, (f) BDE-153 (g) 2'-MeO-BDE-68, (h) 6-MeO-BDE-47 and (i) 6'-MeO-BDE-49. The solid line represents the log-linear regression of the C_B-TL relationship over the entire food web. Data points are geometric means, and error bars represent the range of one standard deviation. PCB-153 concentrations shown for polar bears are for eastern Hudson Bay animals (Belcher Islands) (Norstrom et al. 1998). PBDE concentrations shown for polar bears are for western Hudson Bay animals (Muir et al. 2006a). Redrawn from Kelly et al. (2008b).

The TMF analyses compared PBDEs and PCBs and included polar bears from western Hudson Bay, as well as the biota sampled from the eastern Hudson Bay region. Recalcitrant PCBs all had TMFs significantly greater than 1, ranging from 2.9 (PCB-28) to 11 (PCB-153). In contrast, most PBDE congener TMFs did not differ significantly from 1. Only the lowest (0.44, BDE-66) and highest (1.6, BDE-47) TMFs in the range were significantly less than or greater than 1, respectively.

Previous work in Canadian Arctic top predators demonstrated that, for example, polar bear and ringed seal BMFs for major PBDE congeners exceeded 1 (indicating biomagnification between bear and seal) (Muir et al. 2006a), and the whole food web TMF approach generated the opposite interpretation (i.e., that PBDEs do not biomagnify in the food web).

Where data were available for seals from nearby locations, Muir et al. (2006a) calculated polar bear–ringed seal BMFs for BDE-47, -99, -100, -153 and -154 as well as PCB-153, -180 and -194. Locations, congener-specific and average BMFs are summarized in Table 4.1. Mean PBDE BMFs were greater than 1 for all congeners and locations, except for East Greenland bears, indicating varying degrees of biomagnification of PBDEs across the Arctic. Averaged across all locations, PCB-194 had the highest BMF (73), followed by BDE-153 (71), which was greater than any other PBDE analyzed and greater than the TMFs of PCB-153 and PCB-180 (13 and 32 respectively). BDE-47, -99 and -100 BMFs were much lower than BDE-153 (3.9, 5.8 and 4.7 respectively). In Svalbard, the BDE-47 BMF was 2.5 and was almost equal to the BMF of 2.7 calculated from the data in Wolkers et al. (2004). For Canadian sampling sites, BMFs of polar bear-ringed seal BDE-47, -100 and -153 were greatest in the southeastern Baffin


Photo: Gerald Darnis /ArcticNet

area while BMFs for BDE-99 and BDE-154 were highest in the Lancaster/Jones Sound (Table 4.1). East Greenland had BDE-99, -100 and -154 BMFs < 1, while they were greater than 1 in all other locations. It was hypothesized that a different food web structure and/or differences in the biotransformation processes in the lower trophic levels were contributing to the observed inconsistencies with other locations. On average, BDE-153 had the highest biomagnification potential relative to other PBDEs, and was comparable to known bioaccumulative compounds such as PCB-153.

As shown in Kelly et al. (2008b) the TMFs for recalcitrant PCB congeners are > 1, ranging from 2 to a maximum of 11 (PCB-153). PBDEs do not exhibit the same degree of trophic magnification as PCB congeners with comparable K_{OW}; BDE-47 had the highest TMF of any PBDE with a value of 1.6, while other PBDEs showed very weak trophic magnification or trophic dilution (Figure 4.54 and 4.55).

TABLE 4.1. Biomagnification factors for PBDE and PCB congeners in polar bears assuming ringed seal as the prey species. Reproduced from Muir et al. (2006a).

		Biomagnification factors							
Polar bear population	Ringed seal location	BDE-47	BDE-99	BDE-100	BDE- 153	BDE-154	CB-153	CB-180	CB-194
Amundsen Gulf	Sachs Harbour	3.3	3.4	5.8	130	1.5	13	33	81
Lancaster & Jones Sound	Grise Fiord/ Resolute	4.5	11	6.7	58	2.9	7.0	23	63
Southeast Baffin Is	Pangnirtung	7.4	8.0	8.8	91	1.1	17	39	66
East Greenland	Scoresbysund	1.8	1.0	0.6	8.8	0.2	12	33	82
Svalbard	NE Svalbard	2.5	5.9	1.3	–	–	16	–	–
Average BMF		3.9	5.8	4.7	71	1.8	13	32	73

Methoxy-PBDEs in Eastern Hudson Bay: Kelly et al. (2008b) studied the bioaccumulation and trophic magnification of MeO- and hydroxylated (OH-) PBDEs in a Hudson Bay food web system. The abundance and behaviour of these compounds in Arctic food webs was established and compared to PBDE, PCB and OCP bioaccumulation and trophic magnification.

OH-PBDEs were below method detection limits (MDLs) in sediments and in all biota and tissues, except for beluga whale blubber and milk, where low concentrations of 5 congeners were observed (mean ΣOH-PBDE = 0.1 ng g^{-1} lw). It was suggested that 5-OH-BDE-47 detected in beluga blubber could be a metabolite of BDE-47, which is the most abundant OH-PBDE congener in high trophic level biota (Kelly et al. 2008a), however no correlation between the concentrations of these two compounds was found. In addition, low mean ΣOH-PBDE/ΣPBDE ratios indicated that OH-PBDEs were not formed via biotransformation, taken up from natural sources or retained to any significant degree in belugas.

MeO-PBDE congeners were detected across the eastern Hudson Bay marine food web, with ΣMeO-PBDE concentrations ranging from 1.3 ng g^{-1} lw (eider duck) to 300 ng g^{-1} lw (male belugas). As with PBDEs, MeO-PBDEs showed sex and age specific differences in beluga whales. Generally, MeO-PBDE concentrations were greater in calves and males than in females, which was also the trend observed for PBDEs and tetra-MeO-PBDE congeners in Svalbard belugas (Wolkers et al. 2004). The greatest concentration of any individual MeO-PBDE congener in the food web was for 6-MeO-BDE-47, followed by 2′-MeO-BDE-68 and 6′-MeO-BDE-49. The concentrations of 6-MeO-BDE-47 and BDE-47 were positively correlated in belugas, ringed seal and seaducks, as were some other MeO-PBDEs and their potential source congeners (e.g., 6-MeO-BDE-99 and BDE-99). TMFs of MeO-PBDEs were variable; 6-MeO-BDE-47 and 2′-MeO-BDE-68 exhibited trophic magnification with TMFs = 2.3 and 2.6 respectively, but most MeO-PBDEs had TMF values less than 1. The TMFs of 6-MeO-BDE-47 and 2′-MeO-BDE-68 were greater than that of BDE-47, but are less than most PCB congeners, indicating trophic magnification intermediate to these two classes of compounds (Figure 4.54 and 4.55). However, inter-species comparisons both in the study by Kelly et al. (2008b) and with other marine mammal studies showed that no positive association between BDE-47 and 6-MeO-BDE-47 concentrations could be made (i.e., the greatest BDE-47 concentration in a given animal did not correspond to the greatest 6-MeO-BDE-47 concentration). This suggested that the MeO-PBDEs, particularly ortho-substituted compounds, were bioaccumulated natural products independent of BDE-47 exposure rather than biotransformation products of that congener.

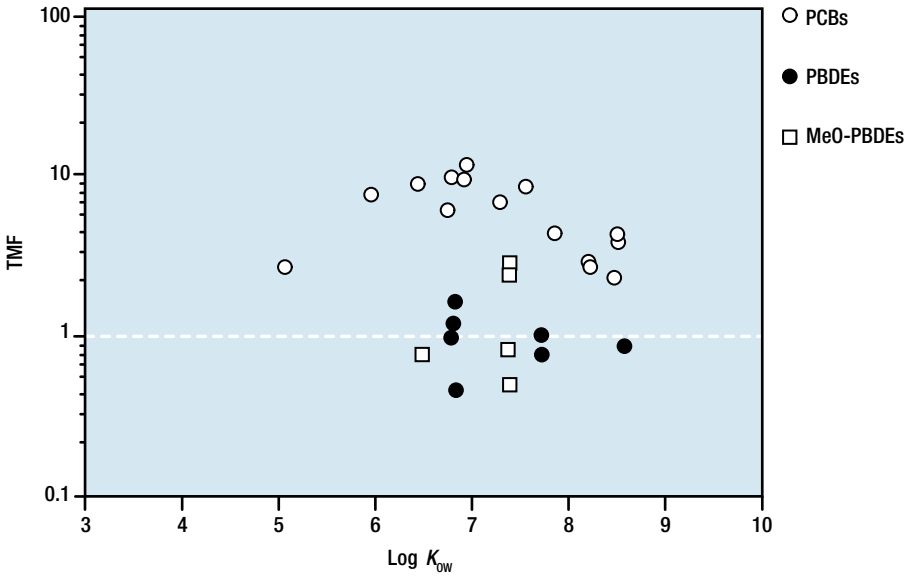

FIGURE 4.55

Observed TMFs for individual PCBs, PBDE and MeO-PBDEs in the arctic marine food web compared to log K_{OW}. Error bars have been omitted for clarity. TMF values greater than 1 (dashed line) indicate biomagnification. See supporting information in Kelly et al. (2008b) for details regarding K_{OW} values.

HBCDD: Tomy et al. (2008b) examined the extent of trophic transfer of the three diastereoisomers HBCDD and seven BDE congeners in components of an eastern arctic marine food web (from eastern Canada (Table 4.2)). The results indicated clear differences in HBCDD isomer and BDE congener profiles with trophic level (TL). Trophic magnification was observed for the α-HBCDD and BDE-47 as concentrations increased with increasing TL in the food web, whereas there was trophic dilution of γ-HBCDD and BDE-209 throughout the food web.

Tomy et al. (2009b) found that the same suite of PBDEs and HBCDD isomers did not biomagnify in food web samples from the southeastern Beaufort Sea (Table 4.2). BDE concentrations in the lower TL animals were generally greater than those measured in the higher TL animals. This result was similar to the observations in the eastern arctic food web and in the eastern Hudson Bay except for BDE-47. The ratios of the HBCDD isomers were strikingly similar in both the studies by Tomy et al. (2008b, 2009b)

Perfluorinated alkyl substances: Tomy et al. (2004) reported a TMF for PFOS of 3.1 in the eastern arctic marine food web. In a related study of the western Canadian arctic marine food web, Tomy et al. (2009b) reported TMFs of 2.1, 3.8, 6.3, 13.7 and 6.3 for PFOA, PFNA, PFDA, PFUnA and PFOS, respectively. Concentrations of PFOSA, with a TMF value of 1.9, were also found to increase with TL.

In addition, Kelly et al. (2009) found that PFAS concentrations (ng g^{-1} ww) increased significantly ($p < 0.05$) with increasing trophic level. Trophic magnification factors based on wet weight concentrations (TMF_{ww}) ranged between 1.43 and 17.4. The TMF_{ww} of PFOS (17.4) was substantially higher than that of PFOSA (5.09) and PFOA (3.28). Observed TMF_{ww} values were consistent with previously reported TMF_{ww} values of PFASs in the western arctic marine food web. Lipid corrected concentrations of PFOSA were also found to increase with TL, with a TMF value of 4.46.

TABLE 4.2. Trophic magnification factors (TMF)[1] for legacy and new POPs in arctic marine food web studies.

	East Hudson Bay		Southeastern Beaufort Sea		Baffin Island (eastern Arctic)		Cumberland South & Baffin Bay		Baffin Bay	
Chemicals	(Kelly et al. 2008a) (Kelly et al. 2009)		(Tomy et al. 2009b)		(Tomy et al. 2008b)		(Tomy et al. 2004); (McKinney et al. 2012)		(Fisk et al. 2001a)	
	TMF	95% CI	TMF	95% CI	TMF	95% CI	TMF		TMF	
PCB-153	11.1	8.6–14					3.17[2]		9.7 ± 1.1	
PCB-180	10	7.2–14					2.65[3]		10.6 ± 1.5	
p,p' DDE	6.28	3.07–12.8					10.1		13.7 ± 1.5	
β-HCH	2.78	2.26–3.42							3.9 ± 1.2	
Mirex	6.87	5.13–9.20							10.4 ± 2.4	
BDE-99	0.76	0.57–1.0	~0.1							
BDE-47	1.6	1.2–2.0	~0.1		2.5	1.6–3.7				
BDE-209	–	–	–		0.3	0.1–0.6				
α-HBCDD	–	–	~0.1		2.1	1.3–3.4				
γ-HBCDD	–	–	~0.1		0.5	0.3–0.9				
PFOA	1.93	1.4–2.64	2.1	1.4–3.2						
PFNA	4.23	2.90– 6.19	3.8	2.9–6.2						
PFDA	4.81	3.31–6.99	6.3	3.3–12.1						
PFUnA	4.79	3.63 –6.32	13.7	5.9–31.2						
PFOS	11	6.90–17.4	6.3	2.4–16.6			3.1			
PFOSA			1.9	1.5–2.3						

[1] TMF = e^B where B= slope of the ln Concentration vs. Trophic Level relationship

[2] TMF for total Hexachlorobiphenyls (mainly CB153) for transient+resident species

[3] TMF for total Heptachlorobiphenyls (mainly CB180) for transient+resident species

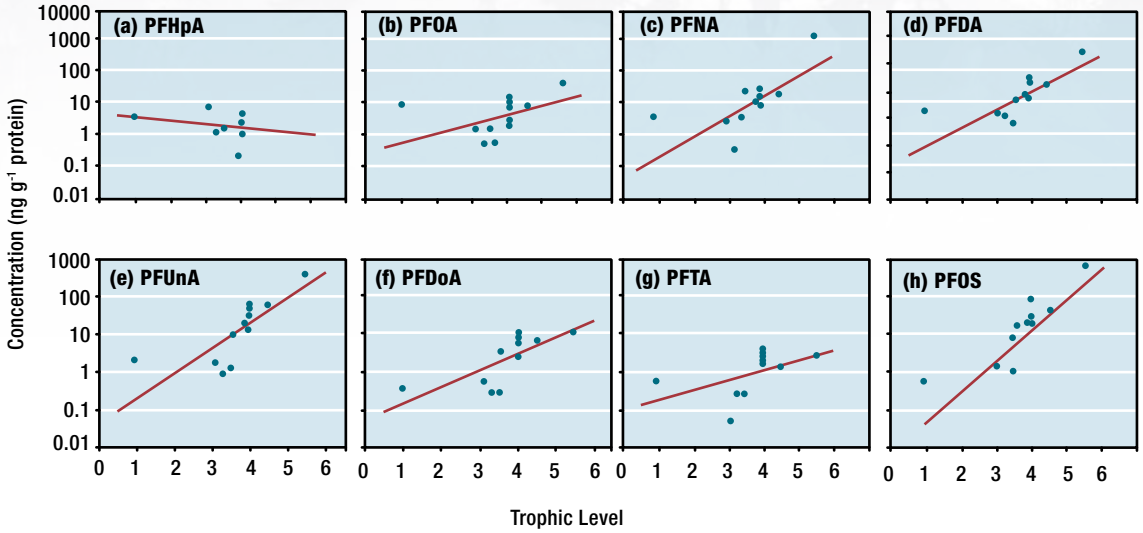

FIGURE 4.56

Chemical concentrations in organisms of the Arctic marine food web versus trophic level (TL) for perfluorinated acids (ng g^{-1} protein), including (a) PFHpA (b) PFOA, (c) PFNA, (d) PFDA, (e) PFUnA and (f) PFDoA, (g) PFTA and (h) PFOS. Data are geometric means ± 1 SD. Data for East Hudson Bay sculpin and polar bears are from (Martin et al. 2004b, Smithwick et al. 2005) and (Norstrom et al. 1998). Solid lines represent log-linear regression of C_B-TL relationship over the entire food web.

Protein corrected concentrations of PFOS and C_8–C_{12} PFCAs increased significantly ($p < 0.05$) with trophic level, while PFHpA and PFTA concentrations were similar ($p > 0.05$) across the eastern Hudson Bay marine food web (Figure 4.56, Annex Table A4-7). TMFs of PFASs based on protein corrected concentrations (TMF_P) ranged between 0.76 and 11.0. Food web bioaccumulation studies of perfluorinated alkyl acids (PFAs) commonly evaluate biomagnification behaviour using wet weight based concentrations in blood, liver tissue and/or whole organisms (Martin et al. 2004b, Haukas et al. 2007, Houde et al. 2006a, Powley et al. 2008, Tomy et al. 2004). However, unlike neutral lipophilic contaminants such as PCBs and OCPs, PFA concentrations exhibit positive correlation with protein content, rather than lipid content in tissues/fluids of the organism (Hoff et al. 2003).

PFA kinetics may be more accurately represented by protein-water and protein-air partition coefficients (K_{PW}, K_{PA}). Hence PFA biomagnification is perhaps best evaluated by assessing trophic magnification factors derived using protein normalized concentrations (i.e., TMF_P).

The low degree of biomagnification of PFHpA ($TMF_P = 0.76$) and PFOA ($TMF_P = 1.93$) may be due to elimination via respiration or urinary excretion of these highly water-soluble compounds (Goecke-Flora and Reo 1996, Martin et al. 2003b). The reduced biomagnification of PFTA ($TMF_P = 1.43$) may be due to reduced bioavailability of this long-chain PFA, given the association with dissolved and colloidal organic matter, low dietary assimilation and/or reduced permeation across gill membranes (Martin et al. 2003a). The observed data indicate that PFAs, with K_{PW}'s between 10^3–10^5 and K_{PA}'s between $10^{4.5}$–10^6, exhibit a high degree of biomagnification in the arctic marine mammalian food web. The corresponding K_{OW} and K_{OA} ranges of these bioaccumulative PFAs (i.e., PFOS and C_9–C_{12} PFCAs) are approximately 10^4 to 10^7 and 10^7 to 10^9, respectively.

In summary, the bioaccumulation behaviour of legacy and new POPs was similar in all the various marine food webs that were studied. Recalcitrant organochlorines such as PCBs, DDTs, and chlordanes exhibited a high degree of biomagnification (McKinney et al. 2012) while measurements of PBDE congeners and HBCDD generally revealed low or negligible biomagnification (TMFs 0.1–2.1) (Tomy et al. 2009b, Tomy et al. 2008b, Kelly et al. 2005). On the other hand, PFOS and several PFCAs were found to be highly persistent environmental contaminants that biomagnified in arctic marine food webs (Kelly et al. 2009). Unlike lipophilic POPs which biomagnify in all food webs, proteinophilic PFAs and the moderately lipophilic β-HCH principally biomagnify in the upper trophic level wildlife of the food web (Table 4.2).

Biomagnification of lipophilic organochlorines (e.g., PCBs, DDTs) is explained by the fact these high K_{OW}-high K_{OA} compounds, which are generally resistant to metabolic transformation, exhibit high gastrointestinal uptake rates and slow respiratory elimination rates in

aquatic water-respiring organisms (i.e., slow lipid-water transport), as well as air-breathing animals (i.e., slow lipid-air transport). β-HCH is moderately lipophilic but relatively non-volatile and hence respiratory elimination of this recalcitrant low K_{OW}-high K_{OA} compound, which is relatively efficient for water-respiring organisms, is very slow in air-breathing animals, resulting in biomagnification in food webs containing air-breathers (Kelly et al. 2007). Other low K_{OW}- high K_{OA} chemicals that exhibit similar food web-specific bioaccumulation behavior are 1,2,4,5 tetrachlorobenzene and β-endosulfan (Kelly et al. 2007). These low K_{OW} – high K_{OA} chemicals are susceptible to biomagnification in air-breathing animals, including humans because of their slow rate of respiratory elimination. Metabolic transformation can ultimately reduce or eliminate the anticipated biomagnification potential but only if the metabolic transformation rate is sufficiently high. The field observations showing biomagnification of low K_{OW} – high K_{OA} chemicals (e.g., β-HCH, 1,2,4,5 tetrachlorobenzene, β-endosulfan) in the eastern Hudson Bay marine food web suggest that metabolic transformation rates of these compounds in Arctic marine organisms is not sufficient to counteract the biomagnification phenomenon.

Similarly, the observed biomagnification behavior of PFASs can be attributed to the high aqueous solubility and low volatility of these compounds. Specifically, the high degree of PFA biomagnification in upper trophic level wildlife (seals, whales and polar bears) is likely due to the combination of (i) efficient dietary assimilation, (ii) strong partitioning into the organic phase (i.e., retention in protein rich tissues/fluids), (iii) high resistance to metabolism and (iv) low volatility of those compounds, which essentially relates to high gastrointestinal uptake and slow elimination rates in air-breathing animals. The low biomagnification potential of PFAs in aquatic organisms is attributed to the relatively high aqueous solubility (> 500 mg L^{-1}) and hydrophilic nature of those compounds, hence efficient respiratory elimination via gills in water-respiring organisms. Further investigations of phase-partitioning (e.g., protein-water and protein-air) and biotransformation/bioformation kinetics of PFAs and PFA precursor compounds are required to better understand the bioaccumulation behaviour of these contaminants.

4.1.6.4. Trophic transfer of isomers and enantiomers in marine food webs

Isomers and enantiomers of contaminants have the potential to identify differences in species biotransformation ability and provide insights into the fate of persistent pollutants in food webs (see section 4.1.5.4). Hoekstra et al. (2003c) addressed the enantiomer-specific accumulation of chiral OCPs (α-HCH and several chlordane components and metabolites) in selected biota in an isotopically characterized food web from arctic Alaska and investigated the utility of EFs to elucidate biotransformation pathways and/or exposure among marine biota. They reported that

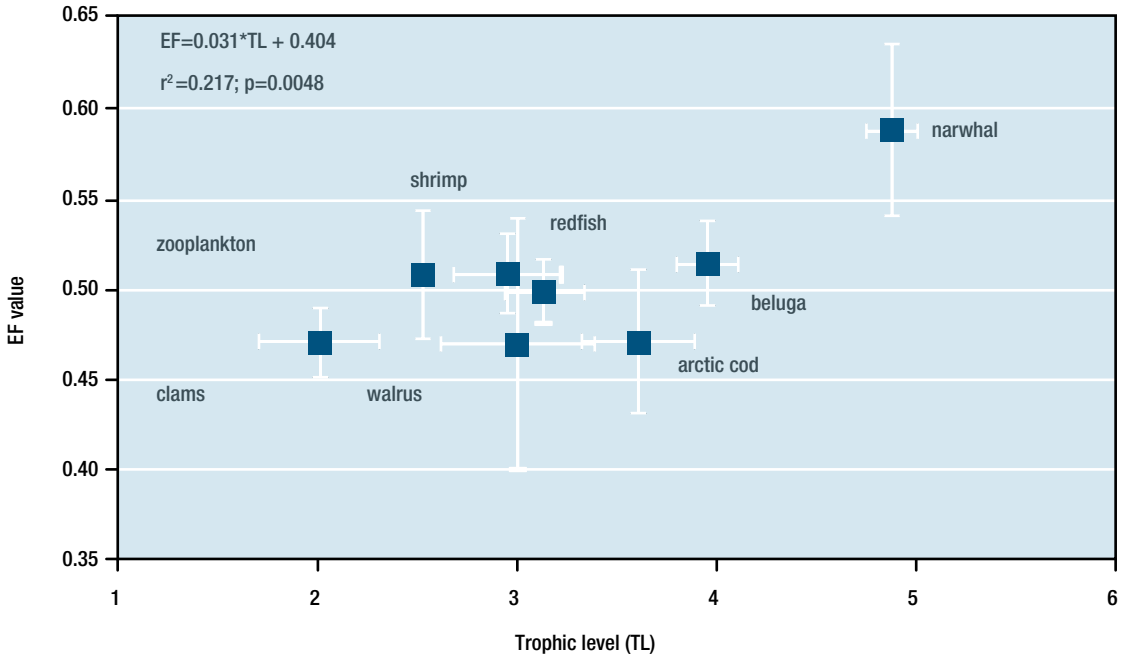

FIGURE 4.57

Plot of enantiomer fraction (EF) of α-HBCDD versus trophic level within the eastern Arctic food web (from Tomy et al. 2008b).

EF values were not significantly correlated with trophic levels and thus concluded that accumulation of chiral OCPs from prey to the predator was not enantiomer specific. More recently, concentrations of HBCDD isomers and enantiomer fractions of individual isomers of HBCDD were determined in an eastern Canadian Arctic marine food web (Tomy et al. 2008b) and results indicated clear differences in HBCDD isomer and BDE congener profiles with TL. Trophic magnification was observed for the α-diastereoisomer as concentrations increased with increasing TL in the food web, whereas there was trophic dilution of γ-HBCDD through the food web. Only the (-)α-enantiomer showed a strong positive relationship between concentration and TL with a trophic magnification factor (TMF) value of 2.2 (Figure 4.57). A small but significant increase in the enantiomeric fraction value of the α-enantiomers with TL was also observed, implying that there is an overall preferential enrichment of the (-)α-enantiomer relative to the (+)α-enantiomer. This is likely due to the greater bioaccumulation potential of the (-)α-enantiomer and/or to the greater susceptibility of the (+)α-enantiomer to metabolism.

As it is reported in previous sections of this report, PFOS is the predominant PFAS in the wildlife in the Arctic. Recently, it has been hypothesized that certain PFOS-precursor isomers (i.e., $C_6F_{13}C^*F(CF_3)SO_2N(H)CH_2(C_6H_4)OCH_3$, namely 1*m*-PreFOS; where * shows chiral center) are chiral, non-racemic proportions of PFOS isomers in biological samples and could be used as a marker of significant exposure to PFOS-precursors. Moreover, these chiral precursors might be utilized to identify the differences in a species biotransformation ability and provide insights into the fate of these chemicals in food webs. However, no data have been reported on enantiospecific uptake or the biomagnifications of PFOS precursors in arctic wildlife, but there was only one in vitro study in human liver microcosms (Wang et al. 2009).

4.1.6.5. Modeling studies

Kelly et al. (2007) developed and tested a model representing POPs bioaccumulation in the east Hudson Bay marine food web. Using a similar modeling approach as earlier work on arctic terrestrial food chains (Kelly and Gobas 2003), a model was employed that used a series of mechanistic equations relating ambient concentrations of organic contaminants (in air and seawater) to resulting concentrations in arctic marine biota, including invertebrates, fish,

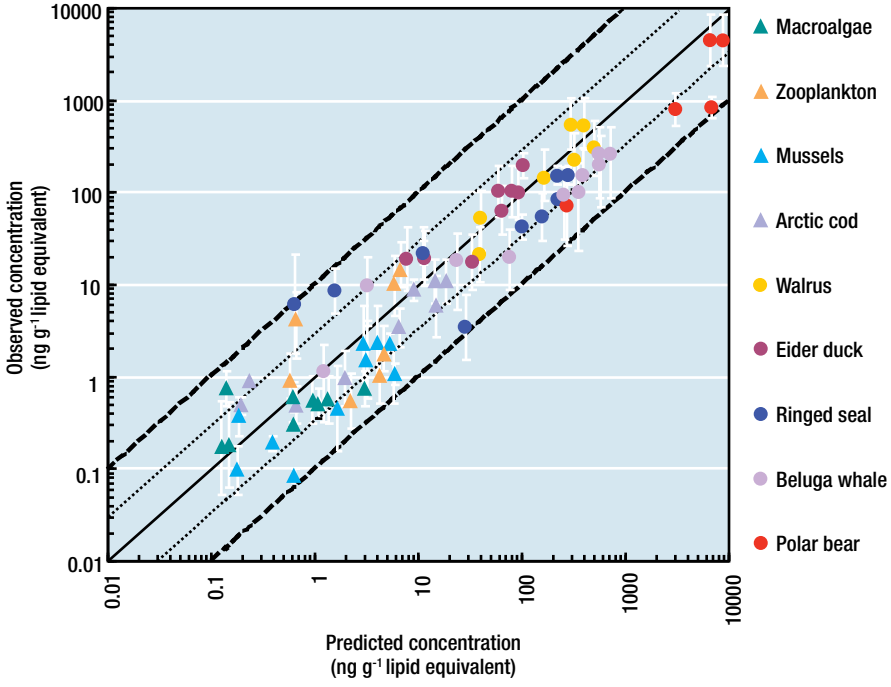

FIGURE 4.58

Model predicted compared to observed concentrations (ng g^{-1} lipid equivalent) in various organisms of the east Hudson Bay marine food web. Observed data represent geometric mean ± one standard deviation. The solid black line represents an ideal model fit (1:1 predicted:observed line). Dashed lines represent a factor of 3 and 10 above and below the ideal fit.

seaducks and marine mammals (Figure 4.58). The same simple two-compartment generic organism model was used to simulate POPs bioaccumulation in the various arctic marine organisms. An important aspect of the model is the respiratory elimination kinetics of POPs in water-respiring organisms (lipid-water exchange) and air-breathing animals (lipid-air exchange) in this food web (Kelly et al. 2007).

The model was parameterized and applied to the eastern Hudson Bay marine food web to predict steady-state concentrations (C, ng g^{-1} lipid equivalent), BMFs and bioaccumulation factors (BAFs) in the various organisms of the food web. Model predictions were compared to current field study data. The results showed model forecasts of POPs internal residue concentrations in east Hudson Bay biota were in good agreement with measured concentrations (Figure 4.58).

The model was used to explore the influence of physical-chemical properties such as K_{OW} and K_{OA} on chemical bioaccumulation behaviour in the arctic marine food web. The results showed that in water-respiring organisms (zooplankton, fish), biomagnification occurs if the K_{OW} of the chemical exceeds approximately 10^5, as respiratory elimination is very slow for these hydrophobic compounds. In the air-breathing organisms (birds, marine mammals), biomagnification can occur when K_{OW} exceeds 10^2 and K_{OA} exceeds 10^6, as these chemicals exhibit very slow elimination via urine and respiration. Figure 4.59 illustrates the relationship between chemical K_{OW}, K_{OA} and the degree of food web magnification in (a) the arctic terrestrial food chain (lichen-caribou-wolf food chain)(section 4.1.4.5) and (b) the marine mammalian food web (i.e., eastern Hudson Bay). In the terrestrial food chain, chemicals with a K_{OW} between 10^2 and 10^{10} and a $K_{OA} \geq 10^6$ can biomagnify up to 400-fold if not metabolized.


Photo: Martin Fortier/ArcticNet

Similar observations are apparent for the marine mammalian food web, which includes water-respiring invertebrates and fish and air-breathing birds and mammals. However, the degree of amplification in this food chain is much greater than the terrestrial food chain. Specifically, in the marine food web, non-metabolizing chemicals with a $K_{OW} \geq 10^5$ and $K_{OA} \geq 10^6$ can attain concentrations in top predators (polar bear) up to 10,000 times higher than in primary producers. Less hydrophobic chemicals with $K_{OW} < 10^5$ and $K_{OA} \geq 10^6$ can also biomagnify with concentrations in polar bears exceeding those in primary producers up to 3,000 fold. Chemicals with $K_{OW} < 10^2$ do not magnify in this food web regardless of their high K_{OA} as the animals can eliminate these compounds efficiently through urinary excretion.

In summary, modeling studies of the east Hudson Bay marine food web provide further insight into the bioaccumulation behaviour of POPs in arctic marine ecosystems. The model demonstrates that less hydrophobic POPs such as HCHs, TeCBz and endosulfans, which have a low log $K_{OW} < 5$ but a high log $K_{OA} \geq 6$ and do not biomagnify in aquatic organisms and food chains, can substantially biomagnify in air-breathing animals. These low K_{OW} – high K_{OA} chemicals are susceptible to biomagnification in air-breathing animals, including humans, because of their slow rate of respiratory elimination. It is important to note that many chemicals can undergo environmental degradation processes and metabolic transformation, which can reduce or eliminate the anticipated biomagnification potential. For example, a recent study of PBDEs in the eastern Hudson Bay marine food web show these compounds exhibit a much lower degree of trophic magnification as compared to recalcitrant Cl_5–Cl_7 PCBs with comparable K_{OW}'s, indicating in vivo metabolism (Kelly et al. 2005). Forecasting the bioaccumulation of such readily metabolizable chemicals will require

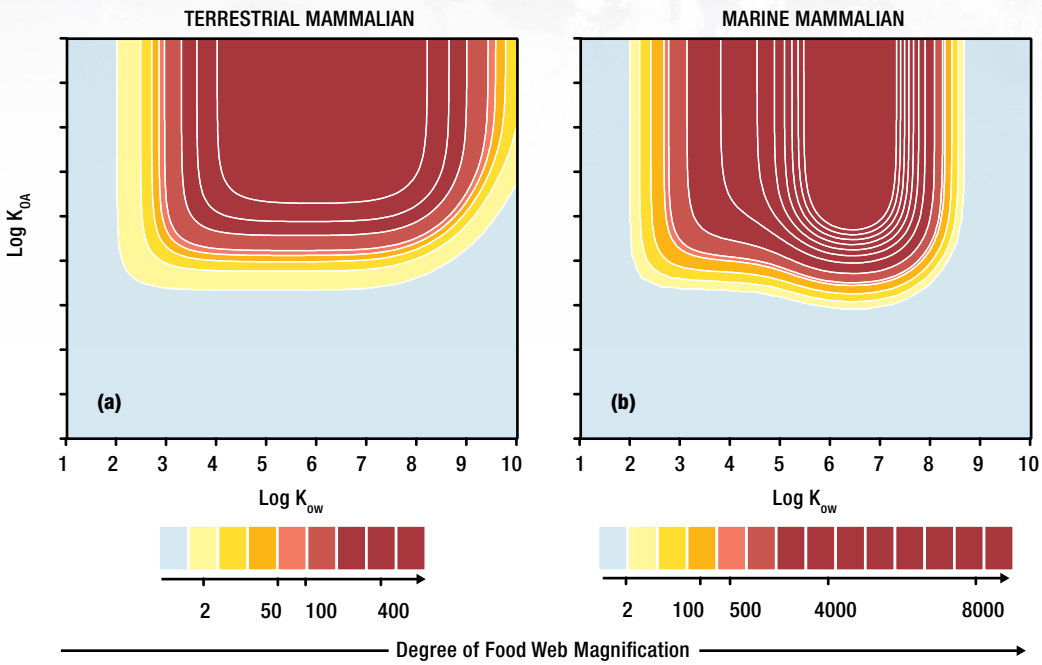

FIGURE 4.59

Results presented as contour plots represent the combined magnification of the chemical concentrations (ng•g^{-1} lipid equivalent) in the top predator over the concentrations at the base of the food web (e.g., primary producers at TL = 1 to polar bear at TL = 5.4). A matrix table was generated using approximately 30,000 K_{OW}-K_{OA} combinations over a log K_{OW} range of 1-10 and a log K_{OA} range of 3-12.

knowledge of the chemical's half-life ($t_{1/2}$) in environmental media, as well as species-specific metabolic transformation rate constants.

4.1.6.6. Summary of marine food web studies and modelling

- Food web studies on PFASs and brominated flame retardants in the arctic marine environment over the past 7 years have helped to assess the extent of biomagnification of these new POPs.
- Measurements of Br_3–Br_7 PBDE congeners (e.g., BDE-28, -66, -99, -100, -118, -153 and -154, -183) revealed negligible biomagnification of these brominated compounds relative to known biomagnifying compounds such as PCB-153. Two MeO-PBDEs, 6-MeO-BDE-47 and 2′-MeO-BDE-68, exhibited trophic magnification with TMFs equal to 2.3 and 2.6 respectively, but most MeO-PBDEs had TMF values less than 1. However, measurements of PFAS demonstrated that PFOS and several PFCAs are highly persistent environmental contaminants and can biomagnify in arctic marine food webs.
- Food web modeling studies have been used to address and explain noted disparities in organic contaminant bioaccumulation in arctic marine and terrestrial systems. Building on observations from their previous studies (Kelly and Gobas 2001, Kelly and Gobas 2003), Kelly et al. (2007) analyzed empirical data and generated physiologically-based toxicokinetic (PBTK) modeling data for 3 distinct food web types from Northern Canada – aquatic/piscivorous, aquatic/marine mammalian and terrestrial/mammalian. The biomagnification of known, highly bioaccumulative compounds such as PCBs and DDTs were compared with the biomagnification of less lipophilic compounds such as HCHs and endosulfans across these three food web systems (Kelly et al. 2007).
- Generally, in aquatic, piscivorous food webs, organic compounds with low biotransformation rates biomagnify when $10^5 \leq K_{OW} \leq 10^8$. Outside of this range, compounds are not absorbed effectively ($> 10^8$) or they are eliminated easily at the gills. In mammalian food webs, compounds that had low biotransformation rates with intermediate to high hydrophobicity ($10^2 < K_{OW} < 10^8$) were shown to biomagnify if the K_{OA} was high enough ($\geq 10^6$) to limit respiratory elimination in air breathing organisms. Compounds with a $K_{OW} < 10^2$ were shown to be sufficiently eliminated via urinary excretion to limit any biomagnification effects regardless of a high K_{OA}.

4.2. Temporal Trends of POPs in Biota

Contributors: Birgit Braune, Marlene Evans, Perihan Kurt-Karakus, Robert Letcher, Melissa McKinney, Derek Muir, Gary Stern, Gregg Tomy

4.2.1. Introduction

Temporal trend studies are important as they can provide a first warning that potentially harmful compounds may be increasing in selected biota (indicator organisms) in the ecosystem. Results are used to assess the fate of contaminants in the environment. These studies can also indicate whether regulatory actions aimed at reducing inputs of harmful chemicals to the environment are proving successful, or whether environmental levels are approaching threshold values. One of the major data gaps identified in the first CACAR assessment was the lack of temporal trend data sets for POPs as, at that time, only a few time series for POPs in biota existed and in most cases, these included only data from a few years. One recommendation from that assessment was to continue monitoring biota in order to obtain longer time series. A major accomplishment of the NCP over the duration of CACAR II was the generation of a set of time series measurements of greater statistical power. One of the conclusions of the CACAR II assessment was that the levels of some legacy POPs were decreasing in most arctic species included in temporal trend monitoring studies, but that the rates varied between locations and species. A recommendation from CACAR II was to continue trend monitoring of POPs in key indicator biota, so that at a minimum, the results of these arctic studies would be available for use in "effectiveness" evaluations of the UNEP Stockholm Convention and UNECE LRTAP POPs Protocol as well as for AMAP Assessment reports. Since CACAR II, databases for temporal trends studies in arctic species have become larger, with many data sets that span from the 1970s to 2011 for legacy POPs and from the 1980s to 2011 for PBDEs and PCDD/Fs. These temporal trend studies have addressed a major data gap identified for both the Canadian and circumpolar Arctic and have provided data sets for comparison to comprehensive long-term studies of contaminants from other regions such as the Great Lakes. Retrospective surveys of archived samples have also added to the temporal trend data sets for both legacy and new POPs.

Long contaminant monitoring time series show random inter-year variations which are not part of a trend (Bignert et al. 1993, Bignert et al. 1994, Bignert et al. 1998, Hebert and Weseloh 2003, Olsson 1995). The probability that a monitoring program will detect a temporal trend in concentrations, in spite of the inter-annual fluctuations or "noise" in the data, represents its statistical power. The probability or power of detecting changes in contaminant levels with time depends both on the pattern and magnitude of those changes (Nicholson and Fryer 1992). The implications of ignoring statistical power include collection of insufficient data to make reliable inferences about temporal trends and/or collection of extraneous data (Braune et al. 2003).

The following sections summarize the most recent temporal trend studies for legacy and new POPs. In most cases, time series results were available up to 2011. Trends (usually expressed as percent annual declines or increases) were analyzed using the statistical package PIA (Bignert 2007) or by simple linear regression of log (mean lipid adjusted concentrations) vs. time (years). All results were lipid adjusted prior to trend analysis (except for PFASs) but well known covariates or factors such as age, sex, or dietary shifts determined by stable nitrogen and carbon isotope ratios, were not included for this assessment. However, contributors have or will include these and other factors in more detailed interpretations of the results. Statistically significant declines or increases refer to probability at the $p \leq 0.05$ level.

4.2.2. Temporal trends in freshwater fish

4.2.2.1. Introduction

Fish accumulate contaminants as they pass water over their gills and from their diet. Unlike mammals, fish have limited capacity to degrade most POPs and excrete many of these chemicals very slowly. Fish are therefore good indicators of freshwater and marine food web contamination from POPs.

4.2.2.2. Sea-run char

4.2.2.2.1. Legacy POPs in sea-run char

The earliest measurements of persistent organic contaminants in sea-run char were made in 1987 including those at Cambridge Bay, Pond Inlet, the Rat River, and Pangnirtung Fjord (Muir et al. 1990). More recent sampling was conducted in the late 1990s in northern Quebec and Labrador (Muir et al. 2000a). Over the period from 2004–2009, long-term trend monitoring sites were established, with Cambridge Bay and Pond Inlet selected as the core long-term trend sites with some sampling continuing at Nain with a focus on mercury. Arctic char could not be reliably harvested in the western Arctic, possibly because of shifting migration patterns due to global warming.

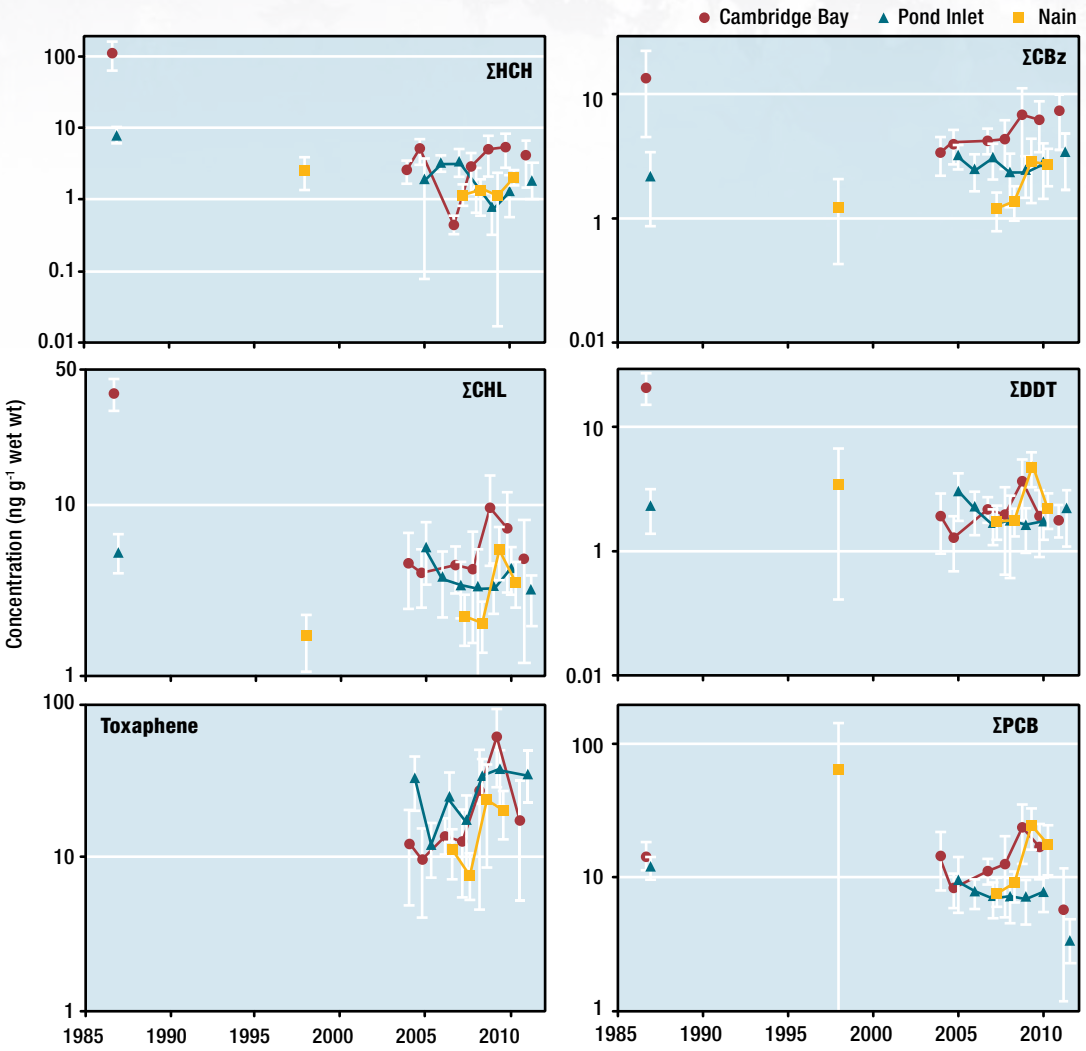

FIGURE 4.60

Mean (± standard deviation) concentrations (wet weight basis) of POPs in sea-run char sampled over the period 1987–2011 at Cambridge Bay, Nain, and Pond Inlet. Analyses are based on dorsal muscle.

Lipid content of sea-run char collected at Cambridge Bay, Nain, and Pond Inlet show no obvious trend pattern with some of the variations associated with the size of the fish caught in each year, e.g., successively larger fish were caught at Nain over the course of the study.

Trend analyses of POPs were conducted at two levels, i.e., a broad comparison of concentrations measured at the earliest date (1987 for Cambridge Bay and Pond Inlet, 1998 for Nain) against 2004–2011 concentrations, and then trends over the period 2004–2011. Considering the comparisons of the earliest measurement point to the 2004–2011 data sets, only HCH concentrations were substantially lower in the latter period than in 1987, the first year of the time series. ΣCHL, ΣCBz and ΣDDT concentrations also declined substantially at Cambridge Bay between these two time points while no decline is evident at Pond Inlet and Nain. Furthermore, ΣCHL, ΣCBz and ΣDDT concentrations were substantially higher at Cambridge Bay than Pond Inlet in 1987 (Figure 4.60).

Cambridge Bay is a former military radar (DEW-line) site and previous studies identified high and localized contamination of PCBs and other organochlorines in Cambridge Bay sediments, benthic invertebrates, and four-horn sculpins (Bright et al. 1995a, Bright et al. 1995b, Jensen et al. 1997) as a consequence of these installations. Thus, it is possible that the lower ΣCHL, ΣCBz, and ΣDDT concentrations measured over the

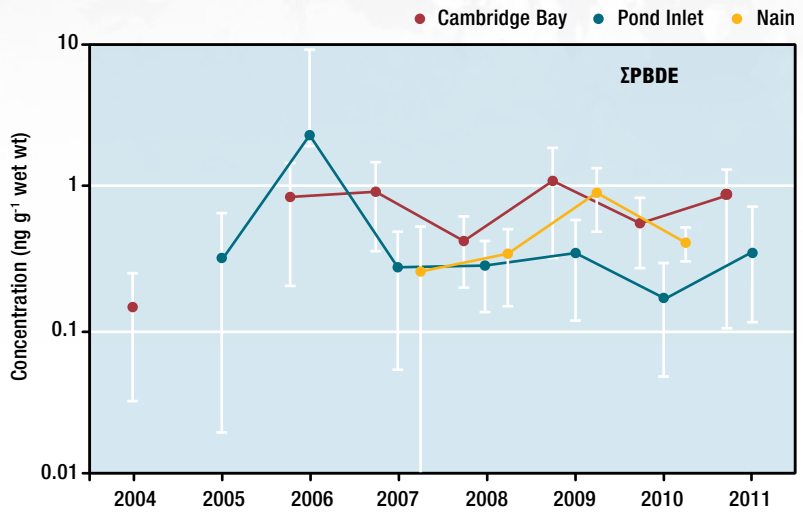

FIGURE 4.61

Concentrations (ng g^{-1} wet weight) of ΣPBDEs in muscle (+skin) of searun char from three communities in the Canadian arctic. Symbols represent average concentrations and vertical bars are standard deviations.

period from 2004–2011 are associated with a decline in localized concentrations. However, ΣPCB concentrations were not particularly high in Cambridge Bay sea-run char in 1987, which suggests that the localized contamination did not affect the more mobile char population. It is unclear why only ΣHCH, ΣCHL, ΣCBz, and ΣDDT concentrations would have been affected. For Nain, ΣCHL and ΣCBz concentrations tend to be higher over the period 2007–2011 than in 1998 whereas no trend is evident for ΣDDT. ΣPCB concentrations were relatively high at Nain in 1998, but have since declined.

Over the 2006–2011 period, there are suggestions of a trend of increasing toxaphene, ΣPCB and ΣCHL concentrations at Cambridge Bay and Nain where the highest concentrations were observed in 2009. The sea-run char data need to be analyzed more closely to assess whether or not these trends are statistically significant. However, they are not associated with major differences in fish size or lipid content.

4.2.2.2.2. New POPs in sea-run char

Average ΣPBDE concentrations in sea-run char increased between 2004–2005 and 2006–2007 at Cambridge Bay and Pond Inlet (Figure 4.61). Since 2007 concentrations have remained the same at these two locations and at Nain. Concentrations based on lipid weight also did not change over the period 2006–2007 and 2011. Temporal trends for other BFRs, PFASs and endosulfan are not yet available for sea-run char due to the limited number of sampling years.

4.2.2.3. Lake trout and burbot in Great Slave Lake

4.2.2.3.1. Legacy POPs in lake trout and burbot in Great Slave Lake

Trends of legacy POPs in burbot and lake trout from the West Basin and East Arm of Great Slave Lake are shown in Figures 4.62 and 4.63. Percent annual change in concentraions of POPs in burbot and lake trout are provided in Table 4.3.

Toxaphene is the major legacy POP in burbot and lake trout and has declined by approximately 8-fold in burbot liver from the East Arm and approximately 4-fold in those sampled from the West Basin over the period 2001 to 2011. Toxaphene has declined about 3-fold in lake trout from the East Arm and West Basin over the period from 1993 to 2011 (Figure 4.62). The decline of toxaphene concentrations from 1993 to 2000 was interrupted in both species in the East Arm, with higher concentrations in 2001. The reason for this anomaly, which was not observed in the West Basin fish, is not known. The percent annual change of toxaphene in burbot and lake trout in the West Basin were very similar (-13% per year and -14% per year, respectively; Table 4.3).

ΣHCH showed a pronounced declining trend in both burbot and lake trout although as with toxaphene, the trend is interrupted in the period 2001–2004 with higher concentrations particularly in the East Arm fish (Figure 4.62 and 4.63). The greatest rate of decline was observed for α-HCH, which is the predominant isomer detected in both species, followed by γ-HCH.

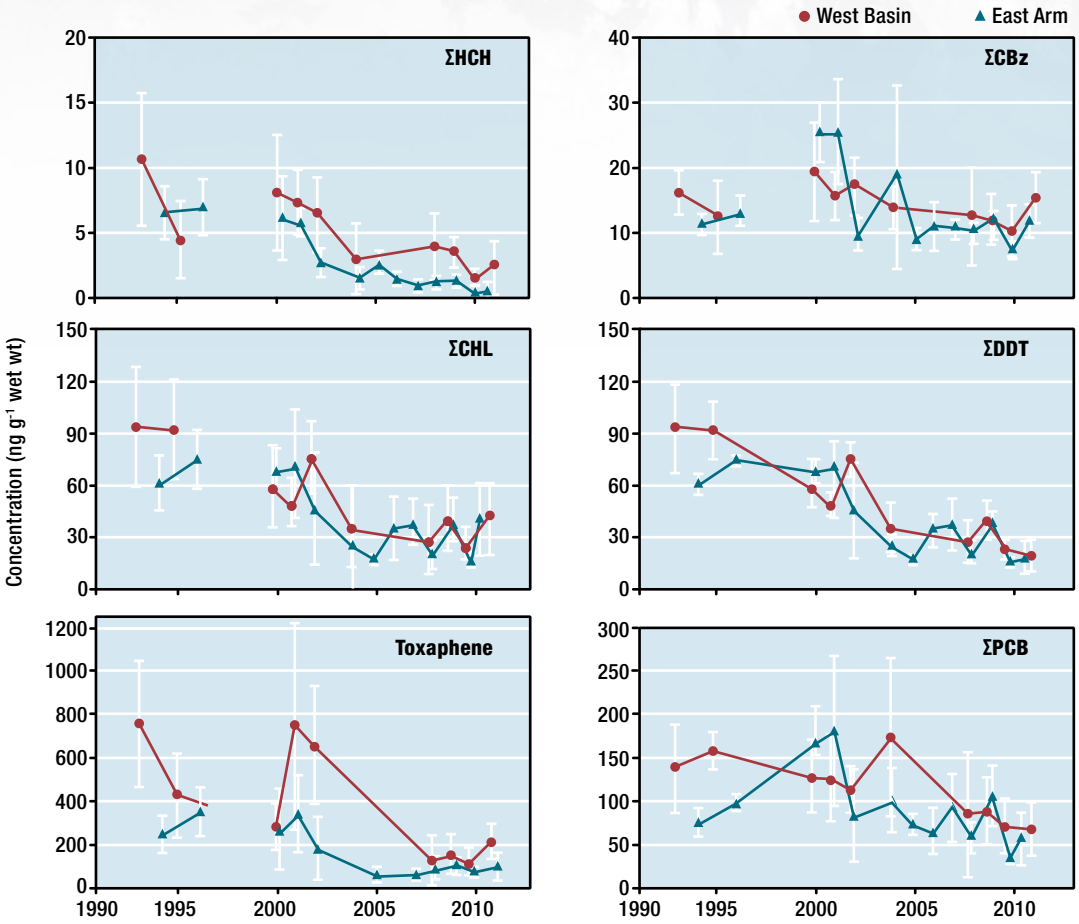

FIGURE 4.62

Trends of ΣHCHs, ΣCBz, ΣCHL, ΣDDT, toxaphene and ΣPCBs in burbot liver collected from the West Basin (Fort Resolution) and East Arm (Lutsel K'e) of Great Slave Lake. Data are presented as the arithmetic mean (± one standard deviation) concentrations (ng g^{-1} ww).

The ΣDDT also showed a significant decrease in burbot samples in both the East Arm and West Basin (Figure 4.62) (-7.2% to -6.8%) and in lake trout (-6.0% to -8.3%) (Table 4.3; Figure 4.63). Lake trout in the West Basin showed a steep decline in *p,p'*-DDT and a somewhat less steep decline in *p,p'*-DDE; thus *p,p'*-DDE has become the predominant DDT degradation product in more recent years. Overall, concentrations of DDT related compounds tend to be higher in the East Arm than in the West Basin.

This may be associated in part with the lower productivity of East Arm waters which results in greater uptake of more persistent organochlorines than in more productive waters where such compounds may become bound to particulates (Houde et al. 2008). The declines are not related to percent lipid or to diet as indicated by carbon or nitrogen stable isotope ratios; all these parameters remained relatively stable over the sampling period (Evans and Muir 2009).

ΣCHL concentrations also declined in burbot (Figure 4.62) at -5.5% per year and -7.8% per year in the East Arm and West Basin, respectively (Table 4.3). In the East Arm, the decline of ΣCHL in burbot liver is greater (2–3-fold) than in lake trout (Figure 4.62; Table 4.3). ΣCBz (mainly HCB and pentachlorobenzene) showed no significant decline in either burbot liver or lake trout muscle over the 17 years. ΣCBz actually increased in the period 2001–2004 relative to other years.

In contrast to most other POPs, ΣPCBs in lake trout showed no statistically significant trend. As noted for toxaphene, ΣCHL, and ΣCBz, the mean ΣPCB concentrations were higher in lake trout in the period 2003–2005 and variability among fish was higher than in the 1990s. The increased concentrations were mainly associated with penta and hexa PCBs, which also are the predominant congeners in lake trout muscle (Figure 4.64).

TABLE 4.3. Percent annual decline or increase per year[1] for legacy POPs in burbot from Fort Good Hope, lake trout and burbot from Great Slave Lake (GSL), lake trout from Lake Laberge and Kusawa Lake, and arctic char from Amituk, Char, Hazen and Resolute lakes.

Species	Location	Years	ΣCBz	ΣHCH	ΣCHL	ΣDDT	ΣPCB	Toxaphene
Lake trout	GSL-West Basin	12	2.0 ns	-15 (8.0–22)	-5.8 (1.0–11)	-8.3 (1.0–16)	-3.9 ns	-14 (4.8–23)
Lake trout	GSL-East Arm	13	0.9 ns	-10 (2.3–18)	-0.6 ns	-6.0 (1.5–13)	-0.1 ns	-9.0 ns
Lake trout	Laberge	13	-7.1 (0.7–14)	-17 (8.8–25)	-12 (5.2–19)	-3.7 ns	-7.5 (0.9–14)	-9.6 (3.7–16)
Lake trout	Kusawa	13	-4.5 ns	-14 (1.0–27)	-13 (5.6–20)	-23 (12–34)	-14 (1.3–26)	-8.5 (1.3–16)
Burbot	GSL-East Arm	10	-0.8 ns	-6.2 (1.9–11)	-5.5 (1.6–9.5)	-7.2 (3.1–11)	-3.6 (0.9–6.3)	-9.4 (2.4–17)
Burbot	GSL-West Basin	13	-4.4 ns	-17.5 (13–22)	-7.8 (2.1–14)	-6.8 (1.7–12)	-5.3 (0.7–9.9)	-13 (5.7–20)
Burbot	Fort Good Hope	15	-6.0 (3.3–8.6)	-11.8 (8.9–15)	-1.2 ns	2.4 ns	-0.5 ns	-6.0 (0.3–12)
Arctic char	Amituk	11	-6.7 ns	-17 (11–22)	-7.6 (3.6–12)	-7.8 (5.2–7.8)	-7.6 (3.2–12)	-9.5 (4.0–15)
Arctic char	Char	11	-3.9 ns	-20 (12–28)	-10.3 (0.7–20)	-11 (6.4–15)	-9.0 (4.9–13)	-6.5 (7.6–14)
Arctic char	Hazen	10	-3.2 ns	-9.7 (7.7–12)	-6.7 (3.2–10)	-12.3 (8.7–16)	-6.4 (3.3–9.4)	-7.6 (0.8–14)
Arctic char	Resolute	13	1.6 ns	-7.9 (4.8–11)	-1.7 ns	-2.7 ns	-3.5 ns	13 (1.8–25)

[1] Percent annual change per year estimated from the half-lives ($t_{1/2}$) that are estimated from log mean concentration ww vs. time (year) using the equation: LN(2)*100/$t_{1/2}$). 95% confidence intervals are in parentheses.
[2] NS = Confidence intervals are not given where there is no statistically significant change in mean concentrations over time for log mean concentration vs. time ($p > 0.05$).

In contrast, ΣPCB concentrations in burbot liver show a more pronounced decline with statistically significant trends (-3.6% per year in the East Arm and -5.3% per year in the West Basin). The reasons for these differing responses for the two species is under investigation but may support the general observation that burbot show more rapid responses to environmental change (e.g., declining inputs of POPs) than lake trout.

4.2.2.3.2. New POPs in Great Slave Lake lake trout and burbot

Concentrations of ΣPBDEs in lake trout and burbot liver in Great Slave Lake have been measured over the periods 2004–2011 and 2006–2011, respectively. PBDEs increased significantly (14% per year) in West Basin lake trout over the period 2004–2009 but did not change significantly in burbot or in East Arm lake trout (Figure 4.65; Table 4.3). Over the period, 2006–2011, HBCDD has been detected in lake trout and in burbot liver, beginning in 2007. Maximum HBCDD concentrations were observed in lake trout in the West Basin in 2011 and in 2010 in the East Basin. West Basin burbot showed an early maxima for HBCDD (2008) and no significant change in concentration over the period 2008–2011 (Figure 4.65).

Concentrations of PFOS and ΣPFCAs in lake trout muscle have declined 20% and 21% per year, respectively, from maxima in 2001 in the East Arm of Great Slave Lake (Figure 4.66).

Although data are more limited for the West Basin, both groups of PFASs have also declined over the period 2004 to 2009 (Table 4.4). Insufficient data were available for samples of burbot liver to assess any trends.

Endosulfan concentrations (sum of α-endosulfan, β-endosulfan and endosulfan sulfate) increased in lake trout to maxima in 2009 in the West Basin and in 2010 in the East Arm (Figure 4.67). In burbot liver, maximum concentrations of endosulfan were found in samples from 2008 and 2009 (Figure 4.67).

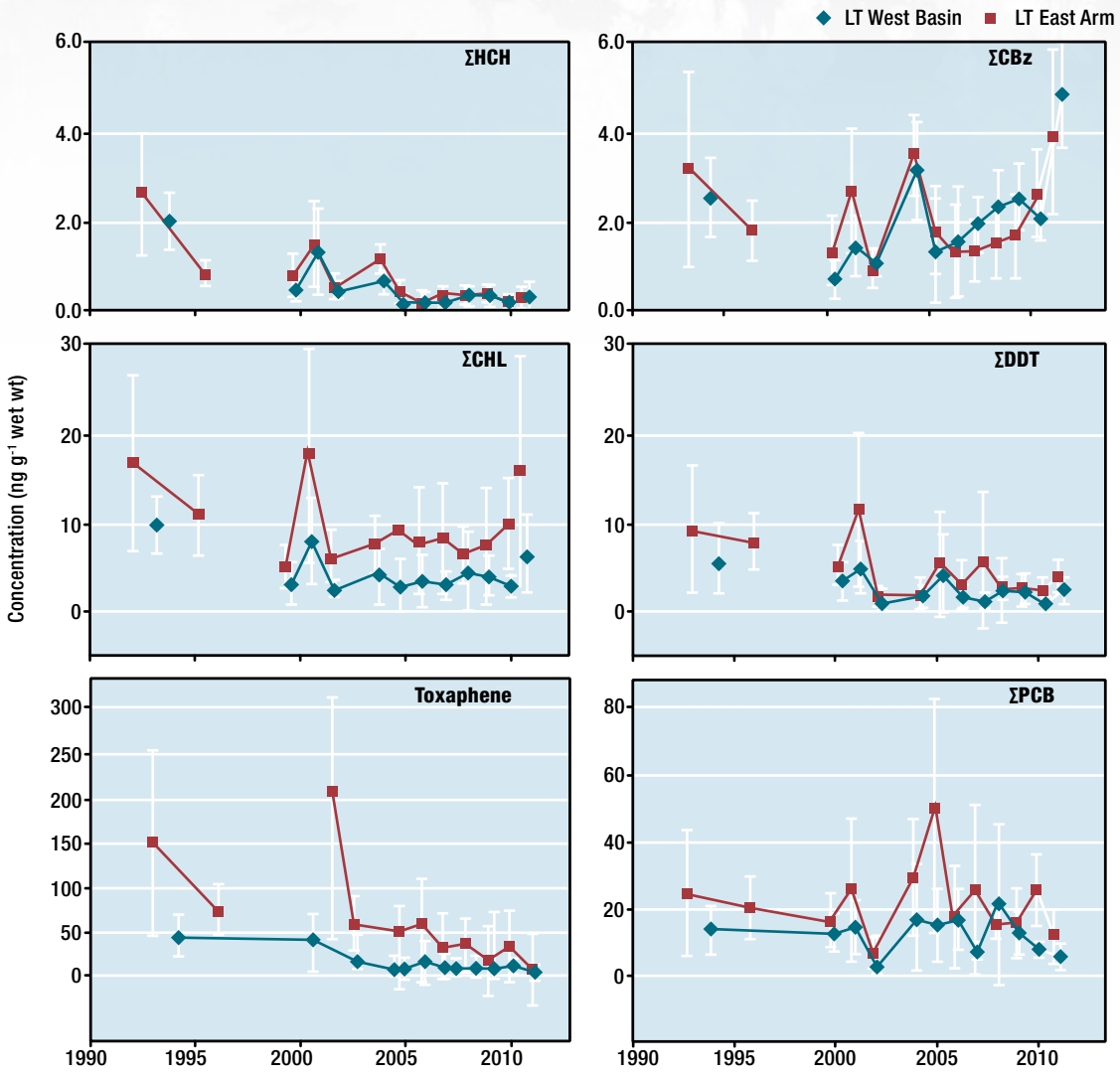

FIGURE 4.63

Trends of ΣHCHs, ΣCBz, ΣCHL, ΣDDT, toxaphene and ΣPCBs in lake trout (fillet) collected from the West Basin (Hay River) and East Arm (Lutsel K'e) of Great Slave Lake.

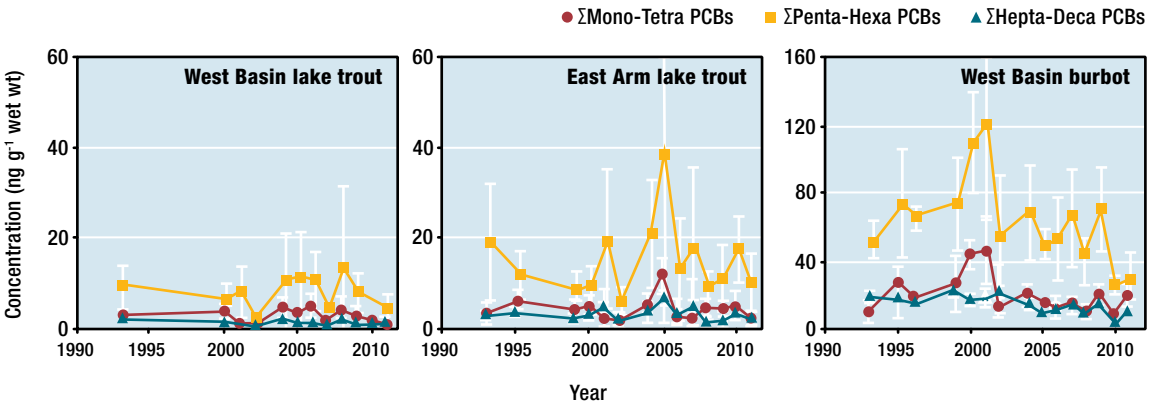

FIGURE 4.64

Time trends of PCB homologs (ng g^{-1} ww ± standard error) in Great Slave Lake lake trout muscle collected from the West Basin (Hay River) and the East Arm (Lutsel K'e), burbot (liver) collected from Fort Resolution. Data are presented as the individual arithmetic means.

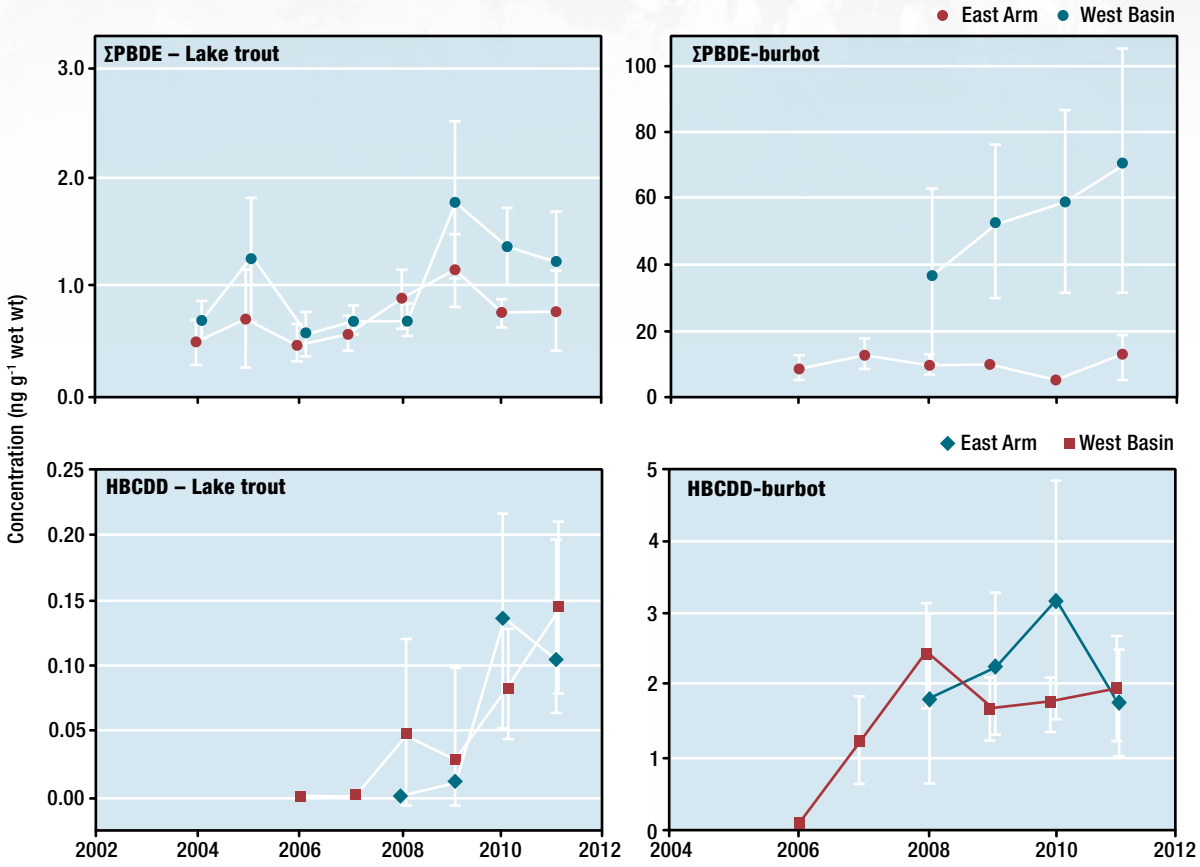

FIGURE 4.65

Trends of ΣPBDEs and HBCDD in lake trout and burbot from the East Arm and West Basin of Great Slave Lake. Symbols represent arithmetic mean concentrations and vertical bars are standard deviations.

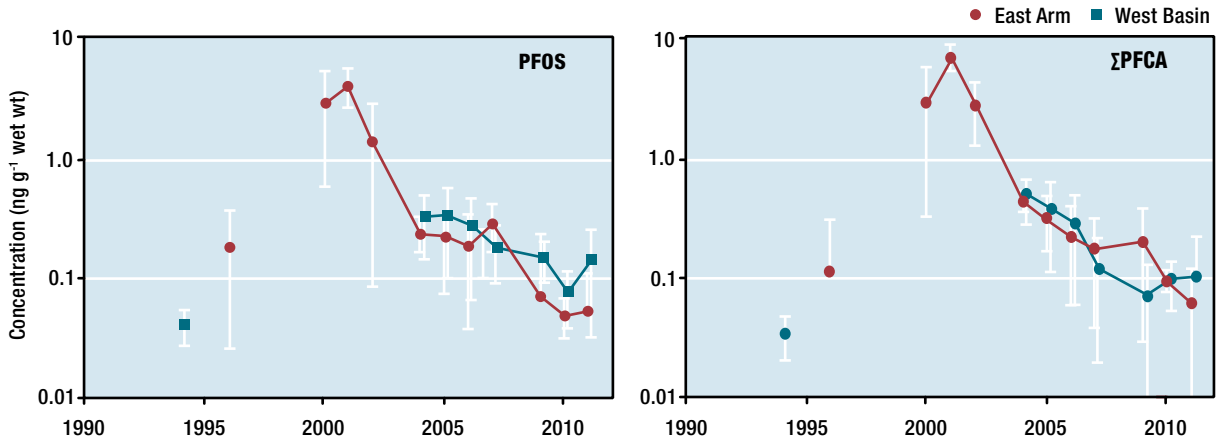

FIGURE 4.66

Trends of PFOS and ΣPFCAs in lake trout from the East Arm and West Basin of Great Slave Lake. Symbols represent arithmetic mean concentrations and vertical bars are standard deviations.

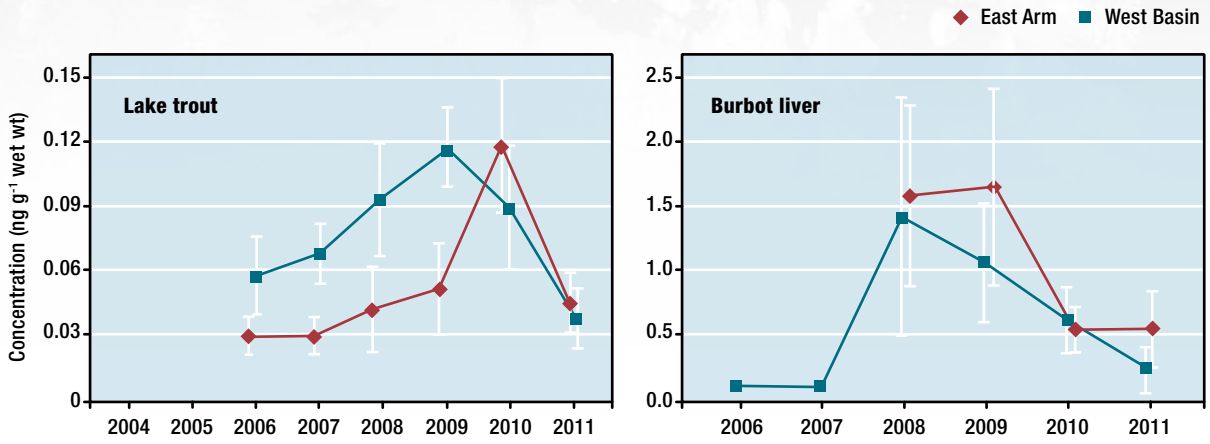

FIGURE 4.67

Trends of total endosulfan in lake trout and burbot liver from the East Arm and West Basin of Great Slave Lake. Symbols represent arithmetic mean concentrations and vertical bars are standard deviations.

TABLE 4.4. Approximate percent annual increase or decline from the maximum for PBDEs and PFASs in burbot liver from Fort Good Hope (FGH) and in muscle of lake trout from Great Slave Lake (GSL), Lake Laberge and Kusawa Lake and arctic char from Amituk, Char, Resolute and Hazen lakes.

Location	Species	PBDEs		PFOS		PFCAs	
		Period	% dec or inc /y[1]	Period	% dec or inc /y	Period	% dec or inc /y
FGH	Burbot	2006–2011	-5.0 ns	2003–2011	-20 (0.5–39)	2003–2011	-19 ns
		1988–2006	+12 (5.8–18)	–	–	–	–
GSL-East Arm	Burbot	2008–2010	+24 ns	–	ND[3]	ND[3]	
GSL-West Basin	Burbot	2007–2011	-6.5 ns	–	ND[3]	ND[3]	
GSL-East Arm	Lake trout	2004–2009	+8.5 ns	2001–2010	-53 (33–73)	2001–2010	-39 (21–58)
GSL-West Basin	Lake trout	2004–2009	14 (-0.3–29)	2005–2010	-20 (13–28)	2004–2010	-42 (32–51)
Kusawa	Lake trout	1999–2007	+5.7	2007–2011	-26 ns	2007–2011	+25 ns
		2007–2011	-100 (19–180)	–	–	–	–
Laberge	Lake trout	2000–2011	-18 (2.4–32)	2007–2011	-1.4 ns	2007–2011	+3.0 ns
Amituk	Arctic char	2003–2011	-17 ns	2007–2009	-9.3 ns	2007–2009	+40 ns
Char	Arctic char	1993–2008	+4.2 (0.3–8.0)	1993–2010	-1.6 ns	1993–2010	-2.1 ns
Hazen	Arctic char	2001–2008	+66 (32–99)	2003–2010	-6.5 ns	2003–2010	-10 ns
		2008–2011	-23 ns	–	–	–	–
Resolute	Arctic char	1997–2005	+21 (8.6–33)	–	ND[4]	–	ND
	Arctic char	2005–2011	-8.7 ns	–	–	–	–

[1] Percent annual change per year estimated from the half-lives ($t_{1/2}$) that are estimated from log mean concentration ww vs. time (year) using the equation: LN(2)*100/$t_{1/2}$). 95% confidence intervals in parentheses.

[2] ns = Non-significant log linear trend. Confidence intervals are not given where there is no statistically significant change in mean concentrations over time for log mean concentration vs. time ($p > 0.05$).

[3] ND = Trends for burbot not determined due to insufficient data.

[4] ND = Trends for PFCAs and PFOS in Resolute Lake not determined due to local source contamination.

4.2.2.4. Mackenzie River burbot at Fort Good Hope

4.2.2.4.1. Legacy POPs in burbot at Fort Good Hope

Burbot have been collected annually from the Rampart Rapids on the Mackenzie River at Fort Good Hope (NT) for the period 1999–2012. Additional archived collections from the 1980s and 1990s are available partly as a result of previous studies (Lockhart et al. 1987, Muir and Lockhart 1994b). Time trends of legacy POPs in burbot liver are presented in Figure 4.68 and additional details are provided in Annex Table A4-2. ΣCBz and ΣHCH show overall consistent declining concentrations (6% per year and 12% per year, respectively) (Table 4.3) with half-lives of approximately 11 y and 5.7 y, respectively. Significant declines also occured for both α-HCH and γ-HCH (10- and 4-fold, respectively) over this 19 year time period, while β-HCH concentrations were below the detection limit in most samples (Stern et al. 2012a).

ΣPCBs, ΣDDT, ΣCHL and toxaphene increased significantly from 2001 until about 2009 (Figure 4.68). Variation in concentrations among burbot collected in the same year was greater over this period than for the more limited number of sampling points in the 1980s and 1990s. The increase in ΣDDT was driven primarily by *p,p'*-DDE, which also implies old or recycled DDT rather than new sources.

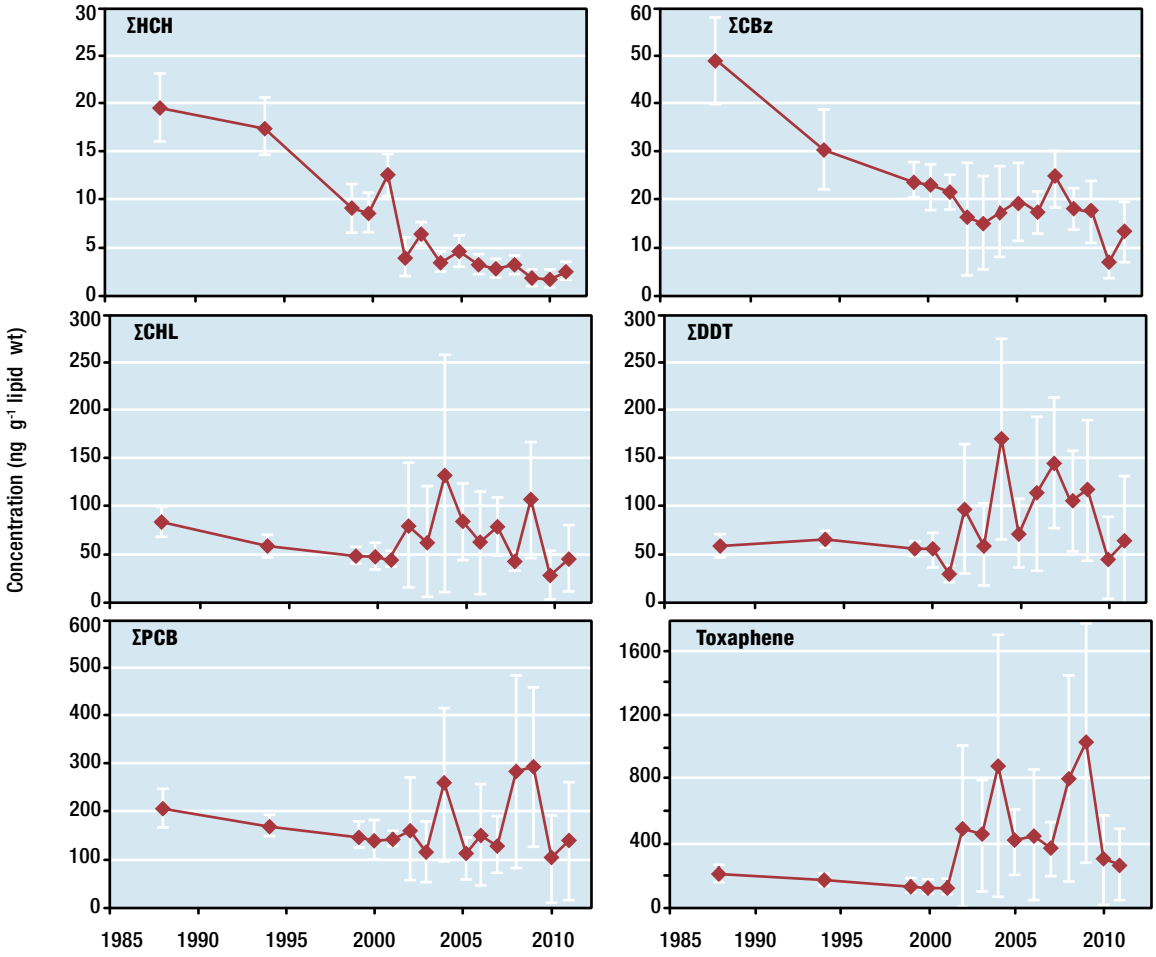

FIGURE 4.68

Trends of ΣHCHs, ΣCBz, ΣCHL, ΣDDT, toxaphene and ΣPCBs in burbot liver collected at Fort Good Hope. Concentrations are arithmetic means (ng g^{-1} lw ± standard deviation). Further details are provided in Annex Table A4-2.

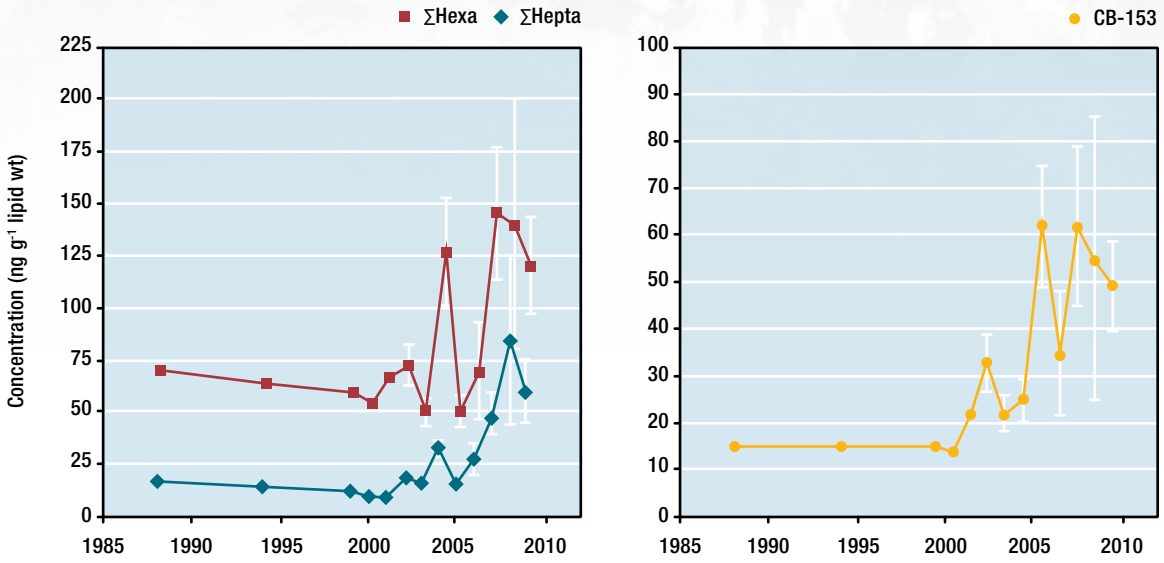

FIGURE 4.69

Mean (± standard error) PCB concentrations in Mackenzie River Burbot. (A) Sum of hexa and hepta PCB congeners, (B) CB-153. Only liver samples with lipid > 10% included. Results to 2009 do not reflect the decline in ΣPCBs in 2010 and 2011 (Figure 4.68).

As was postulated for the increasing levels of total mercury in the same fish (Carrie et al. 2009), the increasing PCB and DDT levels have been attributed to increasing algal primary productivity brought about by climate change in the nearby Hare Indian Lake which makes these POPs more bioavailable to fish and other wildlife (Carrie et al. 2009) (see Chapter 3, section 3.3.1.4). Hexa- and hepta-PCBs were the predominant homolog groups in burbot liver and CB-153 was the most prominent PCB congener (Figure 4.69). PCB congener profiles observed in the burbot resemble those expected for an environmentally recycled source of PCB and not a recent technical mixture. These results are consistent with the fact that there are no known local sources of PCB or DDT that could contribute to the burbot's increasing loads.

The increasing trends of the hexa- and hepta-PCBs as well as *p,p'*-DDE, ΣDDT, ΣCHL and toxaphene in burbot liver were followed by a leveling off or a decline from 2009 to 2011 (Figure 4.68). This is difficult to reconcile with the climate change hypothesis and other possible explanations must be considered such as shifts in the burbot food webs and feeding areas which could also be induced by climate warming.

4.2.2.4.2. New POPs in Mackenzie River burbot

Liver samples from burbot collected near the community of Fort Good Hope (Rampart Rapids) in winter (December–January) between 1988 and 2011 were analyzed for new organohalogen compounds including PBDEs (Stern et al. 2010a). Average ΣPBDE concentrations increased significantly (3.4% per year) from 1988 to 2010 reaching a maximum in 2006 (Table 4.4; Figure 4.70). However, the trend from 1999 to 2011 was not significant. Major PBDE congener levels are currently still close to an order of magnitude less than those of PCBs. The proportion of BDE-47, the major congener in the "penta" BDE commercial product (see Chapter 2, section 2.2.3.1), declined from 39%–57% of ΣPBDE in the period 1988–2000 to 30–36% in the 2009–2010 samples. More highly brominated congeners BDE-99 and BDE-100 increased in proportion (44–53% in 2009–2010). No other BFRs have been reported in the Mackenzie River burbot.

PFASs have been analyzed in the burbot liver samples from Fort Good Hope including archived samples from 1986. PFOS concentrations were very similar in the 1986, 1999 and 2003 samples (approximately 10 ng g^{-1} ww) while samples from 2006–2010 had significantly lower average levels (Figure 4.70). Both PFOS and ΣPFCAs appear to have reached a maximum in 2003 and have declined consistently since then with a half-life of approximately 2.5 y (20% per year).

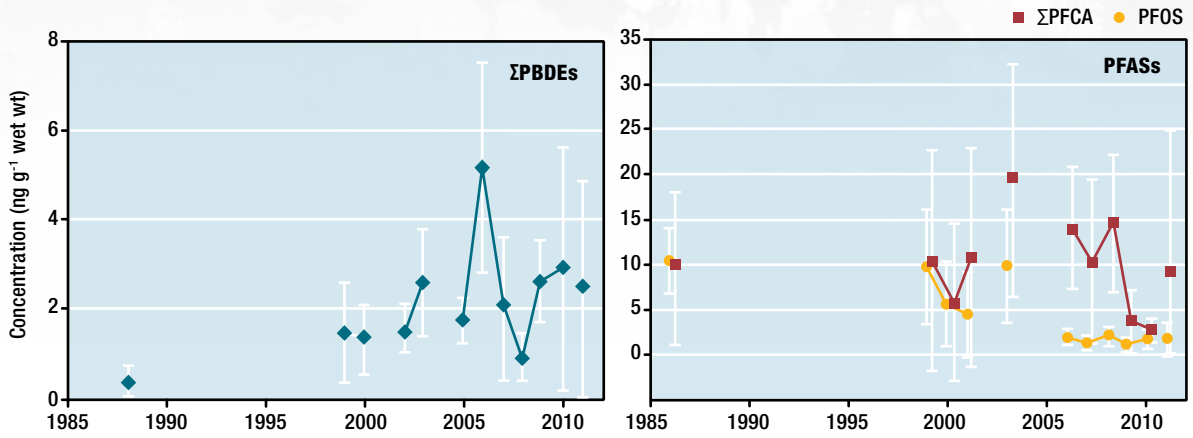

FIGURE 4.70

Time trends of PBDEs and PFASs (PFOS and ΣPFCAs – PFOA, PFNA, PFDA, PFUnA) in burbot liver from Fort Good Hope. Symbols represent arithmetic mean concentrations and vertical bars are 95% confidence limits.

4.2.2.5. Lake trout in Yukon Lakes

4.2.2.5.1. Legacy POPs in Yukon lakes

Concentrations of most legacy POPs declined in lake trout from Lake Laberge, Kusawa Lake and Quiet Lake (Yukon) on the basis of data obtained over a span of 18 years (1992–2010) (Ryan et al. 2005; 2013; Stern et al. 2012a). With annual data available to 2011 for Lake Laberge and Kusawa Lake, these trends can be examined in more detail.

Significant declines over the period 1993 to 2011 were found for ΣHCH, ΣCHL, ΣDDT, ΣPCB, and toxaphene in lake trout from both Lake Laberge and Kusawa Lake. ΣCBz declined in Lake Laberge and not in Kusawa Lake (Figure 4.71; Table 4.3). The percent annual declines of ΣHCH were nearly identical in both lakes (-17% and -14% per year, respectively) and similar to the declining trends in lake trout and burbot in Great Slave Lake (West Basin). ΣDDT declined in Lake Laberge until about 2005 and more recent results show a levelling off; no levelling off of ΣDDT was apparent in Kusawa Lake. For the period 1993–2005, ΣDDT declined rapidly with a half-life of 5.5 y (95% confidence limits 3.9-9.5) in Lake Laberge lake trout. Similarly, the declining trends of all the other 5 groups of POPs in Lake Laberge were more rapid in the 1995–2005 period than for the entire 18-year period (Figure 4.71) due to elevated concentrations in the early 1990s. This was less evident in Kusawa Lake where concentrations were not as high in the 1990s.

No further trends were calculated for OC concentrations for burbot liver in Kusawa Lake or Lake Laberge, beyond those reported in Ryan et al. (2005) because analysis of samples stopped in 2003. For the period 1992 to 2003, there was no evidence of a decline in toxaphene concentrations of the Kusawa Lake burbot, yet a 58% decrease was observed in Lake Laberge samples reflecting high concentrations in the early 1990s. Decreases in ΣHCH and toxaphene in burbot were evident for Lake Laberge fish and for ΣCHL for Kusawa Lake samples.

Ryan et al. (2013) examined the temporal trends of the 6 major groups of POPs (Figure 4.71) in lake trout from Lake Laberge in more detail by considering lipid content and growth rates of the fish, and food web structure. They found that the food web structure had not changed from 1993 (studied by Kidd et al. 1997) to 2001, while OC concentrations in fish declined had significantly declined over this period. Increased growth rates of lake trout and declining lipid content in lake trout and forage fishes may also have contributed to the declining trends of POPs in lake trout.

4.2.2.5.2. New POPs in lake trout in lakes Laberge and Kusawa

PBDEs have also been measured in archived lake trout muscle samples from Lakes Laberge and Kusawa collected in the 1990–early 2000s period as well as in more recent samples. Maximum ΣPBDEs were found in 2000 in Lake Laberge and in 2007 in Kusawa Lake (Figure 4.72). ΣPBDEs declined at a rate of 5.7% per year in Lake Laberge but showed no significant decline in Kusawa Lake (Table 4.4). No other BFRs have been reported in the lake trout of Lake Laberge or Kusawa Lake.

Maximum concentrations of PFOS and ΣPFCAs (sum of PFNA, PFDA, PFUnA) were found in samples of lake trout from Lake Laberge and Kusawa Lake collected in 2007. Due to significant year-to-year variation, no significant trends in PFOS or ΣPFCAs were observed for the period 2007 to 2011 (Table 4.4, Figure 4.72).

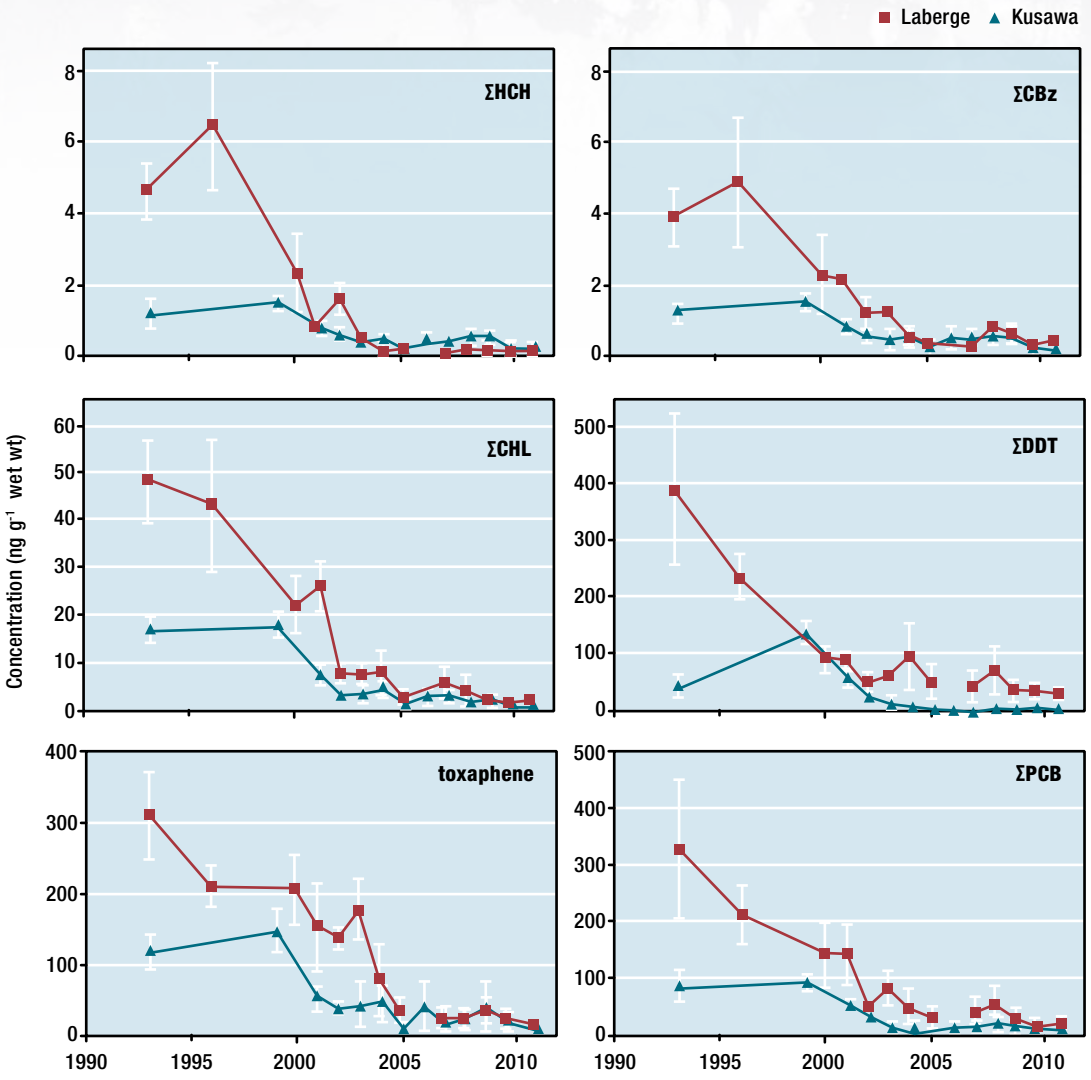

FIGURE 4.71

Trends of ΣHCHs, ΣCBz, ΣCHL, ΣDDT, toxaphene and ΣPCBs in lake trout muscle collected from Lake Laberge and Kusawa Lake. Symbols represent arithmetic mean concentrations (ng g^{-1} ww ± standard deviation). Further details are provided in Annex Table A4-2.

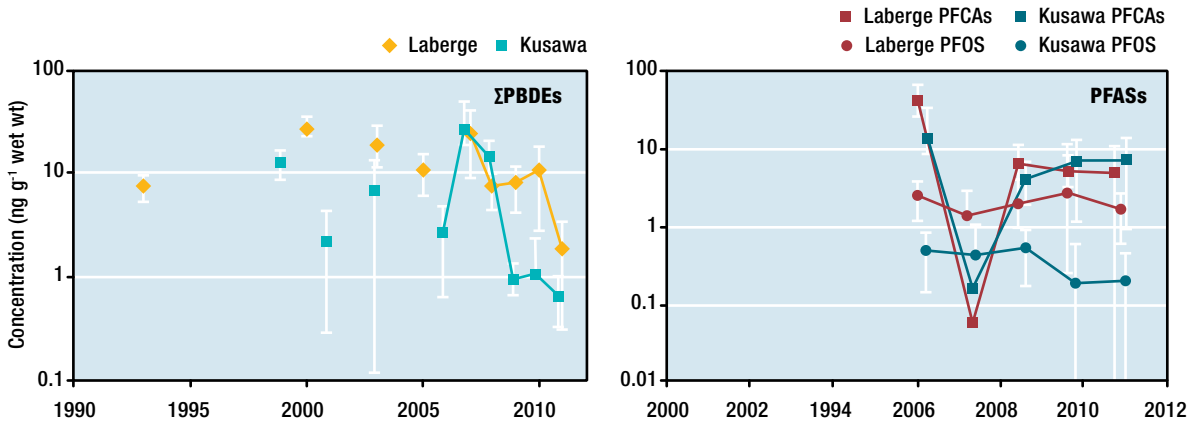

FIGURE 4.72

Trends of ΣPBDEs, PFOS and ΣPFCAs in lake trout from Lake Laberge and Kusawa Lake in the Yukon. Symbols represent arithmetic mean concentrations and vertical bars are 95% confidence limits.

4.2.2.6. Landlocked arctic char in high arctic lakes

4.2.2.6.1. Legacy POPs in landlocked arctic char in high arctic lakes

Time trend data for POPs in landlocked arctic char are available for lakes Amituk, Char, Hazen and Resolute to 2011 with sampling ranging from 10 to 14 years over a period of up to 22 years (Table 4.3; Figure 4.73). Landlocked arctic char collections have been successfully carried out annually in Resolute Lake since 1997 (Köck et al. 2004, Muir et al. 2005) and less frequently in Char, Amituk, and Hazen lakes due to low numbers (Char Lake) or difficult access (Amituk and Hazen Lakes) (see section 4.1.2.1.3).

ΣHCHs declined significantly in all four lakes with percent annual change ranging from -7.9% to -20% per year (Table 4.3). The slowest declines among the six POPs were for ΣCBz, which showed no significant trend due to a leveling off or small increase in concentrations for the period 2009–2011 (Figure 4.73). ΣCHL, ΣDDT, and ΣPCBs declined significantly in Char, Amituk and Hazen lakes but not in Resolute Lake. This may reflect continued minor sources to Resolute Lake (see section 4.1.2.1.3.2). Toxaphene showed increasing concentrations in Resolute Lake over the period 2003–2010 and also showed an upward trend in the other 3 lakes, particularly in Amituk Lake, over the period 2005–2010. This unique trend for toxaphene is not seen in lake trout for the same period although toxaphene levels did increase in Fort Good Hope burbot from 2001–2009 (Figure 4.62).

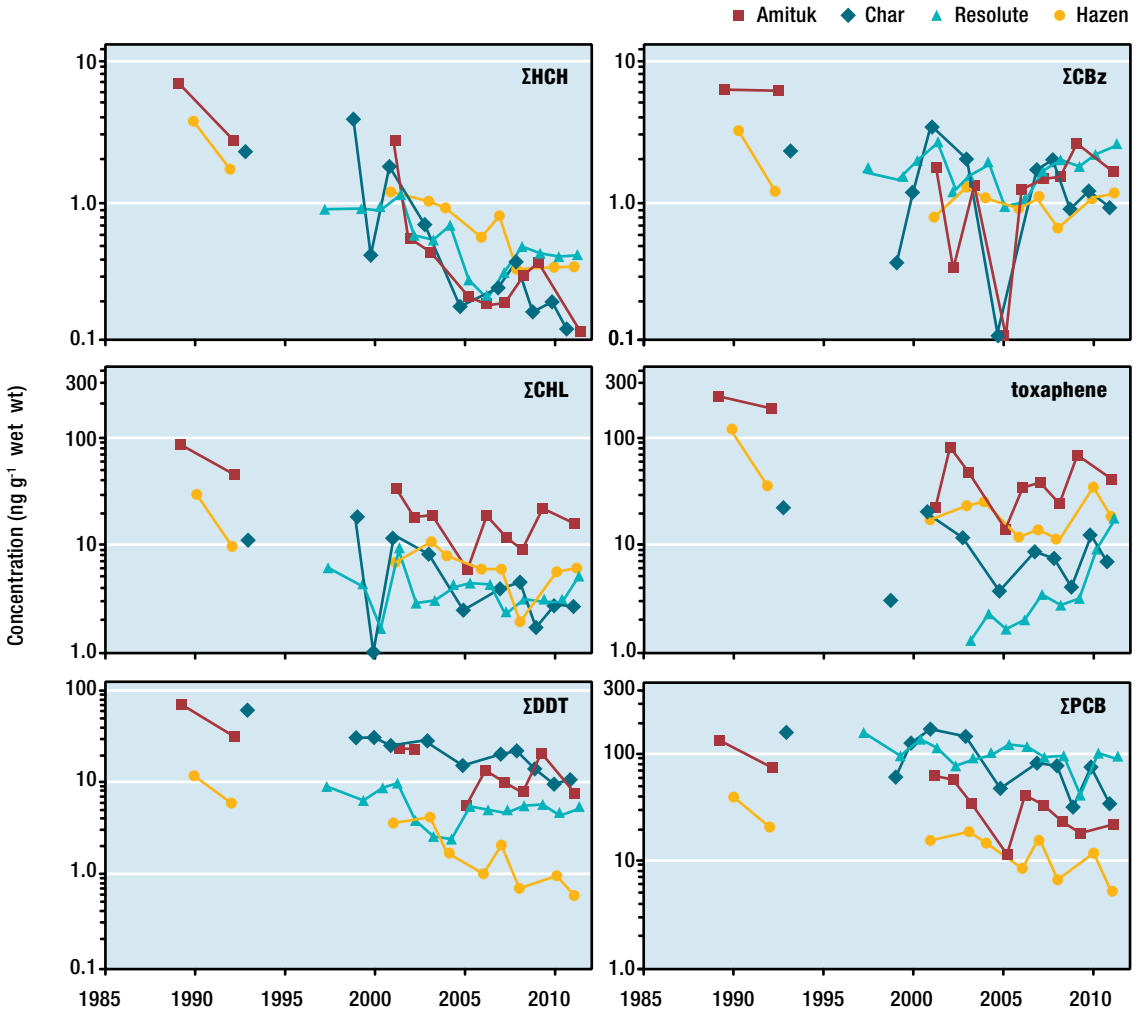

FIGURE 4.73

Trends of ΣHCHs, ΣCBz, ΣCHL, toxaphene, ΣDDT, and ΣPCBs in landlocked char muscle collected from four high arctic lakes. Symbols represent arithmetic mean concentrations (ng g^{-1} wet weight). Error bars are omitted for clarity.

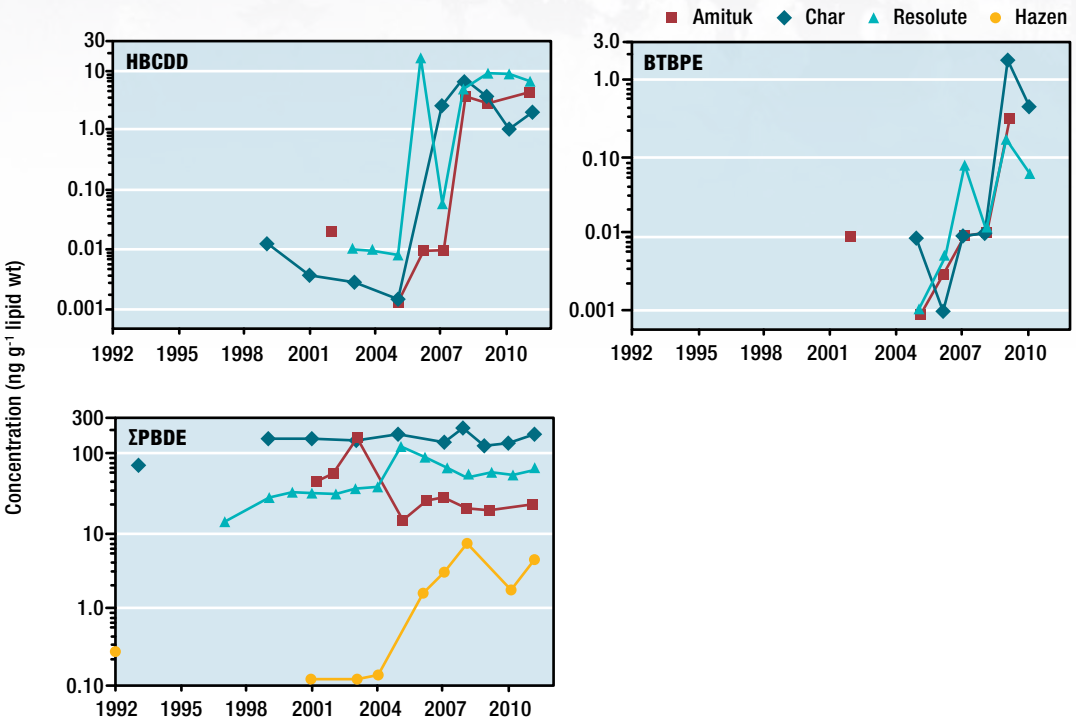

FIGURE 4.74

Trends of HBCDD, BTBPE and ΣPBDEs in landlocked arctic char from Amituk, Char, Hazen and Resolute Lakes. Symbols represent arithmetic mean concentrations. Error bars are omitted for clarity.

4.2.2.6.2. New POPs in landlocked arctic char

Concentrations of PBDEs (mainly tetra- and penta-brominated diphenyl ethers) increased in landlocked arctic char from Amituk, Resolute and Char Lakes, from the 1990s until early 2000s (Figure 4.74). For example, ΣPBDE increased by 21% per year in Resolute Lake from 1997 to 2005. A large increase was also observed in Lake Hazen from 2001 to 2008 (66% per year) (Table 4.4). However, PBDEs in Char Lake have been elevated for a longer time period than in nearby Resolute Lake and have continued to increase although at a much slower rate than in the other lakes. ΣPBDE concentrations appear to have leveled off as of about 2008 in Lake Hazen and Char Lake and show negative, but not statistically significant, trends as of 2011.

Replacement flame retardants HBCDD and BTBPE were also detected in arctic char muscle from Amituk, Char, and Resolute lakes (1992–2011) but were below MDLs in Lake Hazen. Concentrations of HBCDD were near detection limits in all lakes until 2006 when levels increased, particularly in Resolute and Char Lake. Concentrations appear to have leveled off as of 2009. BTBPE was detected in Amituk, Char, and Resolute lakes, but below MDLs in the landlocked arctic char of Lake Hazen. Concentrations remain near detection limits except in Char Lake, where levels reached 1 ng g^{-1} lw in 2009 (Figure 4.74).

Time trends for PFASs in landlocked arctic char are shown in Figure 4.75. Increasing concentrations of PFOS were observed in Char Lake while they remained unchanged in Amituk Lake and Lake Hazen. ΣPFCAs (sum of perfluoro alkyl acids with 9 to 12 carbons) showed little change in concentration 2007–2010 in Lakes Hazen, Char and Amituk. Concentrations in archived char muscle samples from Char Lake from 1993 were also similar to those analyzed 15 years later. Char samples from Resolute Lake were not included in the temporal trend study of PFASs as of 2009 because of high concentrations in char (see section 4.1.2.1.3.2).

Results suggest that α-endosulfan concentrations were increasing during the 1990s and until 2003–2004 in landlocked arctic char, particularly in Amituk and Resolute Lakes (Figure 4.76). No significant increase or decline of α-endosulfan was seen in char from Lake Hazen. β-endosulfan was generally not detected (< 0.01 ng g^{-1}). Endosulfan sulfate was present at similar concentrations as the α-isomer (see Figure 4.10) however temporal trends could not be estimated because it was not determined in samples taken prior to 2007.

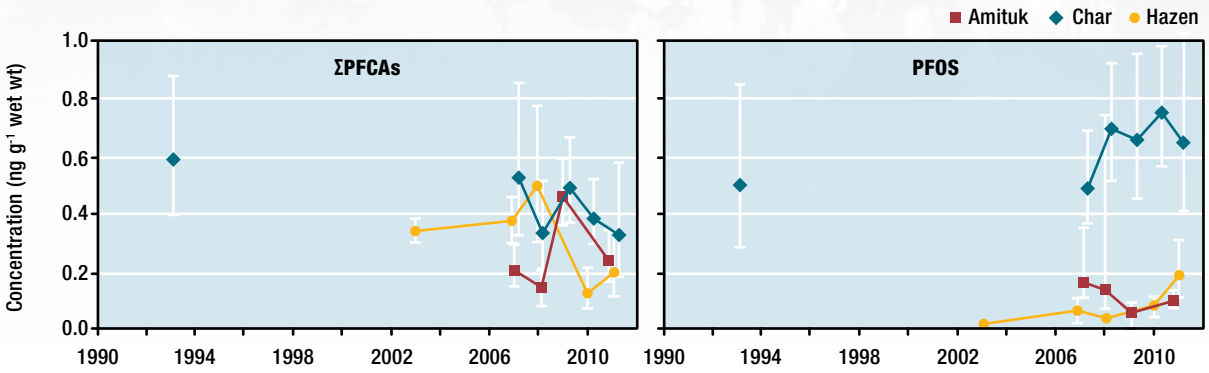

FIGURE 4.75

Trends of ΣPFCAs and PFOS in muscle of landlocked char from Lakes Hazen, Char and Amituk. Symbols are geometric mean concentrations ± 95% confidence intervals.

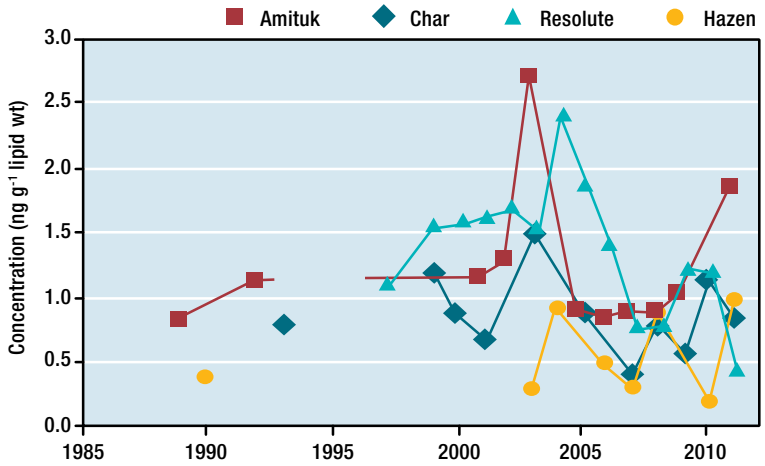

FIGURE 4.76

Trends of α-endosulfan in landlocked arctic char from Amituk, Char, Hazen, and Resolute lakes. Symbols are geometric means. Error bars are omitted for clarity. Endosulfan results from the 1990s and early 2000s are estimated based on a strong correlation between concentrations determined by GC-ECD and those determined by GC-NIMS using equation Log[α-endoMS] = 0.67*log[α-endoECD]-0.109.

4.2.2.7. Assessment of temporal trends in freshwater fishes

- There are declining concentrations of legacy POPs in Canadian Arctic freshwater fishes (burbot, lake trout, landlocked arctic char) and in sea-run char with some important exceptions.
- The results for POPs in fish suggest that overall trends in remote sites (e.g., High Arctic lakes, Kusawa Lake) are mirroring the gradual decline in atmospheric concentrations. However, sites are influenced by local or regional sources, which may be from use or from greater atmospheric deposition in the past, and therefore have more variable and sometimes opposite short term trends.
- When comparing results from the 1980s and 1990s in sea-run char with more recent sampling, chlordane, ΣCBz and ΣDDT concentrations have declined substantially at Cambridge Bay since 1987 while no decline is evident at Pond Inlet and Nain. However, PCBs are much lower at Nain than were reported in 1998.
- It is possible that lower CHL, ΣCBz, and ΣDDT concentrations over the period 2004–2009 compared to 1987 at Cambridge Bay are associated with a decline in localized concentrations given the presence of a former DEW-line site at this location. No change was evident for PCBs, the primary contaminant of concern at DEW-line sites.
- Legacy and new POPs in sea-run char over the period 2004 to 2011, for which annual samples were analyzed, have generally not shown any declining trends.
- Legacy chlorinated pesticides such as ΣDDT, HCH, ΣCHL and toxaphene in lake trout and burbot in Great Slave Lake have generally declined

over the period 1993 to 2011, while ΣPCBs and chlorobenzenes (mainly HCB and pentachlorobenzene) show no significant decline.

- Both PCBs and ΣCBz increased in burbot and lake trout in Great Slave Lake in the period 2001–2005. The reason for this is unknown however, as indicators such as percent lipid and diet (carbon and nitrogen stable isotope ratios) remained relatively stable over this time.
- Burbot sampled at Fort Good Hope on the Mackenzie River showed overall consistent declining concentrations of ΣCBz and ΣHCH. However, ΣPCBs, ΣDDT, ΣCHL and toxaphene increased significantly from 2001 until about 2009. By 2011, concentrations had returned to those observed in 2001.
- In Lake Laberge and Kusawa Lake, significant declines for ΣHCH, ΣPCB, ΣCHL in lake trout were found over the period 1993 to 2011 and unlike the lake trout in Great Slave Lake, no increasing trend was observed over the period 2001–2004 for any POPs.
- The temporary increase in PCBs in burbot at Fort Good Hope in the period 2001–2009 also appears to have occurred in burbot in the West Basin of Great Slave Lake and to a more limited extent in lake trout from both the East Arm and West Basin. Interestingly, these increases did not occur in Yukon lakes. This suggests some process that is influencing the availability of some POPs in the Mackenzie basin. Climate warming has been suggested, however a general warming trend would not explain the increase followed by a decrease in concentrations. Nevertheless, shifts in the burbot and lake trout diet and feeding areas could also be induced by climate warming. Other possibilities include mobilization of legacy sources due to warming, e.g., increased erosion of river sediments. Air concentrations of these POPs measured in the High Arctic generally declined over the same period (see Chapter 3, section 3.1.4).
- Mercury concentrations have also increased in the same fish species at Fort Good Hope and in Great Slave Lake (CACAR III mercury assessment 2013) but unlike the POPs, the increasing trends are continuous with no evident decline, suggesting that different pathways and sources are involved.
- In landlocked arctic char, legacy POPs declined in the study at 3 remote lakes (Char, Amituk and Hazen) but only ΣHCH declined in Resolute Lake.
- The lack of decreasing trends in Resolute Lake may reflect continued minor sources to this lake, which is downstream of Resolute airport and known to have been contaminated with PFOS related substances.
- Resolute Lake char were also distinguished by increasing toxaphene over the period 2003–2010. This upward trend along with the lack of change of PCBs, DDT, and chlordanes in this lake may be an indication of mobilization of old sources of these chemicals that could have been used at the Resolute airport and former military base which is within the lake catchment.
- Trends of PFOS and PFCAs in freshwater fish are quite variable. Sharp declines occurred in lake trout in Great Slave Lake and in burbot liver at Fort Good Hope. Much slower declines (no significant trend) were observed for PFOS in landlocked arctic char.
- PBDEs in freshwater fish have generally reached maximum concentrations in the period 2000–2008 and are leveling off or declining.
- The increase in PBDEs in landlocked arctic char is in general agreement with observations of other biota in the Canadian Arctic Archipelago and for arctic air (Su et al. 2007). A decline would be expected considering that penta- and octa-PBDEs were phased out in Europe in 2004 and in the US by the end of 2005 (de Wit et al. 2010).
- HBCDD has increased after 2006 in Great Slave Lake and in the high arctic lake char although concentrations remain low compared to ΣPBDEs, illustrating that high production volume chemicals with similar properties and uses as PBDEs will inevitably appear in arctic biota.

4.2.3. Temporal trends in seabirds

4.2.3.1. Legacy POPs in seabirds

The time series for POPs in seabird eggs represents one of the longest trend datasets in the Canadian Arctic with archived samples available as far back as the mid-1970s at Prince Leopold Island (Braune 2007). Most of the legacy POPs have decreased in the eggs of thick-billed murres and northern fulmars monitored at Prince Leopold Island since 1975 (Braune 2007). Distinct declines are apparent for ΣDDT, ΣPCB, and ΣCBz (Table 4.5; Figure 4.77). ΣCHL concentrations showed an overall decline until 2008 in northern fulmar and then increased in the period 2008–2011. The trend over the period 1975–2011 for ΣCHL in fulmars was not statistically significant. The polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have also declined. Concentrations of ΣDDT and ΣPCBs also appear to be levelling off, albeit with some interannual fluctuation (Figure 4.77).

TABLE 4.5. Analysis of time trends of legacy POPs[1] in eggs of thick-billed murres and northern fulmars at Prince Leopold Island using the PIA program (Bignert 2007).

Species	Years[2]	N	Parameter	ΣCBz	ΣCHL	ΣDDT	Σ_{69}PCB	ΣPCDD	ΣPCDF
Thick-billed Murre	15	65	% decline [3]	-2.6	-1.2	-2.5	-4.0	-3.4	-2.6
1975–2011			LDC (%) @ Power 80% [4]	6.1	4.5	4.2	4.7	6.7	5.7
Northern Fulmar	14	66	% decline	-2.6	-1.5 ns	-4.7	-3.8	-5.4	-4.6
1975–2011			LDC (%) @ Power 80%	5.6	5.4	4.6	6.1	8.0	6.8

[1] ΣCBz = Sum Chlorobenzenes (tetra-, penta- & hexachlorobenzene); ΣCHL = Sum Chlordanes (oxychlordane, *cis*- & *trans*-nonachlor, *cis*- & *trans*-chlordane, heptachlor epoxide); ΣDDT = Sum *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT; Σ_{69}PCB = Sum of 69 congeners;

[2] Number of 3-egg pools analyzed for all but ΣPCDD and ΣPCDF which were analyzed as 5-egg pools over 13 sampling years for PCDDs and 12 for PCDFs (n=36 for murres and n=34 for fulmars)

[3] ns = no statistically significant log-linear change ($p > 0.05$) in mean concentrations over time using the PIA program (Bignert 2007). Percent annual decline or increase is significant ($p < 0.05$) unless otherwise noted.

[4] LDC = Lowest detectable change in current time series at power of 80%.

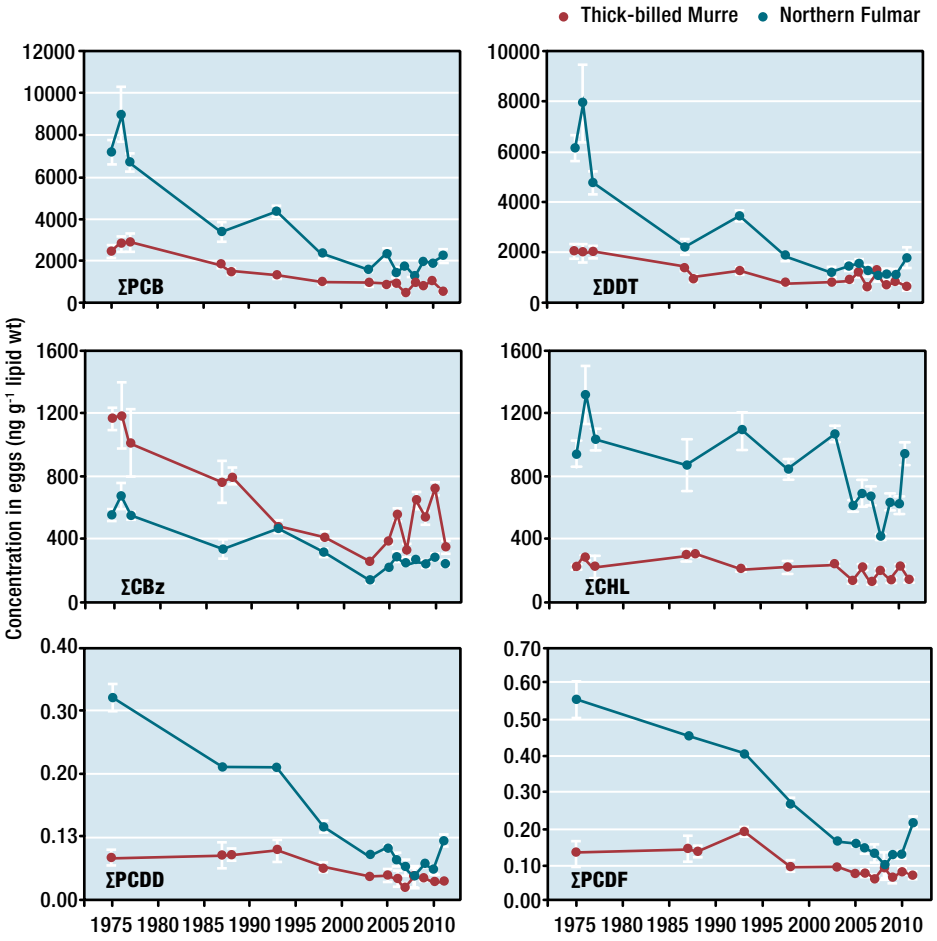

FIGURE 4.77

Mean concentrations (± standard error) of ΣPCB, ΣDDT, chlorobenzenes (ΣCBz), chlordanes (ΣCHL), polychlorinated dibenzo-*p*-dioxins (ΣPCDD) and dibenzofurans (ΣPCDF) in eggs of northern fulmars and thick-billed murres from Prince Leopold Island, 1975–2011.

Concentrations of the legacy organochlorines as well as PCDDs and PCDFs in eggs of the ivory gull collected from Seymour Island also either decreased or showed little change between 1976 and 2004 (Braune et al. 2007).

4.2.3.2. New POPs in seabirds

Brominated flame retardants: Polybrominated diphenyl ethers (PBDEs) were first detected in Canadian arctic seabird liver and eggs by Braune and Simon (2004). Subsequent retrospective analyses and continued monitoring showed that concentrations of ΣPBDEs in the eggs of thick-billed murres and northern fulmars from Prince Leopold Island steadily increased from 1975 to 2003 after which levels started to decrease (Braune 2008) driven largely by BDE-47 (Figure 4.78). The overall trend over the period 1975 to 2011 is a non-significant increase of 3.0% per year in northern fulmar and 2.4% per year in thick-billed murre (Table 4.6).

An increase in ΣPBDE concentrations between 1976 and 2004 is also reflected in eggs of the ivory gull (*Pagophila eburnea*) collected from Seymour Island in the Canadian Arctic (Braune et al. 2007). BDE-47 was the predominant congener in thick-billed murres and northern fulmars, as well as in the ivory gull eggs (Braune et al. 2007) followed by BDE-99 and BDE-100 in all years analyzed. The increase in ΣPBDE concentrations observed in the seabird eggs between the mid-1970s and 2003–2004 agrees well with the pattern of significant increase in the use of PBDEs seen for the period spanning the early 1970s to the early 2000s in North America (Hale et al. 2003, Law et al. 2003). The declining concentrations observed in the fulmar and murre eggs after 2003 may reflect the phasing out of penta-mix BDE usage in North America after 2005 (de Wit et al. 2010).

Perfluorinated alkyl substances: Retrospective analyses showed that PFAS concentrations in livers of thick-billed murres and northern fulmars from Prince Leopold Island had increased significantly from 1975 to 2003–2004 (Butt et al. 2007a). PFASs analyzed included C_7–C_{15} PFCAs, 8:2 FTCA and FTUCA, 10:2 FTCA and FTUCA, C_6, C_8, C_{10} perfluorinated sulfonates and PFOSA. Considering PFCAs, the concentration increases over both sampling periods (1975–1993 and 1993–2004) were significant for thick-billed murres but the trends were not as clear for the northern fulmars. For northern fulmars, PFCAs showed either maximum concentrations in 1993 or statistically similar concentrations in 1987, 1993 and 2003, suggesting a levelling off in PFCA levels beginning in the early 1990s. Doubling times could be calculated for both species since the increase over the entire study period was significant. The doubling times in thick-billed murres ranged from 2.3 y for PFPA to 9.9 y for PFDoA, and from 2.5 y for PFPA to 11.7 y for PFDA in northern fulmars. PFOS levels were statistically similar in both populations between 1993 and 2003–2004.

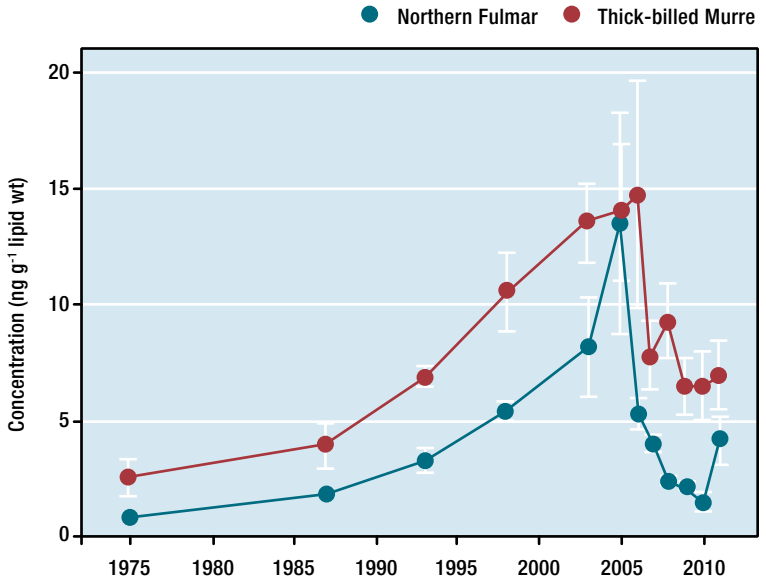

FIGURE 4.78

Mean annual concentrations (± standard error) of BDE-47 in eggs of thick-billed murres and northern fulmars from Prince Leopold Island, 1975–2011.

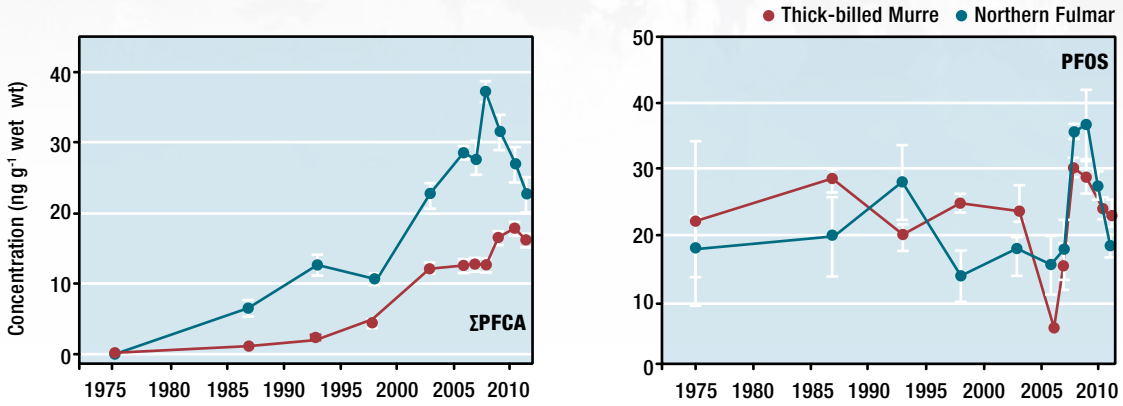

FIGURE 4.79

Mean annual concentrations (± standard error) of ΣPFCAs and PFOS in eggs of thick-billed murres and northern fulmars from Prince Leopold Island, 1975-2009. ΣPFCA = C_6 to C_{15} inclusive.

TABLE 4.6. Analysis of time trends for new POPs in eggs of thick-billed murres and northern fulmars at Prince Leopold Island using the PIA program (Bignert 2007).

Species	Years[1]	Parameter	N	ΣPBDE[2]	N	PFOS	N	ΣPFCA[3]
Thick-billed Murre 1975–2011	12	% decline [4]	48	+3.0% ns	50	-0.30% ns	50	+14%
		LDC (%) at Power 80% [5]		18%		14%		7.9%
Northern Fulmar 1975–2011	12	% decline	48	+2.4% ns	52	-0.09% ns	52	+13%
		LDC (%) at Power 80%		24%		12%		25%

[1] Number of egg pools. ΣPBDE which were analyzed as 5-egg pools 1975–2003 and as 3-egg pools 2005–2011.

[2] ΣPBDE = Sum BDE-17, -28, -49, -47, -66, -100, -99, -85, -153, -138, -183

[3] ΣPFCA = Sum C_6 to C_{15}.

[4] ns = no statistically significant log-linear change ($p > 0.05$) in mean concentrations over time using the PIA program (Bignert 2007). Percent annual decline or increase is significant ($p < 0.05$) unless otherwise noted.

[5] LDC = Lowest detectable change in current time series at power of 80%.

Recent annual analyses of PFASs in eggs indicates that concentrations of ΣPFCAs increased from 1975 to 2008 in eggs of both northern fulmars and thick-billed murres from Prince Leopold Island but declined from 2008 to 2011. PFOS levels did not change significantly over the same time period although as of 2009 concentrations appear to be declining (Figure 4.79). The overall trend for the period 1975 to 2011 was for no significant change in PFOS (< 1% per year; Table 4.6) and significant annual increases in ΣPFCAs (13% in murres and 14% in fulmars)(Table 4.6).

Polychlorinated naphthalenes: PCNs were first detected in Canadian arctic seabird eggs by Muir (2004). Subsequently, PCNs were monitored in eggs of thick-billed murres from Prince Leopold Island between 1975 and 2012 (Birgit Braune, Environment Canada, unpublished data). The tetra- and penta-CNs together accounted for 80-88% of total PCNs (Σ_{68}PCN) in all years. Σ_{68}PCNs significantly decreased in eggs of thick-billed murres from 1975 to 2012 ($p < 0.0001$) which is consistent with trends reported elsewhere (e.g. Gewurtz et al. 2009, Järnberg et al. 1993, Sinkkonen and Paasivirta 2000).

4.2.3.3. Assessment of temporal trends in seabirds

- Concentrations of most of the legacy organochlorines (e.g., PCBs, DDE) have decreased in Canadian arctic seabirds since 1975 and now appear to be levelling off.
- In recent years, ΣCBz and ΣCHL have increased concentrations in northern fulmars and thick-billed murre eggs sampled from Prince Leopold Island in Lancaster Sound. Similar increases have been observed in ringed seals from the same region. An explanation for these increases is lacking at the present time.

- Perfluorinated carboxylic acids (PFCAs) have increased since 1975 in eggs of both northern fulmars and thick-billed murres whereas perfluorooctane sulfonate (PFOS) levels do not show any discernible trend. However, recent measurements (2009–2011) suggest concentrations of PFOS and PFCAs are now declining.
- The trend for PFCAs mirrors the global production and emissions of PFOA and PFCA precursors which is known to have increased substantially in the period 1990–2005, although they likely declined after 2005 (Armitage et al. 2009). PFOS concentrations in eggs do not mirror global production, which declined as of 2002.
- Concentrations of ΣPBDEs increased in northern fulmars and thick-billed murres between 1975 and 2003, and now appear to be decreasing in both species. The trends in these species mirror the known use in North America where "penta" PBDEs were phased out as of 2004 (de Wit et al. 2010).
- ΣPCNs increased in eggs of thick-billed murres but showed no significant trend in northern fulmars over the last 2–3 decades.
- The annual sampling undertaken in recent years (2005 onwards) for the arctic seabird eggs has greatly improved the power of the time series for legacy POPs and provided evidence for increases and declines of new POPs such as PBDEs and PFOS which would have been less evident with sampling at 5 year intervals.
- Trends of other BFRs, toxaphene and endosulfan are unknown for seabirds.

4.2.4. Temporal trends of POPs in marine mammals

4.2.4.1. Legacy POPs in ringed seals

Temporal trend studies on POPs in Canadian arctic ringed seals draw on a large database consisting of results for samples collected for the period 1972 to 2011. Most samples are from the period 1998–2010, except at Ulukhaktok where results in archived samples from the 1970s, 1980s and 1990s are available (Addison et al. 2009, Gaden et al. 2012). Temporal trends of selected legacy POPs in ringed seal blubber have been previously reported for Ulukhaktok (Addison et al. 2005, Addison et al. 2009, Addison et al. 2013, Addison and Smith 1998, Addison and Zinck 1986) and for the Lancaster Sound area to 2005 (Lohmann et al. 2007). Rigét et al. (2010) included results to 2006 for seals from Lancaster Sound and Ulukhaktok (Holman) in an assessment of overall temporal trends. Annual sampling at three locations, Sachs Harbour, Resolute Bay and Arviat, since 2004 has significantly increased the sample numbers for these three locations (Muir et al. 2010, Muir et al. 2012). For this assessment, the results from Sachs Harbour and Ulukhaktok ("Beaufort"), Resolute, Grise Fiord and Arctic Bay ("Lancaster"), Arviat and Inukjuaq ("Hudson Bay") were combined in order to strengthen the statistical power of the data to assess temporal trends. Statistical analysis showed that most PCBs and OCP concentrations were similar for nearby communities and differed significantly among regions. The trends for Σ_{10}PCB (sum of 10 major congeners), ΣDDT, ΣCHL, toxaphene and ΣCBz are shown in Figure 4.80 and for α-HCH, β-HCH, HCB in Figure 4.81. Table 4.7 presents results of statistical analysis for 6 major POPs using the PIA program (Bignert 2007). Additional data are available in Annex Table A4-1.

Overall, there are declining trends of POPs in ringed seals with the relative magnitude of ΣDDT > α-HCH > Σ_{10}PCB ≈ ΣCHL ≈ toxaphene. Rigét et al. (2010) reached similar conclusions working with a large set of time series for arctic marine mammals from Alaska, Canada, and Greenland. ΣDDT declined significantly in ringed seals from all 4 regions (Figure 4.80; Table 4.7). Chlordane-related compounds declined in the East Baffin and Hudson Bay regions (Table 4.7). However, the declines of Σ_{10}PCB and ΣCHL in the Beaufort and Lancaster regions were not statistically significant despite the relatively large numbers of sampling years now available, suggesting continued inputs. HCB declined significantly in the Hudson Bay and Beaufort regions. Toxaphene did not show a significant decline in any region and actually increased in concentration in the Lancaster and East Baffin samples over the period 2008–2010 (Figure 4.80).

To examine temporal trends of toxaphene, results from recent samples analyzed by GC-ECNIMS were combined with older data for ringed seals (e.g., Muir 1996) that used GC-ECD for quantification. This is potentially problematic because GC-ECD is a non-specific detector and chlordane and even PCBs can interfere in the analysis. However, the earlier work focussed on specific chlorobornane peaks in marine mammal tissues identified by GC-ECNIMS (Bidleman et al. 1993) or by ECD after nitric-sulfuric acid treatment to remove PCB interferences (Muir et al. 1992a). The NIST cod liver oil certified reference material (1588a) was used as of 1993 and results for total toxaphene in CRM samples from that era are within ± 20% of current measurements of technical toxaphene analyzed by GC-ECNIMS. Thus, there is some confidence that older and more recent data can be combined.

The HCH isomers showed divergent trends. α-HCH declined significantly in ringed seals from all 4 regions (Figure 4.81; Table 4.7) while β-HCH increased significantly at Sachs Harbour, Ulukhaktok and Resolute but not in Hudson Bay or East Baffin. Using their extensive dataset for seals at Ulukhaktok, Addison et al. (2009) showed that β-HCH was continuing to increase while α-HCH and γ-HCH showed no significant change over the period 1978–2006. β-HCH concentrations increased significantly, about 8- to 10-fold in females (16% per year) and 4- to 5-fold in males (12% per year). It was concluded that although global emissions of both α-HCH and β-HCH have declined since the early 1980s, the "signal" of HCH emission changes has not yet resulted in a "response" in ringed seal residue concentrations.

This regional difference for β-HCH may be due to the influence of Pacific Ocean waters traversing the Archipelago which influences the contaminants accumulated by ringed seals in the Beaufort Sea and Lancaster Sound. The declines of HCB, ΣDDT, Σ_{10}PCB, ΣCHL and toxaphene were all greater in Hudson Bay, which may reflect generally higher concentrations in the 1980s and 1990s as well as the limited importance of Pacific Ocean waters in this region compared to the Archipelago.

Ikonomou et al. (2002) examined temporal trends of mono-ortho and non-ortho (MO and NO or coplanar) PCBs and PCDD/Fs in male ringed seals from Ulukhaktok. Concentrations of MO+NO PCBs (149–174 ng g^{-1}) and PCDD/F (8.6–14.6 pg g^{-1}) in ringed seals aged 0 to 15 years remained approximately constant from 1981 to 2000. No further results for planar PCBs or PCDD/Fs in ringed seals are available.

Gaden et al. (2012) examined temporal trends of PCBs and selected OCPs in ringed seals from Ulukhaktok for the period 1993 to 2008 with the objective of determining if the date of the spring sea-ice break-up affected trends. A longer ice-free period could expand the open water foraging range for the seals. HCB and age- and blubber-adjusted concentrations of *p,p'*-DDT and toxaphene (determined by GC-ECD) significantly decreased over the study period. Six of the 22 POPs analyzed were higher with earlier break-up (at least 12 days earlier than the 1993–2008 mean break-up date) (*p,p'*-DDE and CBs 31, 118, 138, 153, and 180) after adjustment for age and body condition. However, significant temporal trends of declining body condition (a metric calculated from seal length) were also observed particularly for seals collected after 2000 and could have influenced the results. Nevertheless, the results were consistent with other studies (McKinney et al. 2012, Hallanger et al. 2011), which suggest that additional trophic levels in the food web or different prey species due to changing ice conditions, could influence contaminant levels in top predators.

TABLE 4.7. Results of analysis of time trends of POPs in female and juvenile ringed seals

Region[1]	Yrs[2]	N	Parameter[3]	α-HCH	β-HCH	HCB	Σ_{10}PCB	ΣDDT	ΣCHL	Toxaphene[4]
Hudson Bay	13	157	% decline or increase	-9.2	-2.7 ns	-2.8	-5.4	-7.3	-7.4	-6.1 ns
1986–2011			LDC (%) at Power 80%	10	17	5.4	9.4	9.4	11	27
East Baffin	10	87	% decline or increase	-7.4	+1.2 ns	-1.6 ns	-4.1	-3.0	-2.9 ns	-2.8 ns
1986–2011			LDC (%) at Power 80%	10	18	8.6	12	8.1	10	99
Lancaster	17	212	% decline or increase	-4.3	+4.5	-0.87 ns	-2.2	-3.0	-1.2	+0.30 ns
1972–2011			LDC (%) at Power 80%	6.7	7.5	3.6	4.5	4.2	5.0	25
Beaufort	8	91	% decline or increase	-1.9	+5.4	-0.86	-0.54 ns	-2.7 ns	+0.32 ns	-1.8 ns
1972–2011			LDC (%) at Power 80%	23	18	7.9	18	28	30	33
Ulukhaktok[5]	7	79	% decline or increase	-2.4	+16	-3.8	-2.2	-4.2	–	–
1972–2010										

[1] Hudson = Arviat + Inukjuaq; Lancaster = Resolute Bay + Gjoa Haven + Arctic Bay + Grise Fiord. Beaufort = Sachs Harbour and Ulukhaktok; East Baffin = Pangnirtung + Qikiqtarjuaq

[2] Number of sampling years

[3] Calculated using the PIA program except for results from Addison et al. (2009,2013) which were calculated using simple log linear regression. LDC = Lowest detectable change in current time series at power of 80%. ns = no statistically significant log-linear change ($p > 0.05$) in mean concentrations over time. Percent annual decline or increase is significant ($p < 0.05$) unless otherwise noted.

[4] Sample numbers are smaller for toxaphene. Hudson Bay = 103; Lancaster = 81; East Baffin = 35; Beaufort = 96

[5] Results in female ringed seals from Addison et al. (2009) for HCH isomers over the period 1978 to 2006 (n=36) and from Addison et al. (2013) for ΣPCBs (sum 7 congeners), ΣDDT and HCB (n=79) over the period 1972–2010.

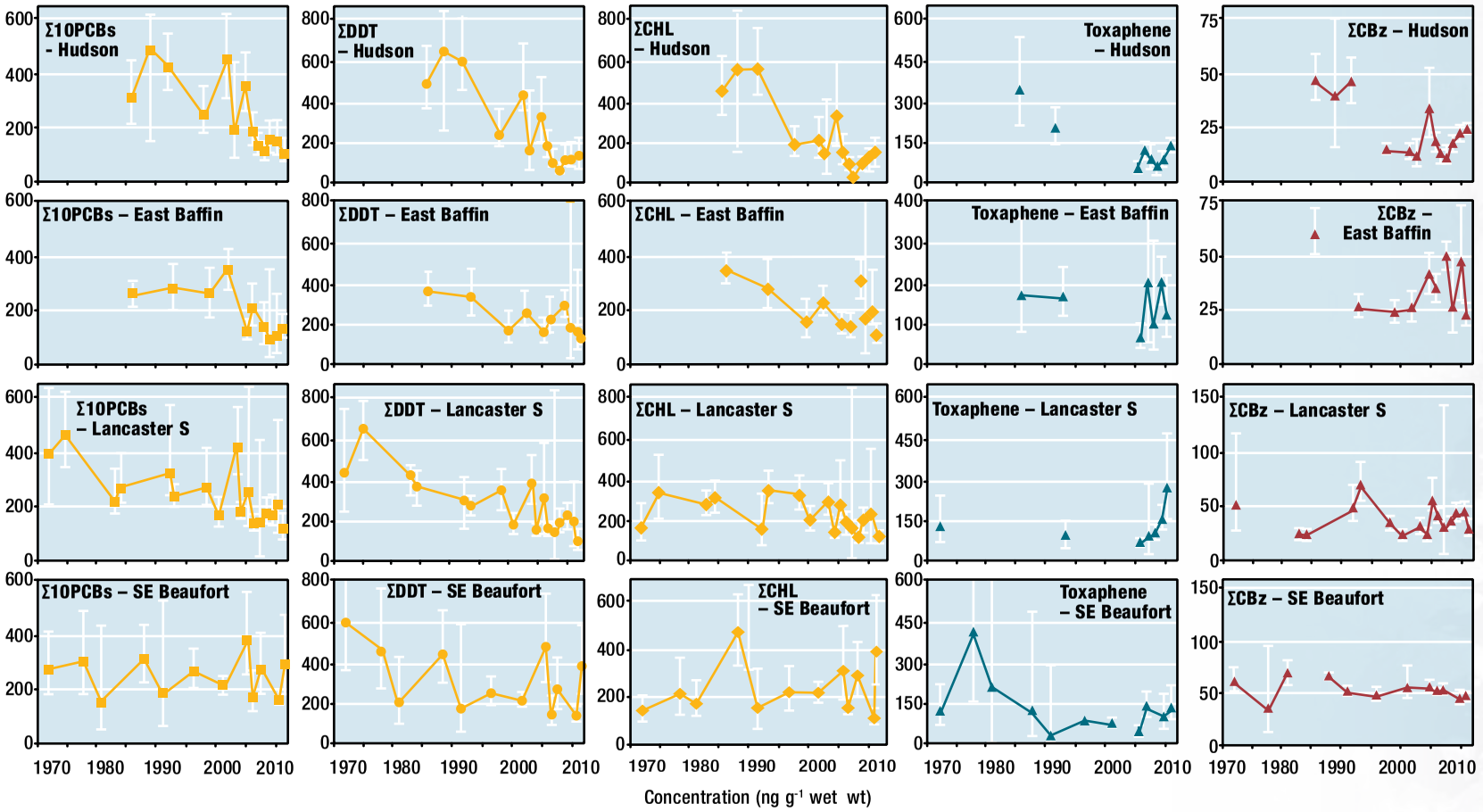

FIGURE 4.80

Trends of Σ_{10}PCBs (sum of CB 28, 31, 52, 101, 105, 118, 138, 153, 156, 180), ΣDDT, ΣCHL, toxaphene and ΣCBz in blubber of female (+ juvenile) ringed seals from 4 regions (see Table 4.7 for communities within each region). Symbols represent geometric mean concentrations (ng g^{-1} lipid weight) and vertical lines are 95% confidence intervals.

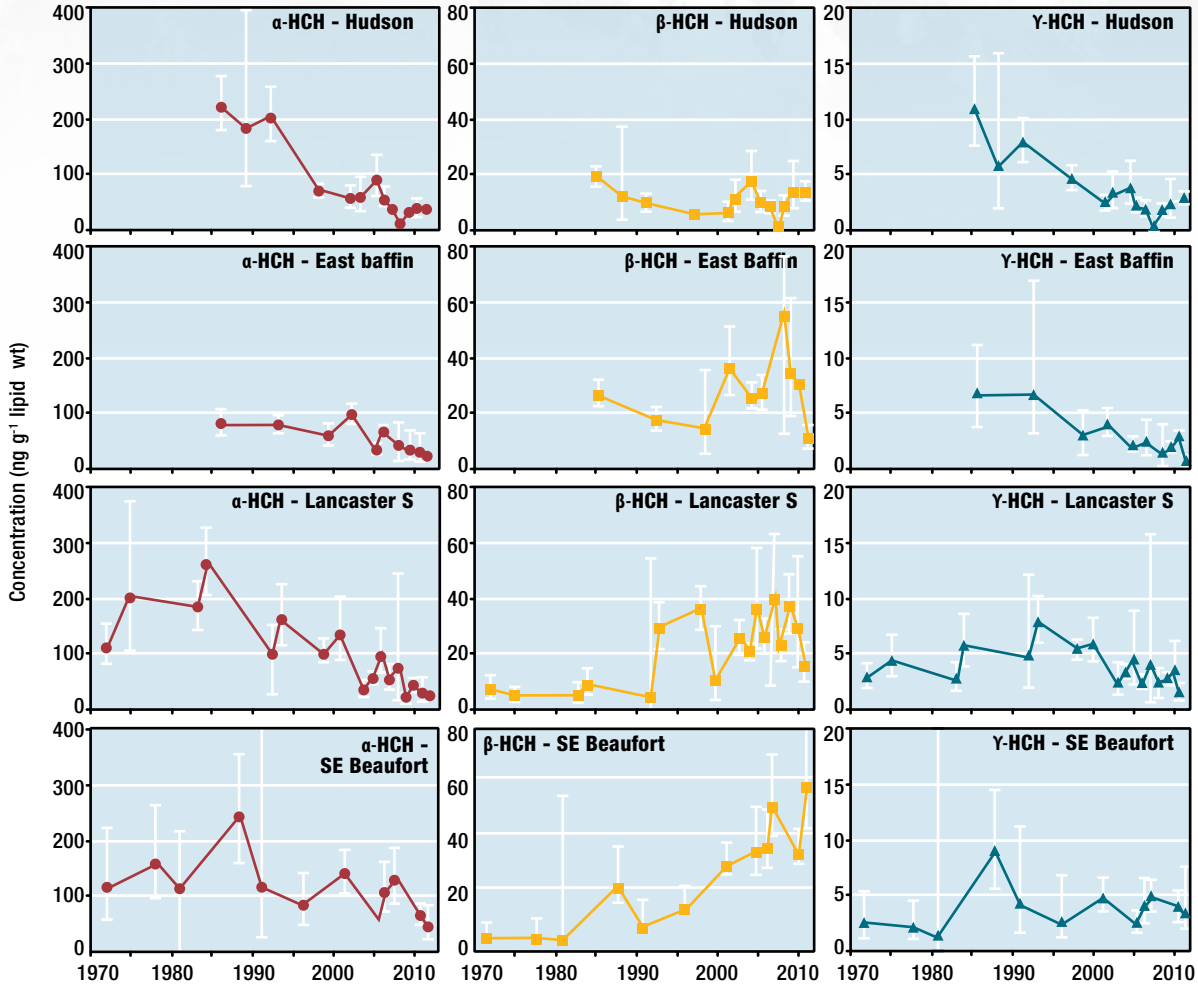

FIGURE 4.81

Trends of α-, β and γ-HCH in blubber of female ringed seals from 4 regions (see Table 4.7 for communities within each region). Symbols represent geometric mean concentrations (ng g^{-1} lipid weight) and vertical lines are 95% confidence intervals.

4.2.4.2. New POPs in ringed seals

Brominated flame retardants: The CACAR II report (Fisk et al. 2003) summarized PBDE temporal trends in male ringed seal blubber (age class: 0–15 y) from Ulukhaktok collected between 1981 and 2000 (Ikonomou et al. 2002) with additional samples collected during 2002 and 2003 (Ikonomou et al. 2005). These studies reported overall increasing ΣPBDE concentrations with trends that mirrored global penta-BDE production. Doubling times for ΣPenta-BDEs (4.7 y) and ΣHexa-BDEs (4.3 y) were similar, whereas a longer doubling time was shown for Tetra-BDEs (8.6 y).

As of 2004, PBDEs were determined annually in ringed seals from 4 other locations (Sachs Harbour, Arviat, Pangnirtung, Resolute), and in samples from other communities, as well as in archived samples from the 1970s and 1990s. The results for penta- and octa-BDEs (sum congeners 47, 99, 100, 153, 154, 183) for four regional groups of locations (Beaufort, Lancaster, Hudson and East Baffin (Qikiqtarjuaq + Pangnirtung)) are shown in Figure 4.82. ΣPBDEs continued to increase significantly in the southern Beaufort at an annual rate of +9.2% and also in the East Baffin and Lancaster Sound samples (non-significant increases). However, in Hudson Bay ΣPBDEs declined (-7.4% per year; 2002–2011) although the trend was also not significant (Table 4.8).

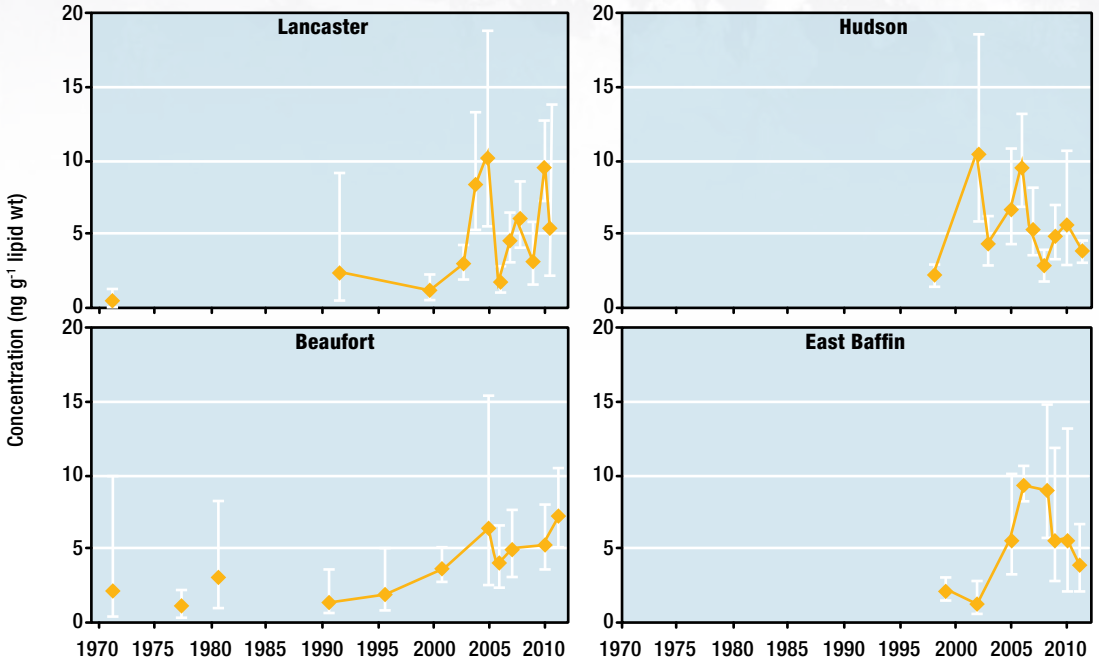

FIGURE 4.82

Temporal trends of ΣPBDEs at in ringed seal blubber from 4 regions from the 1970s to 2010. Results from neighboring communities have been combined. Symbols represent geometric mean concentrations and vertical lines are 95% confidence intervals.

ΣPBDE appeared to reach maximum levels in 2005 and 2006 in the Resolute area (Lancaster) however, the overall trend from 1972–2010 is significant (+7.4% per year).

Increasing concentrations of HBCDD and BTBPE have been found in seal blubber since 2006 (Figure 4.83; Table 4.8). The rate of increase of HBCDD appears to be rapid in Beaufort Sea, Lancaster Sound and Hudson Bay samples (+45 - 162% per year), however the sampling years are limited. The blubber samples were also analyzed for PBEB, HBB and DBDPE, but the compounds were infrequently detected and, when detected, were at levels close to instrumental detection limits.

TABLE 4.8. Approximate percent annual increase or decrease for PBDEs and HBCDD in blubber of female ringed seals and for PFASs in ringed seal liver samples.

Location	ΣPBDEs		HBCDD		PFOS		PFCAs	
	#Years & range[1]	% dec or inc / y[2]	#Years & range	% dec or inc /y	#Years & range	% dec or inc /y	#Years & range	% dec or inc /y
Beaufort	(8) 1991–2011	+9.2 (6.1–12)	(5) 2001–2011	+45 ns	(7) 1972–2011	+3.6 ns	(7) 1972–2011	+3.0 ns
Lancaster Sound	(10) 2000–2011	+10 ns	(6) 2000–2011	+162 (106–219)	(4) 1972–2003	+4.8 ns	(4) 1972–2003	+8.0(3.7–12)
Lancaster Sound	–	–	–	–	(9) 2003–2011	-21(4.4–38)	(9) 2003–2011	-18(7.3–28)
East Baffin	(8) 1999–2011	+10 ns	–	–	(5) 1999–2011	-14 ns	(3) 2006–2011	-6.6 ns
Hudson Bay	(9) 2002–2011	-7.4 ns	(5) 2007–2011	+100 ns	(9) 2002–2011	-9.0 ns	(9) 2002–2011	-7.0 ns
Hudson Bay	–	–	–	–	(3) 1992–2002	+14 ns	(3) 1992–2002	+18 ns

[1] Number of sampling years within the interval.

[2] Percent decrease from maximum or percent increase over the period indicated. Where the trend is statistically significant, 95% confidence intervals are given in parentheses. ns = no statistically significant change in mean concentrations over time ($p < 0.05$) using the PIA program (Bignert 2007) or regression of log concentration vs. time.

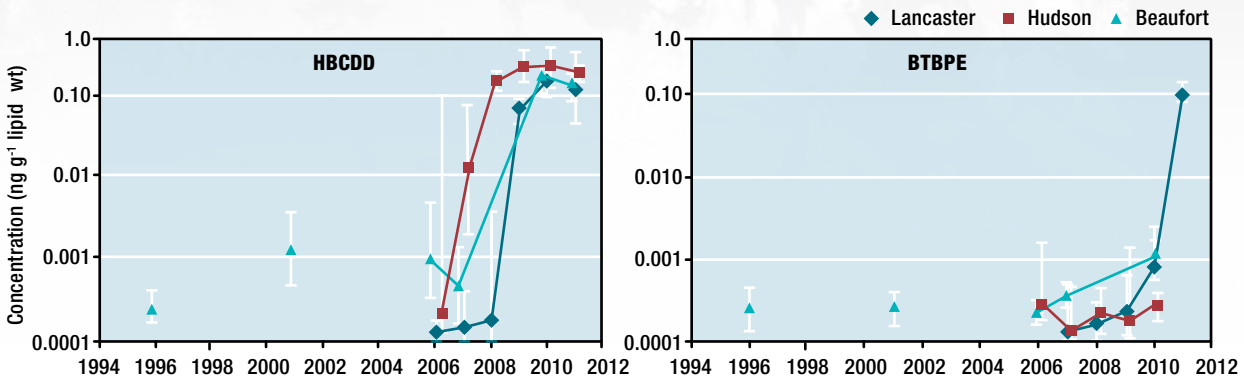

FIGURE 4.83

Temporal trends of HBCDD and BTBPE in female ringed seals from the three regions. Symbols represent geometric mean concentrations and vertical lines are 95% confidence intervals. Values below 0.001 ng g^{-1} lw are less than method detection limits.

Perfluorinated alkyl substances: PFASs concentrations in ringed seal livers in the Canadian Arctic increased over the period from the 1970s to early 2000s (Figure 4.84). Butt et al. (2007b) reported on temporal trends of PFASs in ringed seal liver from Arviat (1992, 1998, 2004 and 2005) and Resolute Bay (1972, 1993, 2000, 2004 and 2005). Overall, the C_9–C_{15} PFCAs increased during the time intervals investigated with calculated doubling times ranging from 19 years to 16 years for PFDoA and 10 to 7.7 years for PFNA in the Arviat and Resolute Bay populations, respectively. However, it was noted that the PFCA concentrations in more recent time points, in both populations, were not statistically different from each other and may suggest a leveling off of PFCA levels in ringed seals in the Canadian Arctic. In contrast, PFOS levels peaked during 1998 and 2000 at Arviat and Resolute Bay, respectively, followed by statistically significant declines to 2005. The Arviat population showed two consecutive statistically significant declines: from 1998 to 2003, and then from 2003 to 2005. However, in the Resolute Bay population, the 2000 to 2004 decline was not statistically significant, but the overall 2000 to 2005

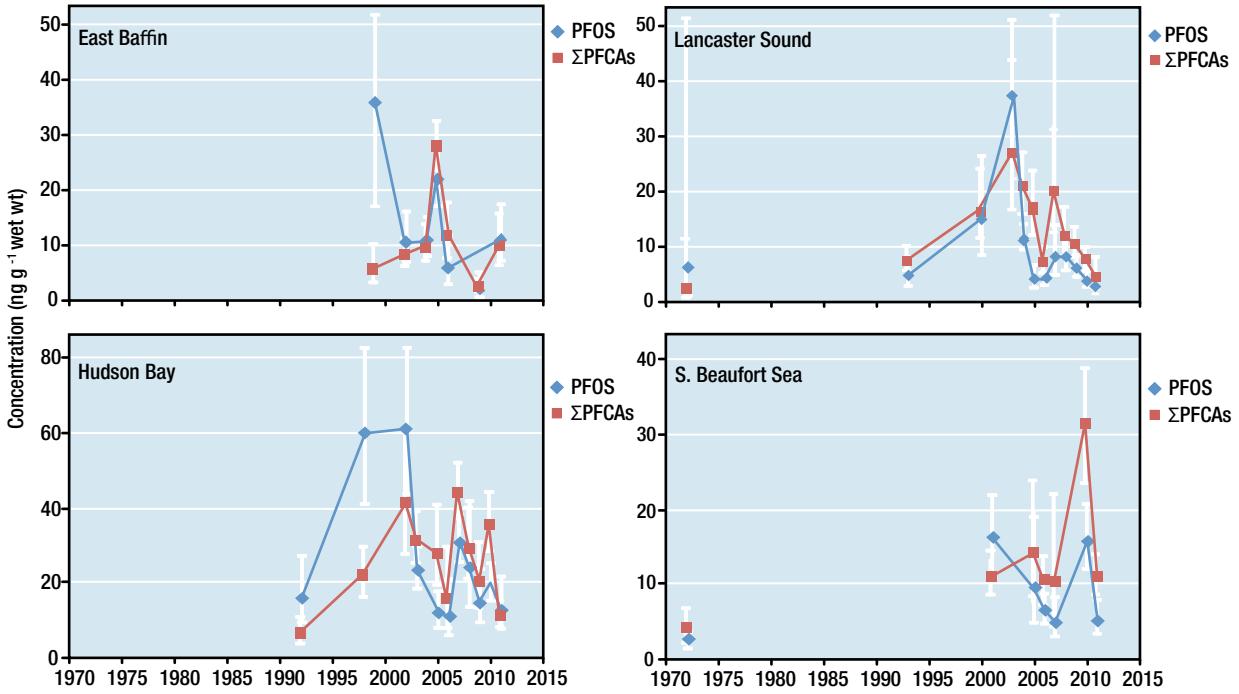

FIGURE 4.84

Temporal trends of PFOS and ΣPFCAs in ringed seal liver from 4 regions. Results from neighboring communities have been combined. Symbols represent geometric mean concentrations and vertical lines are 95% confidence intervals.

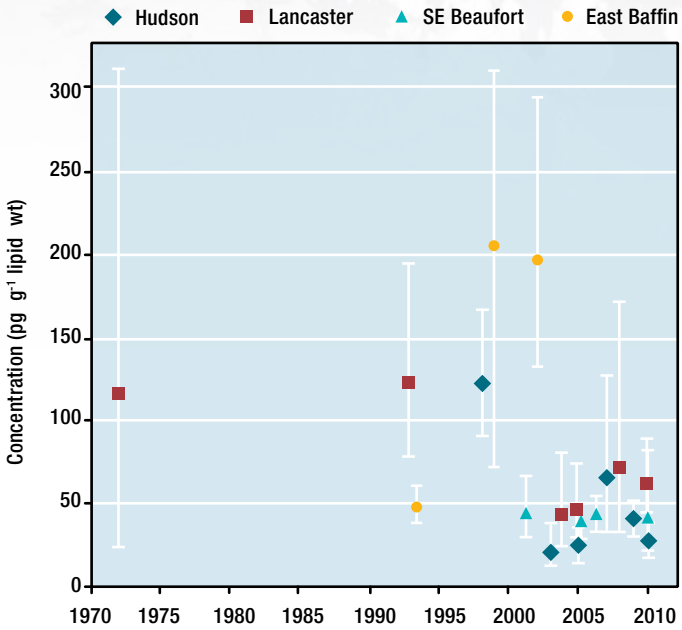

FIGURE 4.85

Temporal trends of chlorinated naphthalenes in ringed seal blubber (females and juvenile males only) from four regions (see Figure 4.80). Results from East Baffin (Pangnirtung) are from Muir et al. (2004) and Helm et al. (2002). Symbols represent geometric mean concentrations and vertical lines are 95% confidence intervals.

decline was significant. The apparent PFOS disappearance half-life rates were 3.2 ± 0.9 years and 4.6 ± 9.2 years for Arviat and Resolute Bay, respectively. These results indicated that the ringed seals and their food web were rapidly responding to the phase out by the manufacturer of perfluorooctane sulfonyl fluoride based compounds in 2001 (Paul et al. 2009).

Continued annual monitoring has shown that PFOS concentrations in ringed seal liver declined over the period 2003 to 2011 as shown in Figure 4.84 and Table 4.8. The decline in Lancaster Sound (Resolute) over the period 2003–2010 is about -21% per year and -9.0% per year in Hudson Bay for the period 2002–2011. ΣPFCAs are also declining in Lancaster Sound (-18% per year) and in Hudson Bay (-7.0% per year; not statistically significant). In the southern Beaufort Sea locations, both PFOS and ΣPFCAs continue to increase (+3.0% per year, 1972–2011) although at slower rates than those found in the 1990s to early 2000s in Lancaster Sound and Hudson Bay. Interestingly, this decline in PFOS is not evident in ringed seals in Greenland based on results to 2006 (Bossi et al. 2005, Butt et al. 2010).

Polychlorinated naphthalenes: Temporal trends of PCNs are available for ringed seal blubber from the Hudson Bay (Arviat), Lancaster (Resolute Bay), East Baffin (Pangnirtung), and Beaufort Sea (Sachs Harbour) sampling programs (Figure 4.85) (Muir et al. 2010). The PCN concentrations are relatively low compared to legacy POPs and PBDEs and appear to have declined at Resolute Bay, where samples from 1972 and 1993 were analyzed, and at Arviat based on samples from 1998. Results for Pangnirtung for samples from 2002, previously reported in Muir et al. (2004) and from 1993 reported by Helm et al. (2002) are also shown. Recent samples from Arviat and Resolute Bay appear to show declines from levels measured in samples from the 1990s.

4.2.4.3. Legacy POPs in beluga

As a result of an ongoing whale sampling and stock identity program, supported by the Nunavut Wildlife Management Board, the Fisheries Joint Management Committee and Fisheries and Oceans, a unique long-term dataset exists for POPs in southeastern Beaufort Sea beluga harvested from the Husky Lakes and Hendrickson Island area and also from the Cumberland Sound (southeast Baffin Island) stock harvested at Pangnirtung (Stern et al. 2012c). Temporal trends for legacy POPs in these two stocks are shown in Figure 4.86 and detailed results for male and female beluga are provided in Annex Table A4-1. Results for Cumberland Sound are limited after 2006, with only four animals on average collected and analyzed annually, making interpretation of the results difficult.

Earlier studies (Stern and Addison (1999); Stern and Ikonomou (2003)) of temporal trends of legacy POPs in blubber of beluga from 1982 to 2002 showed that several POPs declined over that period (ΣDDT, α- and β-HCH, dieldrin) while others did not change (ΣPCBs, ΣCHL) or increased (ΣCBz). With 8 more years of data, it is now clear that most legacy POPs achieved maximum concentrations in beluga in the mid-1990s and levels have since declined in both sampling locations (Figure 4.86). An exception was ΣHCH, which reached a maximum in the Beaufort Sea beluga in 2004. Declining concentrations for the period of 1995 to 2005 for toxaphene, ΣPCBs, ΣDDT, ΣCHL and ΣCBz were followed by a period of higher concentrations, from 2004–2005 to 2008–2009. Thus, although the overall trends suggest a decline (Table 4.9), using the full dataset, there are no statistically significant temporal trends for legacy POPs in the southern Beaufort Sea dataset. In Cumberland Sound, significant declines were found for ΣCBz (-10% per year), ΣHCH (-7.1% per year), ΣDDT (-11% per year) and ΣPCB (-6.0% per year) over the period 1995 to 2009 based on regression of annual mean concentrations against time (Table 4.9).

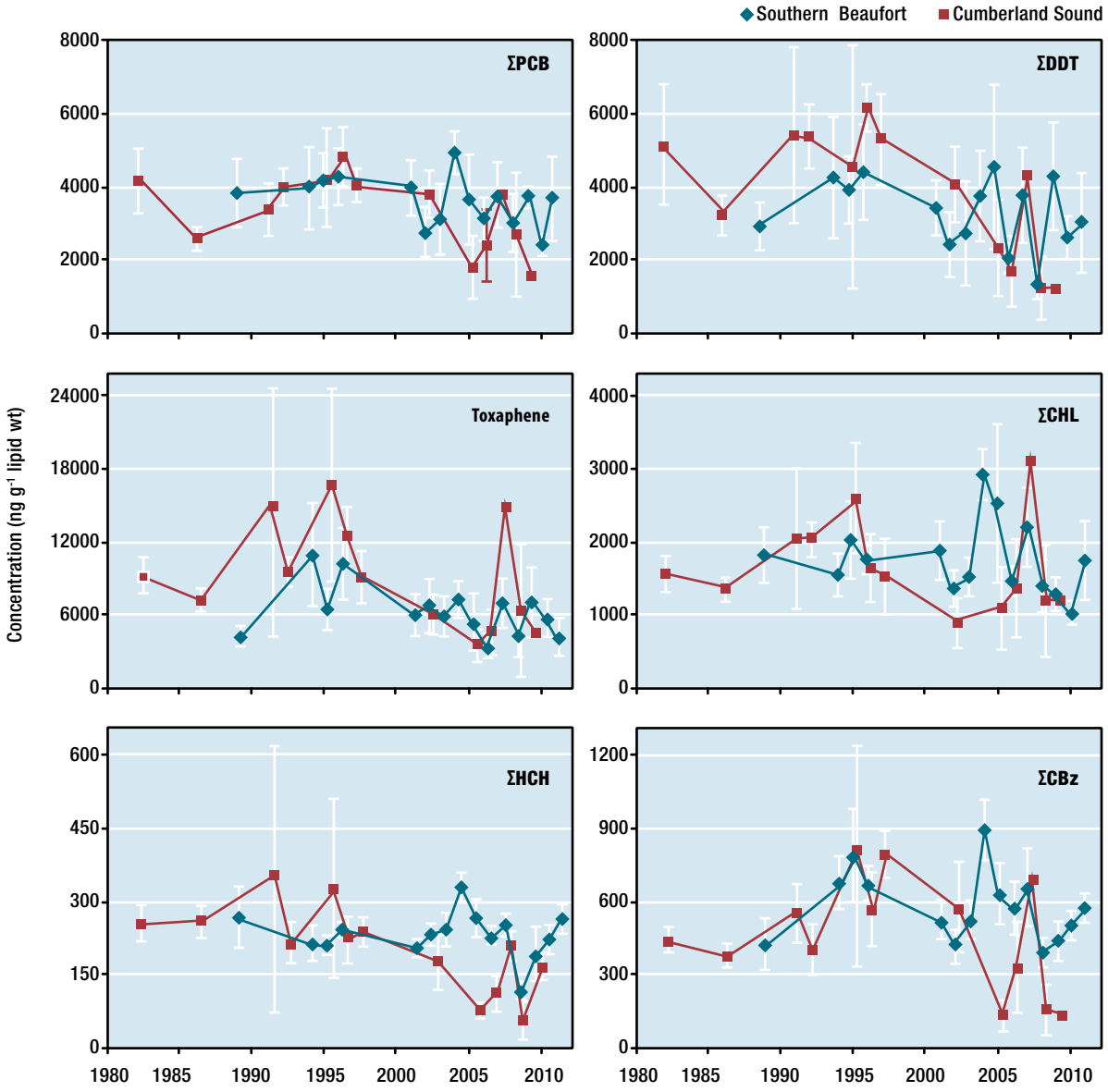

FIGURE 4.86

Trends of ΣPCBs, ΣDDT, toxaphene, ΣCHL, ΣHCH and ΣCBz in blubber of male beluga whales from the southern Beaufort Sea and Cumberland Sound stocks (Stern et al. 2012c). Symbols represent arithmetic mean concentrations (ng g^{-1} lw) and vertical lines are 95% confidence intervals. Note that sample numbers for Cumberland Sound range from 1–4 for 2007–2009.

TABLE 4.9. Declines (percent per year) of legacy POPs in male belugas from Southeast Beaufort Sea and Cumberland Sound stocks.

	Beaufort Sea				Cumberland Sound			
	Years	n	% per year	SE (%)	Years	n	% per year	SE (%)
ΣCBz	1995–2011	13	-2.0 ns	1.3	1995–2009	9	-10.2 ns	3.7
ΣHCH	1996–2011	12	-1.2 ns	1.8	1995–2009	9	-7.1 ns	2.9
ΣCHL	1996–2011	12	-2.0 ns	2.0	1995–2009	9	-2.0 ns	2.6
ΣDDT	1996–2011	12	-2.4 ns	2.9	1996–2009	8	-10.8 ns	2.9
ΣPCB	1996–2011	12	-1.7 ns	1.4	1996–2009	8	-6.0 ns	2.3
Toxaphene	1996–2011	12	-4.0 ns	1.7	1995–2009	9	-5.9 ns	3.0
Dieldrin	1996–2011	12	-0.2 ns	1.8	1995–2009	9	-6.8 ns	3.6
Oxychlordane	1996–2011	12	-0.6 ns	2.3	1995–2009	9	-0.7 ns	4.5

Calculated using simple linear regression of log transformed mean concentrations for each year. Half-lives ($t_{1/2}$) converted to percent per year using %=LN(2)*100/$t_{1/2}$

However, small sample sizes for beluga in Cumberland Sound from 2007–2009 make these trends uncertain.

As was postulated for mercury, the lack of response, in western arctic beluga, of HCH to the declining levels in the arctic atmosphere and ocean could be, at least in part, attributed to recent changes in ice cover, which may for example, alter the foraging of the beluga whales or their prey (Gaden et al. 2009, Gaden and Stern 2010, Kuzyk et al. 2010, Loseto et al. 2006, Loseto et al. 2008a, Loseto et al. 2008b, Stern and Macdonald 2005). The ΣHCH trends in beluga in the western Arctic are similar to those in ringed seals (Addison et al. 2009).

Hoguet et al. (2013) reported on temporal trends of legacy POPs in beluga from the Chukchi Sea population in northwestern Alaska for the period 1989 to 2000. Similar to observations for the Hendrickson Island beluga, Hoguet et al. (2013) found no significant temporal trends for ΣPCBs, ΣDDT and ΣCHL. However, ΣHCH and ΣCBz declined significantly. Comparison of more recent trends between the two populations was not possible.

4.2.4.4. New POPs in beluga whales

Brominated flame retardants: Temporal trends of HBCDD and PBDEs were investigated in beluga blubber from the southern Beaufort Sea stock (Hendrickson Island) and Cumberland Sound stock (Pangnirtung) (Tomy et al. 2009a, Tomy et al. 2011b). The Beaufort Sea population showed a statistically significant increase in ΣPBDE (BDE-47, -85, -99, -100, -153 and -154) levels from 1993 to 2004 with an annual increase of 8.8% per year (or doubling time of 8 y) while at Pangnirtung the increase from 1982 to 2008 was 5.9% per year (Figure 4.87; Table 4.10).

ΣPBDE concentrations appeared to decline in the Beaufort population over the period 2004–2009 (-8.8% per year) although the trend was not statistically significant. An increase in the ΣPBDEs was also reported by Hoguet et al. (2013) for beluga from the Chukchi Sea population over the period 1989 to 2000 which paralleled increases seen in the southern Beaufort Sea population for the same period.

Levels of ΣHBCDD (α- and β-isomers) increased significantly in the Hendrickson Island beluga samples over the period 1993–2004 (13% per year) and in Cumberland Sound from 1982–2010 (8.7% per year) (Table 4.10). Temporal trends of other BFRs detected in beluga blubber are not available (see section 4.1.5.3.3.2). Hoguet et al. (2013) also found a significant increase in α-HBCDD in the Chukchi Sea belugas over the period 1989 to 2000.

Perfluorinated alkyl substances: Tomy et al. (2004) reported increasing trends in PFOS and PFOSA concentrations in the liver of beluga from the Canadian Arctic between 1982 and 2002. Since then, annual analysis of samples from the southern Beaufort Sea and Cumberland Sound stocks has greatly enlarged this dataset (Tomy et al. 2011b).

A declining trend of ΣPFCA (C_8–C_{12} PFCAs) was observed in both the Beaufort Sea and Cumberland Sound beluga (Figure 4.88). This decline in ΣPFCA was statistically significant in the Beaufort Sea population (11% per year) (Table 4.10), which had higher levels in the 1980 and 1990s. In Cumberland Sound beluga, maximum concentrations were achieved in the year 2000 and then declined. The higher PFCA concentrations in beluga in the 1980s and 1990s in the Beaufort Sea stock is unusual and differs from observations of ΣPFCAs in ringed seals (section 4.2.4.2) and seabirds (section 4.2.3.2).

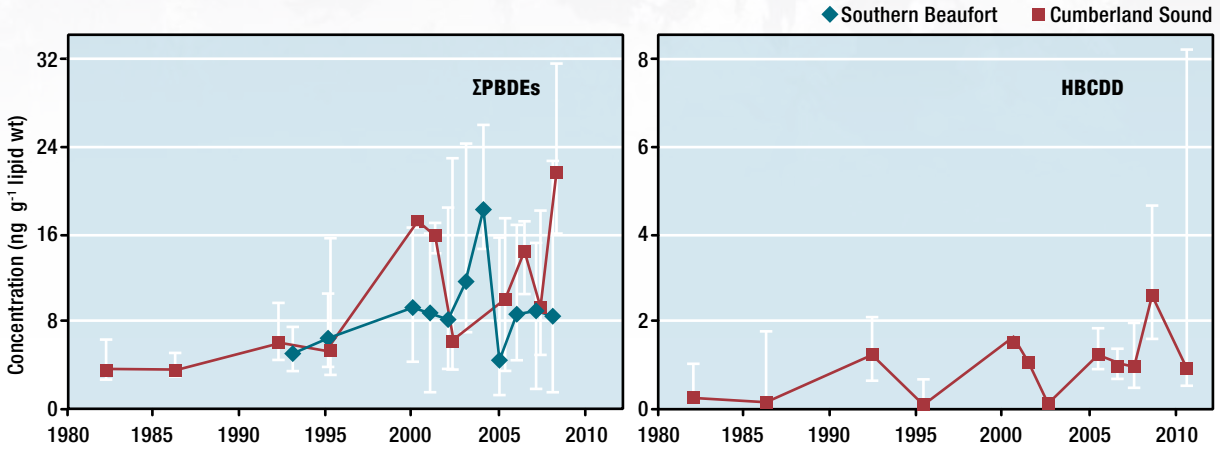

FIGURE 4.87

Temporal trends of ΣPBDEs and HBCDD in male beluga whales from the southern Beaufort Sea and Cumberland Sound stocks. Symbols represent arithmetic mean concentrations and vertical lines show minimum and maximum concentrations (Tomy et al. 2011b).

PFOS concentrations from both the southern Beaufort Sea and Cumberland Sound populations increased from the 1980s to 2000 with annual increases of 6.5% per year and 4.7% per year, respectively (Table 4.10). Interestingly, PFOS levels showed statistically significant decreases post-2000 in the Cumberland Sound animals with an annual decrease of 9.8% from 2000 to 2010. PFOSA levels also significantly decreased from 2002 to 2010. At Hendrickson Island the decline of PFOS was lower over the period 2000–2011 (2.4%) and not statistically significant. The post-2000 PFOS decreases in the Hendrickson Island and Pangnirtung beluga whales are consistent with the trends reported for ringed seals from Arviat and Resolute Bay (Butt et al. 2007b) (Table 4.8). The trends in the two beluga populations in the Canadian Arctic differ from those of belugas in the Chukchi Sea where rapid increases were observed for PFCAs (11–14% per year) and PFOS (9.4% per year) over the period 1989 to 2006 (Reiner et al. 2011).

Chlorinated paraffins: SCCPs appeared to reach highest levels in beluga in the late 1990s and declined rapidly to near detection limits by 2007 (Figure 4.89). No data are yet available for results post-2007 to assess the direction of further trends. The decline in concentrations may reflect reduced use of SCCPs in North America and Western Europe (Fiedler 2010). However, production of chlorinated paraffins (including SCCPs) has increased substantially in China during the period 2000–2007 (Fiedler 2010). Whether this will eventually impact the Canadian Arctic is unknown.

TABLE 4.10 Approximate percent annual increase or decreases for PBDEs, HBCDD and PFASs in beluga samples[1]

Location	ΣPBDEs		HBCDD		PFCAs		PFOS	
	#Years & range	% dec or inc /y[1,2]	#Years & range	% dec or inc /y			#Years & range	% dec or inc /y[1,2]
Beaufort	(7) 1993–2004	+8.8	(7) 1993–2004	+13	(13) 93–10	-11	(4) 1984–2000	+6.5
Beaufort	(5) 2004–2009	-8.8 ns	(6) 2004–2009	-3.3 ns	–	–	(11) 2000–2010	-2.4 ns
Cumberland Sound	(7)1982–2008	+5.9	(11) 1982–2010	+8.7		-7.8 ns	(8) 2000–2010	-9.8
Cumberland Sound	–	–	–	–	–	–	(5) 1982–2000	+4.7

[1] Results are based on simple linear regressions of log (geomean concentrations) vs. time (years).

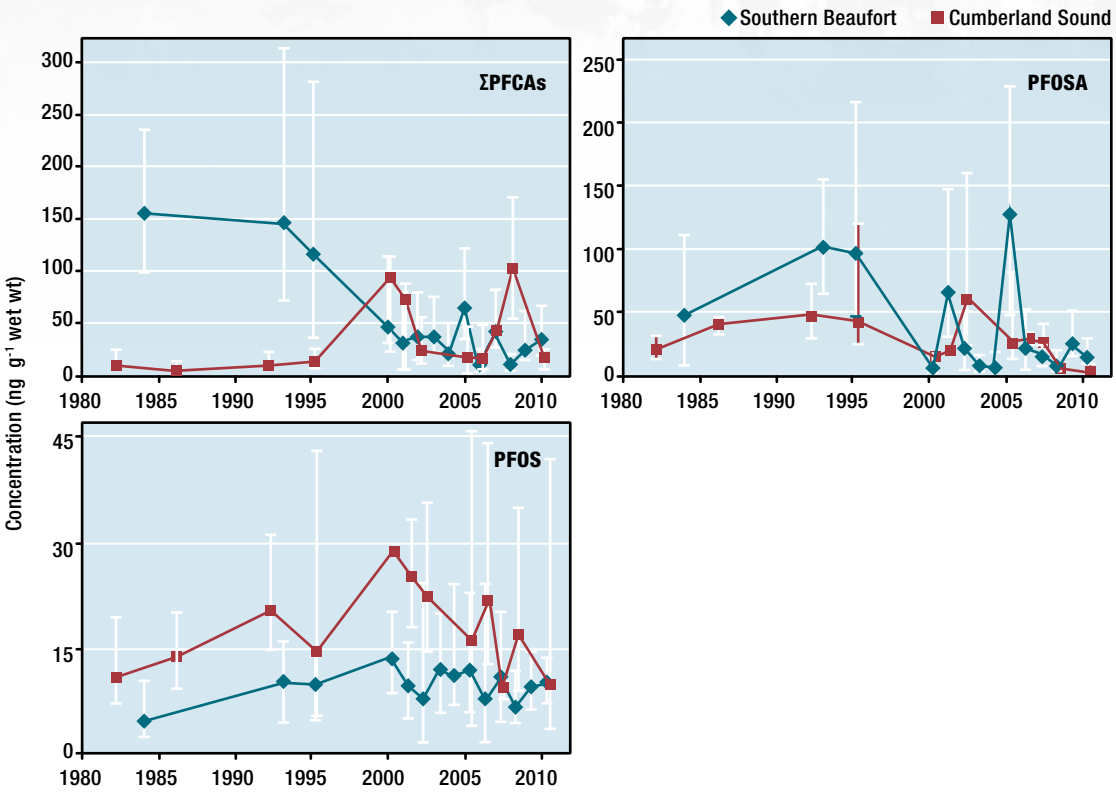

FIGURE 4.88

Temporal trends of ΣPFCAs, PFOSA and PFOS in beluga liver samples from the southern Beaufort Sea and Cumberland Sound stocks. Symbols represent arithmetic mean concentrations and vertical lines show minimum and maximum concentrations (Tomy et al. 2011b).

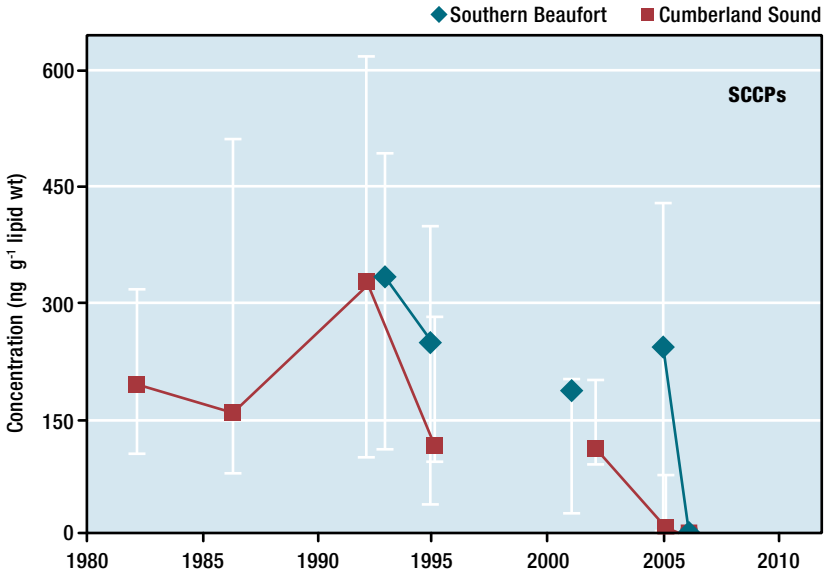

FIGURE 4.89

Temporal trends of SCCPs in beluga blubber samples from the southern Beaufort Sea and Cumberland Sound stocks. Symbols represent arithmetic mean concentrations and vertical lines show minimum and maximum concentrations (Tomy et al. 2011b).

Photo: Benedikt Guomundsson/ArcticNet

4.2.4.5. Legacy POPs in polar bears

Time period comparisons over the period of 1989–2008 were recently reported for 7 polar bear subpopulations in Canada as shown in Figure 4.90. Due to different sampling times for each subpopulation, they are based on year ranges. As shown in Figure 4.91, studies of POPs in polar bears from western Hudson Bay over the period 1991–2007 enabled temporal trends to be examined over a 17-year period (McKinney et al. 2009, McKinney et al. 2010).

McKinney et al. (2011b) reported that ΣCHL and *p,p'*-DDE levels decreased consecutively from the period 1989–1993 (Norstrom et al. 1998) to 1996–2002 (Verreault et al. 2005c) and from 2005–2008 in most Canadian bear subpopulations. The 2005–2008 levels were lower relative to 1989–1993 levels in all subpopulations. The only exception was ΣCHL levels in western Hudson Bay bears. In 2001–2002, concentrations were suggested to have levelled off in this region (Verreault et al. 2005c); however, nearly a 4-fold decline was observed in ΣCHL levels in southern Hudson Bay bears in the 2005–2008 study relative to a 1989–1993 study (Norstrom et al. 1998). The relatively stable ΣCHL levels in western Hudson Bay may be related to diet and food web changes within this region as indicated by dietary tracer changes of stable carbon isotope ratios and fatty acid profiles that have been correlated with sea-ice changes in Hudson Bay (McKinney et al. 2009). In contrast, western Hudson Bay *p,p'*-DDE levels substantially decreased compared to temporal patterns in most subpopulations. McKinney et al. (2009) concluded that this may be related to a previous local source and contrasting ecological distribution of DDT in this region relative to other contaminants.

McKinney et al. (2011b) also found higher ΣPCBs in all samples collected in the period 2005–2008 compared to 2001–2002 (Verreault et al. 2005) except for southern Hudson Bay (Figure 4.90). Overall ΣPCB levels appeared to have levelled off in the 2000s in most subpopulations, subsequent to the declines observed in the 1990s (Norstrom et al. 1998). Dieldrin levels also showed no overall declines, consistent with other temporal studies (Verreault et al. 2005c). The only available comparisons for ΣHCH, ΣCBz, and mirex were between 2005–2008 and 2001–2002. These showed higher ΣCBz in all subpopulations in 2005–2008 samples, e.g., by 2 times in Davis Strait and western Hudson Bay, while mirex and ΣHCH were generally unchanged i.e., within < 20% change (Figure 4.90). Unfortunately, previous studies (Norstrom et al. 1998) found that analytical variation associated with recovery losses of relatively volatile α-HCH and CBzs led to erroneously lower adipose levels, confounding temporal comparisons between studies (McKinney et al. 2010).

Longer-term trends were assessed by McKinney et al. (2009, 2010) in the western Hudson Bay subpopulation of polar bears at intervals from 1991 to 2007. They examined temporal trends of PCB and OCP levels both on an individual and sum(Σ) contaminant basis. Results are summarized Table 4.11 and in Figure 4.91. Over the 17-year period, ΣDDT (and *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT) decreased (–11% per year); α-HCH) decreased (–12% per year); β-HCH increased (+8.3% per year); and ΣPCB and ΣCHL, both contaminants at highest concentrations in all years, showed no distinct trends even when compared to previous data for this subpopulation dating back to 1968. Some of the less persistent PCB congeners decreased significantly (–1.6% per year to –6.3% per year), whereas CB153 levels tended to increase (+3.3% per year) (McKinney et al. 2010). Parent CHLs (*cis*-nonachlor, *trans*-nonachlor) declined, whereas non-monotonic trends were detected for metabolites (heptachlor epoxide, oxychlordane). ΣCBz, octachlorostyrene, mirex, $\Sigma MeSO_2$-PCB and dieldrin did not significantly change. Including earlier results from Norstrom for samples from 1968, 1972 and 1989 showed that ΣPCB, ΣCBz and ΣCHL had remained unchanged over the period from 1968 to 2007, although large gaps in the time series in the 1970s and 1980s make this uncertain (Figure 4.91).

McKinney et al. (2009, 2010) assessed whether long-term ecosystem changes affecting contaminant levels might also affect contaminant patterns. They examined the influence of year (i.e., aging or "weathering" of the contaminant pattern), dietary tracers (carbon stable isotope ratios, fatty acid patterns) and biological (age or sex) group on congener/metabolite profiles. Patterns of PCBs and CHLs were correlated with dietary tracers and biological group, but only PCB and CHL patterns were correlated with year. DDT patterns were not associated with any explanatory variables, possibly related to local DDT sources. Including stable carbon isotope ratios, and fatty acid indices representing mainly fatty acids α-linolenic acid and *cis*-7,10,13,16,19-docasapentaenoic acid (index 1) and *cis*-4,7,10,13,16,19-docasahexaenoic acid (index 2) resulted in an improved relationship of the contaminant concentrations over time compared with simple regression (Table 4.12).

Overall, the results suggested there would be trends toward higher actual contaminant concentrations with increased harp and harbour seal diets of the polar bear versus those if diet remained constant. It was concluded that contaminant pattern trends may be useful in distinguishing the possible role of ecological or diet changes on contaminant burdens from expected dynamics due to atmospheric sources and weathering.

TABLE 4.11. Trends of legacy POPs in western Hudson Bay polar bears over the period 1991 to 2007 with and without correction for diet (McKinney et al. 2009, McKinney et al. 2010).

	Simple regression[1]		Multiple regression with year and diet tracers[2]					
Contaminant	r^2	% change	r^2	year	$\delta^{13}C$	FA-Index1	FA-Index2	% change
α-HCH	0.83	-12	0.83	-0.91	0.01	-0.003	0.006	-12
β-HCH	0.90	+8.3	0.64	0.64	-0.15	0.2	-0.19	+6.4
ΣPCB	0.04	+1.7	0.36	-0.11	0.02	0.6	0.23	-0.92
Σ_{10}PCB	0.33	+2.0						
CB153	0.55	+3.3						
ΣCHL	0.00003	0.04	0.14	-0.16	-0.17	0.3	-0.36	-1.1
t-nonachlor	0.74	-4.1						
ΣCBz	0.13	-0.92						
HCB	0.19	+1.6						
ΣDDT	0.57	-11	0.68	-0.46	0.21	-0.43	0.15	-6.7
p,p'-DDE	0.87	-9.7						
mirex	0.52	+1.4						

[1] Based on log contaminant concentration vs. time. Simple regressions are from McKinney et al. (2009); others from McKinney et al. (2010). All regression coefficient (R^2) values are statistically significant ($p < 0.05$) except for simple regression of log ΣCHL vs. year.

[2] Diet tracers are stable carbon isotope ratios $\delta^{13}C$ and fatty acid indices (FA).

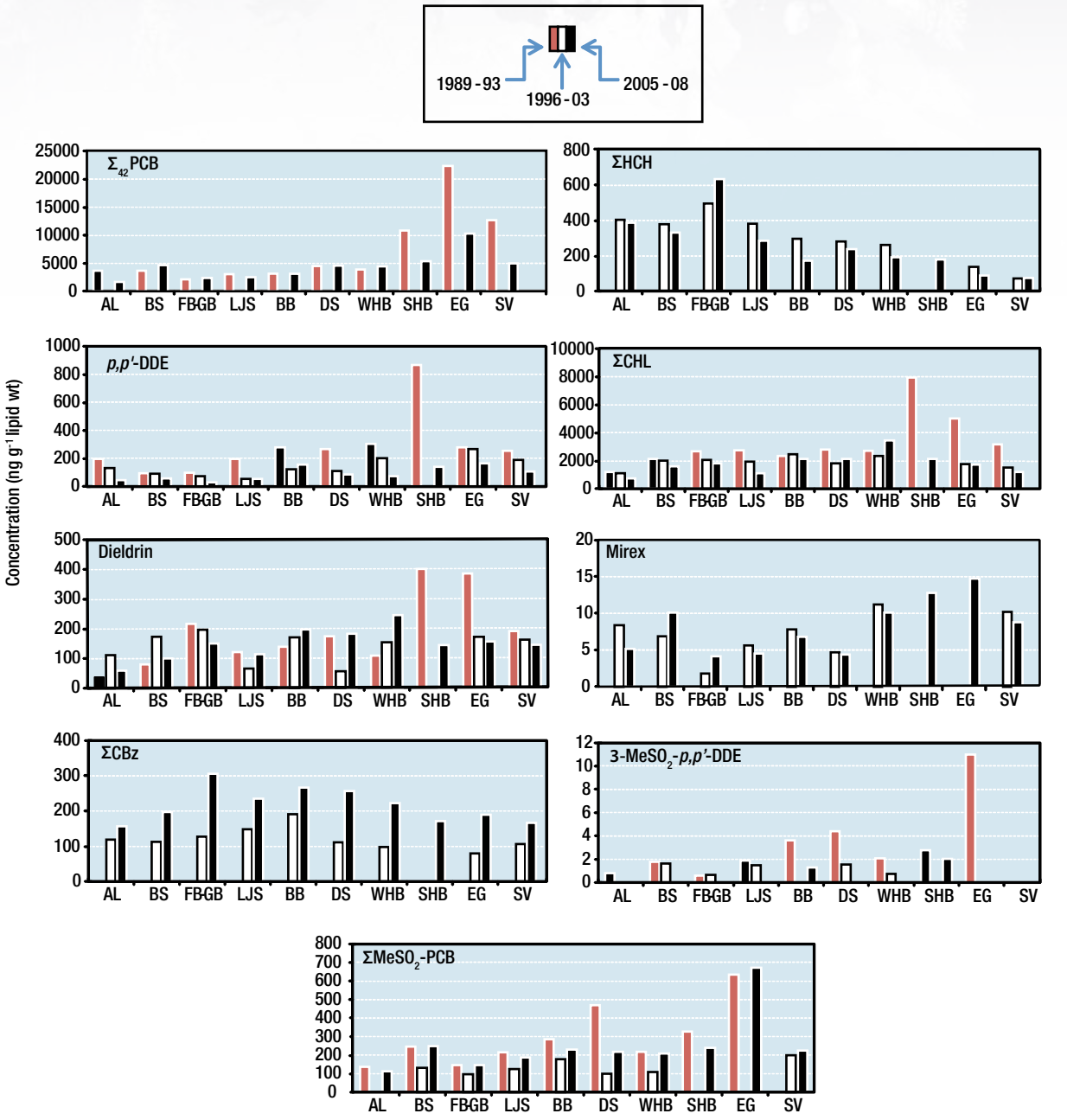

FIGURE 4.90

Temporal comparisons of legacy POPs in 7 polar bear subpopulations in Canada collected in 1989–1993 Letcher et al. 1995; Norstrom et al. 1998), 1996–2002 Verreault et al. 2005) and 2005–2008 (McKinney et al. 2011b). BS= eastern Beaufort Sea, GB= Gulf of Boothia, LJS=Lancaster & Jones Sound, BB= Baffin Bay, DS = Davis Strait (East Baffin Island), WHB = Western Hudson Bay, SHB = Southern Hudson Bay. Bars represent geometric mean concentrations in subcutaneous fat.

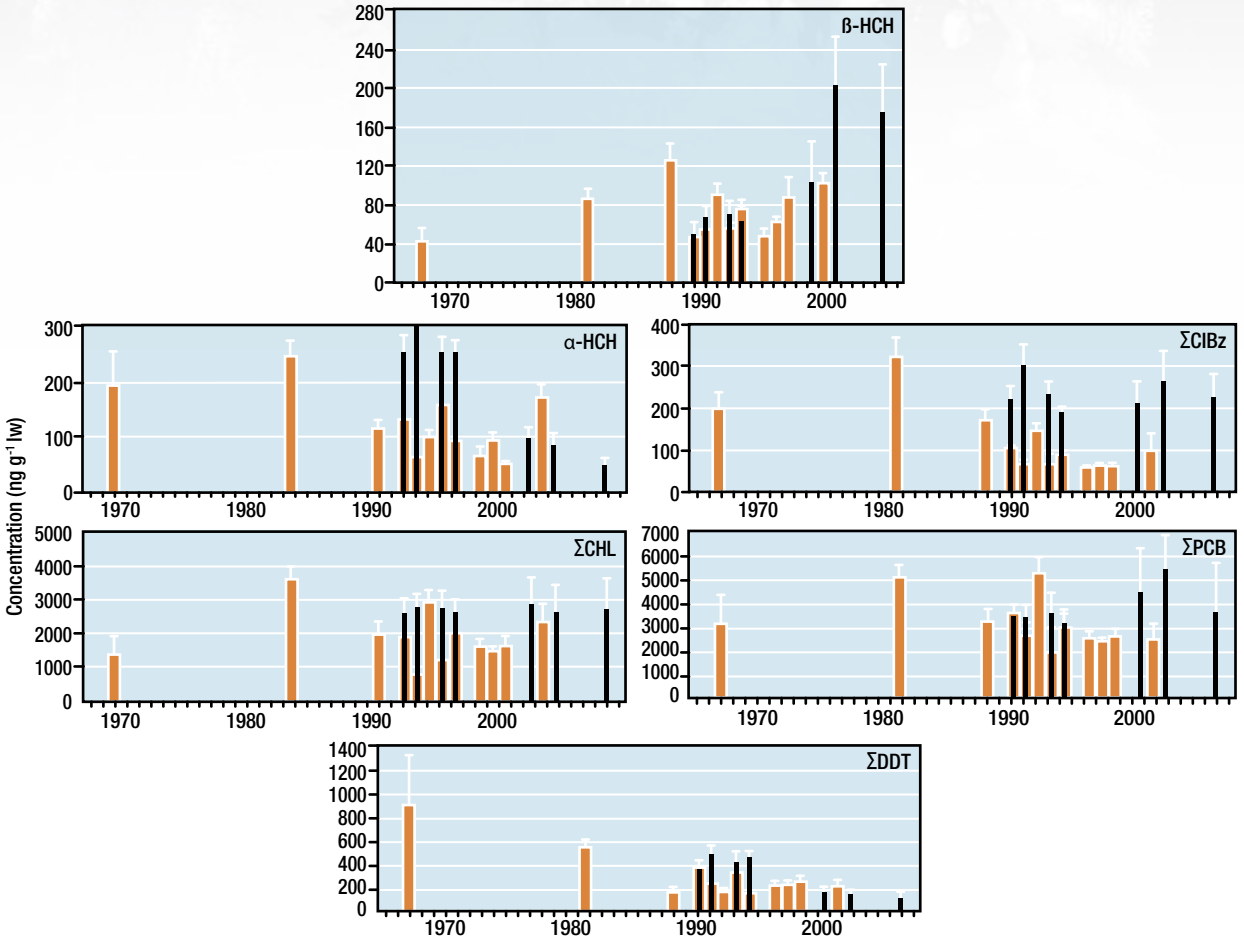

FIGURE 4.91

Levels (geometric mean, +95% confidence interval) of PCBs and organochlorine pesticides in adipose of polar bears from western Hudson Bay collected in 1968–2007 (adapted from McKinney et al. 2010). Orange bars are from de Wit et al. (2004) with original data from Norstrom (2001) and Verreault et al. (2005). Overlaid black bars are from re-analysis of archived samples.

4.2.4.6. New POPs in polar bears

Brominated Flame Retardants: Temporal trends of brominated flame retardants were reported in adipose tissue from the western Hudson Bay (WHB) polar bear subpopulation between 1991 and 2007 (1991, 1992, 1994, 1995, 2001, 2003 and 2007) (McKinney et al. 2010). Sample sizes ranged from 9–15 individuals with primarily adult females analyzed in the early years. The suite of BFRs analyzed included 37 PBDE congeners, HBCDD, PBBs (BB-101 and BB-153), PBT, PBEB, HBB, BTBPE and DBDPE. The Σ_{37}PBDE levels increased in a log-linear manner from 1991 to 2000 with an overall annual increase of 13% (Table 4.12). Similar trends (annual increase of 13%) were found for Σ_4PBDE (BDE-47, BDE-153, BDE-99 and BDE-100). These compounds were the only congeners consistently detected and contributed 90% of the Σ_{37}PBDE concentration. BDE-209 was infrequently detected (< 9% of all samples) in the WHB polar bear subpopulation. Generally lower levels of PBDEs were observed in 2007 as compared to 2003 (with the exception of BDE-47) and may indicate stabilizing or decreasing concentrations as the result of penta-BDE and octa-BDE commercial mixture phase-out in late-2004. For example, Σ_{37}PBDE levels increased from 29.3 ng g^{-1} lw (mean) in 2001 to 50.8 ng g^{-1} lw in 2003, decreasing to 38.8 ng g^{-1} lw in 2007. However, the authors noted that ΣPCB levels were also elevated in 2003, relative to 2001 and 2007, and thus the apparent recent declines may be the result of inter-annual variability. Additional years of monitoring are necessary to confirm temporal trends.

HBCDD was generally not detected in the 1990s in Western Hudson Bay bears, but was frequently detected in the 2000s sampling times. Similar to PBDE levels, HBCDD concentrations peaked in 2003 (mean = 11.7 ng g^{-1} lw) relative to 2001 (3.9 ng g^{-1} lw)

and 2007 (3.1 ng g^{-1} lw). PBEB, HBB and DBDPE were very infrequently detected, at low- to sub-ng g^{-1} ranges, and thus temporal trends were not assessed. The influence of specific diet tracers (carbon stable isotope ratios, fatty acid patterns) on the PBDE congener pattern was investigated using principal component analysis. It was shown that higher and lower proportions of BDE-153 and BDE-47, respectively, were associated with a higher fatty acid index that represents higher proportions of harp or harbor seals and lower proportions of bearded seals in the diet. This meant that the concentration of ΣPBDE increased at a significantly faster rate than if the diet had not changed.

The same suite of BFRs were analyzed in polar bear adipose samples, collected between 2005 and 2008, from 8 locations across the Canadian Arctic (McKinney et al. 2011b). Temporal trends were assessed by comparing the study results with those previously reported from 1996–2002 (Muir et al. 2006a) (Figure 4.92). Only PBDE trends could be investigated since the other BFRs were not comprehensively monitored.

The ΣPBDE levels were lower during the period 2005–2008 in 5 out of 7 populations (1996–2002 levels for southern Hudson Bay were not available), as compared to the period of 1996–2002. The exceptions were western Hudson Bay, which showed

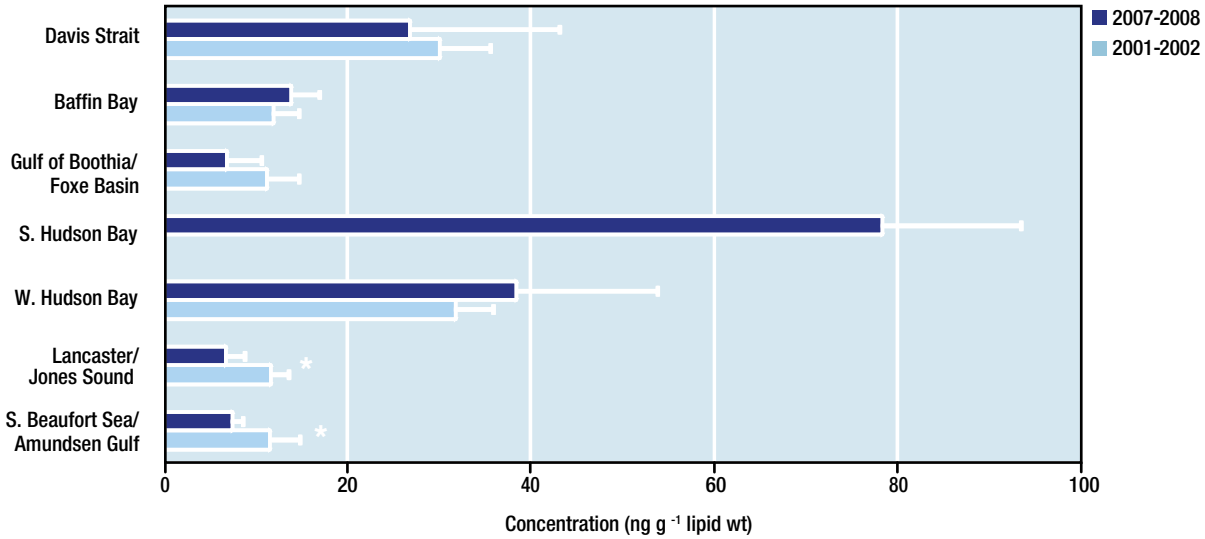

FIGURE 4.92

Two point temporal comparisons of Σ_4PBDE (sum of BDE-47, -99, -100, -153) concentrations in Canadian polar bear populations between 2001–2002; (Muir et al. 2006a), Southern Hudson Bay data not available) and the present 2007–2008 levels (McKinney et al. 2011b). Asterisks mark significant ($p < 0.05$) decreases from 2001–2002 to 2007–2008.

Photo: Thorsten Mauritsen/ArcticNet

TABLE 4.12. Trends of brominated flame retardants in western Hudson Bay polar bears over the period 1991 to 2007 (McKinney et al. 2009, McKinney et al. 2010).

	Simple regression[1]		Multiple regression with year and diet tracers[2]					
Contaminant	r^2	% change	r^2	year	$\delta^{13}C$	FA-Index[1]	FA-Index[2]	% change
Σ_{37}PBDE	0.91	13	0.82	0.67	-0.15	0.29	-0.12	+9.4
BDE-47	0.93	13						
BDE-99	0.86	13						
BDE-153	0.84	17						
BB-153/BDE-154	0.23	5.5						

[1] Based on log contaminant concentration vs. time. All regression coefficient (R2) values are statistically significant ($p < 0.05$) except for simple regression of log BB-153/BDE154 vs. year.

[2] Diet tracers are stable carbon isotope ratios δ13C and fatty acid indices (FA).

increasing levels, and Davis Strait, which showed steady concentrations. Overall, these trends may indicate stabilizing or decreasing concentrations in top arctic marine predators as the result of penta-BDE and octa-BDE commercial mixture phase-out in late-2004.

A study by McKinney et al. (2011c) assessed and compared the oxidative and reductive biotransformation of PBDEs (including BDE-209) and DBDPE using an in vitro system based on liver microsomes from various arctic marine-feeding mammals: polar bear, beluga whale and ringed seal, and in laboratory rat as a mammalian model species. Greater depletion of fully brominated BDE-209 (14–25% of 30 pmol) and DBDPE (44–74% of 90 pmol) occurred in individuals from all species relative to depletion of lower brominated PBDEs (BDE-99, -100, and -154; 0–3% of 30 pmol). No evidence of simply debrominated metabolites was observed. Investigation of phenolic metabolites in rat and polar bear revealed formation of two phenolic, likely multiple debrominated, DBDPE metabolites in polar bear and one phenolic BDE-154 metabolite in polar bear and rat microsomes. For BDE-209 and DBDPE, observed metabolite concentrations were low to nondetectable, despite substantial parent depletion. It was concluded that these findings may suggest a possible underestimation of the ecosystem burden of total BDE-209, as well as its transformation products, and that there is a need to research to identify and characterize the persistence and toxicity of major BDE-209 metabolites. Similar cause for concern may exist regarding DBDPE, given the similarities of physicochemical and environmental behavior to BDE-209, current evidence of biotransformation, and increasing use of DBDPE as a replacement for BDE-209.

Perfluorinated alkyl substances: Temporal trends of PFASs in polar bears, between 1972 and 2002, from two regions in the North American Arctic were originally reported by Smithwick et al. (2006a) and were summarized in Butt et al. (2010). The "eastern" population (1972, 1975, 1982, 1984, 1993 and 2002) consisted of samples collected near northern Baffin Bay, and the "western" population (1972, 1982 and 2002) consisted of samples collected near Barrow, Alaska. Significant increases in PFOS and C_9–C_{11} PFCA levels were shown in both populations over the study period. Significant PFHxS increases were only observed in the western population. Similarly, significant PFOA increases were only observed in the eastern group. PFOSA showed decreasing trends in both populations, but was only significant in the eastern population. Doubling times ranged from 3.6 ± 0.9 y for PFNA in the eastern group to 13.1 ± 4.0 y for PFOS in the western group. It was shown that the mean doubling times were much shorter in the eastern population (5.8 y) as compared to the western population (9.1 y). Further, it was suggested that the PFOS doubling times in the polar bears (9.8 y and 13 y in the eastern and western populations, respectively) was in agreement with the PFOSF production doubling time of approximately 11 y.

PFASs in polar bear liver samples from more recent collections (2007 and 2008) were reported from 7 Canadian management zones (Letcher et al. 2010a, Letcher et al. 2009). The PFASs analyzed included C_4, C_6, C_8 and C_{10} PFSAs, C_6–C_{15} PFCAs, PFOSA, 6:2, 8:2 and 10:2 FTOH, and the 6:2, 8:2 and 10:2 FTUCA. Temporal trends were assessed by comparing the 2007–2008 levels to those from 2001–2002 reported by Smithwick et al. (2006b) (Figure 4.93). Overall, the trends showed lower PFOS levels in 2007–2008 as compared to 2001–2002 with the exception of south Hudson Bay, which showed increases. However, the observed decreases were only statistically significant for Baffin Bay, Davis Strait and GB/FB (Figure 4.93). The results differ from those of East Greenland polar bears (Dietz et al. 2008, Dietz et al. 2013). In those studies, PFOS concentrations continued to increase exponentially over time beginning in the late 1990s and up to 2010.

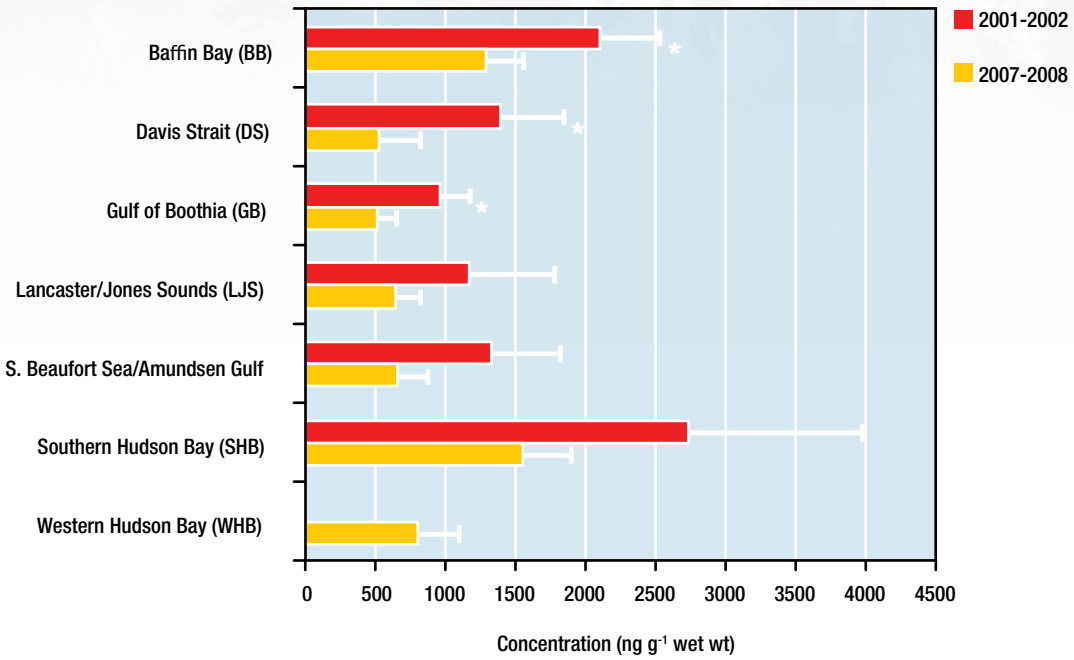

FIGURE 4.93

Two point temporal comparisons of PFOS concentrations in liver of 7 polar bear populations between 2001 and 2002 (Smithwick et al. 2005; western Hudson Bay data not available) and levels in 2007–2008 (Letcher et al. 2010a). Asterisks denote significant ($p < 0.05$) decreases from the 2001–2002 period to the 2007–2008 period.

4.2.4.7. Assessment of temporal trends in marine mammals

- Beluga, ringed seals and polar bear are showing similar overall trends for legacy POPs with the relative magnitude of ΣDDT > α-HCH > Σ_{10}PCB > ΣCHL similar to that found by Rigét et al. (2010) for all time series in arctic marine mammals, in general. There have been limited or no significant changes in concentrations of ΣPCBs and ΣCHL in most regions but general, relatively rapid decreases for DDT and α-HCH.
- Fewer significant trends are observed in beluga, which may reflect the long period of maternal transfer of stored POPs compared to seals.
- The case of increasing β-HCH in seals in the Beaufort and Lancaster region (as well as in sea-bird eggs) highlights the importance of ocean water moving through the Arctic Archipelago from the Pacific Ocean via the Bering Sea and possibly Russian freshwater inputs.
- The lack of decline of PCBs, CHL and toxaphene likely reflects continuing inputs via atmospheric and oceanic pathways as the temporal trends of PCBs and CHL in atmospheric samples from Alert also show only slow declines.
- However, the slow or non-significant declines could also reflect dietary changes associated with recent changes in ice cover. This could alter foraging of beluga, ringed seals and polar bears. The study by McKinney et al. (2010) suggested that for polar bears there would be trends toward higher actual contaminant concentrations with increased harp and harbour seal diets of the polar bear compared to those if diet remained constant.
- While legacy POPs are showing overall similar trends in beluga, ringed seals and polar bears as well as in seabirds, this is not the case for ΣPBDEs and PFASs. PBDEs were increasing in polar bears in west Hudson Bay while remaining stable or declining in ringed seals as of 2002.
- Significant declines of ΣPBDEs were found in bears sampled from the Beaufort Sea and Lancaster/Jones Sound whereas ΣPBDEs increased in ringed seals in both areas. However, the comparison for bears was limited to 2 time points compared with annual sampling for ringed seals and thus trends cannot be fully compared. The trends of ΣPBDEs in beluga in the southern Beaufort Sea also differ from ringed seals, having reached an apparent maximum earlier than for seals.
- The higher PFCAs in beluga in the 1980s and 1990s in the Beaufort Sea stock is unusual and differs from observations of ΣPFCAs in ringed seals (section 4.2.4.2) and seabirds (section 4.2.3.2). Also, the

global production of PFCA precursors is thought to have increased until at least the mid 2000s (Armitage et al. 2009). Possibly, the fact that these beluga are migratory, overwintering in the Bering and Chukchi seas and thus having greater exposure to Pacific Ocean influenced waters with varying PFCA concentrations there compared to the Arctic Ocean, plays a role in these different trends.

- On the other hand, the doubling times for PFOS concentrations in seals, beluga and polar bears during the 1990s to early 2000s was similar to the doubling time of production of perfluorooctanesulfonyl fluoride (PFOSF)-based products during the 1990s indicating a rapid response to global emissions. The decline of PFOS appears to differ in beluga, ringed seals and polar bears particularly in the western Canadian Arctic where PFOS appears to be declining in beluga, stable in polar bears, and increasing slowly in ringed seals.
- Annual sampling of beluga and ringed seals, implemented under the NCP "Blueprint" as of 2004, has been instrumental in demonstrating the rise of HBCDD in ringed seals and beluga, which appears to be rapid beginning as of about 2006. Data are too limited and levels to close to detection limits to assess whether other BFRs are increasing.
- Time trend information is also limited for other POPs such as endosulfan (available only for seals), toxaphene (seals and beluga), chlorinated paraffins (currently only for beluga), planar PCBs and PCDD/Fs (seals, seabirds), and chlorinated naphthalenes (seals, seabirds).
- The statistical power of the time series for legacy POPs and for PBDEs and PFASs has improved relative to results in CACAR 2003 (Fisk et al. 2003) which were typically for 2 or 3 time points. The ability to detect a 5% change at 80% power has been achieved for selected POPs at Lancaster Sound (seals and seabirds).
- No new temporal trend data are available for narwhal or walrus.
- The geographic coverage of temporal trend studies is limited–for seals it does not currently include any eastern Arctic locations and for beluga it does not include Hudson Bay. In the case of polar bears a strong temporal trend dataset is available only for the western Hudson Bay subpopulation.
- Species coverage is limited for seals. With reports of increasing numbers of harbour and harp seals, some attention should be given to determining contaminant levels in these species.

4.2.5. Statistical power of seabird egg and ringed seal temporal trend datasets

As discussed in earlier sections, annual sampling was initiated in 2004 for selected marine and freshwater species in the NCP environmental trends program in order to examine the inter-year variation in contaminants data, and to improve the statistical power of the temporal trend data series. To illustrate the improvement for seabird eggs and ringed seals, the PIA statistical package (Bignert 2007) was used to analyze trends in these time series datasets by comparing results with annual sampling to those with sampling on a five-year cycle. The results show that the recent annual sampling has greatly increased the ability to detect change. For both ΣDDT and ΣPCBs in seabirds, the power was nearly doubled (e.g., thick-billed murre 24% to 52%) and least detectable change lowered (e.g., 11% to 6.3% in northern fulmars) compared to results if sampling had continued on a five-year cycle (Table 4.13). For ΣDDT and ΣPCB in ringed seal blubber, statistical power is already high due to the much larger dataset (n=212 samples; 17 sampling years). But the lowest detectable change is 2-fold lower with the additional sampling compared to sampling approximately every 5 years (Table 4.13).


Photo: Adam Morris

TABLE 4.13. Results from power analysis of ΣDDT and ΣPCB in thick-billed murre and northern fulmar eggs from Prince Leopold Island (1975–2008) and ringed seals from Resolute Bay (1972–2011) comparing recent annual sampling with an every 5-year sampling regime over 30–40 years for each species.

		Thick-billed murre		Northern fulmar		Ringed seals	
	Statistial parameter[1]	Including annually 2005–2008	Every 5 y	Including annually 2005–2008	Every 5 y	Including annually 2005–2008	Every 5 y
		n=50; #y=12	*n*=35; #y=9	*n*=51; #y=11	*n*=36; #y=8	*n=212, #y=17*	*n=131, #y=10*
ΣDDT	% decline or increase	-2.5	-2.5	-4.9	-5.1	-3.0	-2.4
	Power	52	24	54	17	78	93
	LDC (%) @ Power 80%	7	11	6.8	15	4.2	8.1
	Y required to detect 5%	15	15	14	15	21	21
ΣPCB	% decline or increase	-3.8	-3.4	-4.8	-5.0	-2.2	-1.7
	Power	65	38	61	27	73	90
	LDC (%) @ Power 80%	6	8.6	6.3	11	4.5	8.6
	Y required to detect 5%	14	13	13	13	26	26

[1] Power of current time series to detect a log-linear trend of 5%; LDC = Lowest detectable change in current time series; Y required = Number of years required to detect an annual change of 5% with a power of 80%.

4.2.6. Climate change effects on contaminants trends in biota

An intensely focused environmental stress element in the Arctic is climate change caused by global warming and/or temperature changes (Graversen et al. 2008). There is an established link between recent climate change and phenological, geographical and compositional changes to ecosystems across many regions of the world (Parmesan and Yohe 2003). Although the magnitude of warming is regionally variable, it has been reported that for the Arctic, the magnitude is nearly twice that of the global average (Graversen et al. 2008, Johannessen et al. 2004). Records of increasing temperatures, melting glaciers, reductions in extent and thickness of sea-ice, thawing permafrost and rising sea level all are results of a warming Arctic. Observations suggest that precipitation has increased by roughly 8% across the Arctic over the past 100 years. Much of the precipitation appears to be coming as rain, mostly in winter, and the increasing winter rains, which fall on top of existing snow, result in faster snowmelt. Sea-ice is one of the most important climatic variables and it is a key indicator and agent of climate change. In the Arctic, ice is a supporter of life bringing the sea animals to the arctic lands by becoming an extension of the land. Over the past 30 years, the annual average sea-ice extent has decreased by about 8% whereas sea-ice extent in summer has declined more dramatically than the average annual, with a loss of 15–20% of the late-summer ice coverage. As the decline in arctic sea-ice opens closed passages, this will increase marine access for transport. Along with increasing access to shipping routes and resources, it will bring increasing risk of environmental contamination caused by these activities, especially due to oil spill and other industrial accidents. Climate change is also projected to cause vegetation shifts due to rising temperatures which favour taller, denser vegetation, and will thus promote the expansion of forests into the arctic tundra and tundra into the polar deserts. A changing environment can affect wildlife populations under abnormal and possibly increased stressor conditions that are outside of cyclic/seasonal conditions, ranging from habitat loss and alteration to new and more virulent diseases.

Climate-related change that will influence POPs may result in increased levels, and at the minimum, perturbations of contaminant exposure at various levels of the food web. Contaminants including POPs reaching the Arctic as a result of LRAT from the other regions are among the major environmental stresses interacting with climate change. Particular arctic animals that are high on the marine food chain currently show high levels of POPs such as DDT and PCBs since POPs become increasingly concentrated

as they move up the food chain. As a result, top predators such as polar bear and arctic fox have the highest levels of contaminants followed by various seals, whales, fish, seabirds and birds of prey. Air masses carry contaminants and precipitation deposits them onto the land and sea. Temperature has a major role in determining the distribution of contaminants between air, land and water. Therefore, climate change-related alterations in wind patterns, precipitation and temperature can change the routes of contaminant entry, locations and amounts of deposition in the Arctic. More extensive melting of multi-year sea-ice and glaciers would result in rapid release of large pulses of pollutants that were captured in the ice over years or decades. Moreover, climate change would increase bio-transport of contaminants to the Arctic as recent evidence suggests that salmon migrations undergo large, climate- related variations and that Pacific salmon may respond to change by moving northward into arctic rivers. As contaminants are subject to accumulation and biomagnifications in salmon in the Pacific Ocean, they are transported to arctic waters by means of bio-transport by salmon. For some arctic lakes, fish may bring more POPs than does atmospheric deposition. Similarly, changing bird migrations might also act as bio-transporters of POPs to particular watersheds of the Arctic.

Changes in the distribution and bioaccumulation of contaminants are expected to be caused by climate change. Climate change can affect air and water masses and consequently modify contaminant transport. This is particularly true in arctic wildlife and food webs where arctic warming and impacts on sea-ice conditions is generally occurring, and more intensely in specific areas such as Baffin Bay and Hudson Bay. Although very limited, studies have linked Arctic warming climate change to region-specific or temporal shifts in food web structure and thus dietary influences on the level and pattern of contaminant exposure in mammals and birds. Thick-billed murres have been monitored for contaminants since 1993 at Coats Island in northern Hudson Bay, and since 1975 at Prince Leopold Island in the High Arctic (Braune et al. 2002). A decrease in trophic position, as indicated by $\delta^{15}N$, has occurred in eggs of thick-billed murres breeding at Coats Island, whereas murre eggs from Prince Leopold Island have not shown any consistent change over time Braune (2007). Arctic cod is the main prey of thick-billed murres at Prince Leopold Island in the High Arctic (Davidson et al. 2008, Gaston and Bradstreet 1993) and, until the mid-1990s, was the most common prey item found in the diet of nestling murres throughout the Canadian Arctic (Gaston and Jones 1998). However, dietary studies have shown that there has been a shift from arctic cod and benthic fish species to capelin and sandlance in the diet of thick-billed murres at Coats Island in northern Hudson Bay between 1980 and 2002 (Gaston et al. 2003). Warming ocean conditions and longer ice-free periods have been documented for Hudson Bay (Davidson et al. 2008, Gaston et al. 2009) leading Gaston et al. (2003) to suggest that the decline in arctic cod and increase in capelin and sandlance were associated with a general warming of Hudson Bay waters. In contrast, there has been no trend reported in summer ice cover at Prince Leopold Island (Davidson et al. 2008). Adjusting the egg concentrations of ΣPCB and ΣDDT for trophic position at both murre colonies results in little change at Prince Leopold Island but reduces the rates of decline at Coats Island (Table 4.13) suggesting that the shift in diet which occurred in the murres at Coats Island has affected the contaminant temporal trends for that colony.

TABLE 4.14. Temporal trends in egg organochlorine concentrations at two thick-billed murre colonies, Prince Leopold Island (1975–2008) and Coats Island (1993–2008)[a]

		unadjusted data			adjusted data			
Contaminant	Colony	r	p	slope	r	p	slope	% rate
ΣPCB	Prince Leopold Island	-0.84	<0.0001	-0.0409	-0.84	<0.0001	-0.0410	100
	Coats Island	-0.70	<0.0001	-0.0470	-0.67	<0.0001	-0.0425	90
ΣDDT	Prince Leopold Island	-0.66	<0.0001	-0.0241	-0.65	<0.0001	-0.0236	98
	Coats Island	-0.49	0.0031	-0.0333	-0.35	0.0376	-0.0213	64

[a] Trends were calculated using lipid-corrected, unadjusted (ln-transformed concentrations) and adjusted data (ln-transformed and adjusted for temporal change in murre trophic position; i.e., $\delta^{15}N$). Percent rate is the relative rate of temporal decline of the adjusted data relative to the unadjusted data.

Photo: Gita Laidler

For polar bears from Hudson Bay and across the Alaskan, Canadian and East Greenland Arctic, studies have shown that for various chlorinated and brominated contaminants, shifts in diet (and their food webs) has had contaminant-specific effects on spatial or temporal trends of contaminants (McKinney et al. 2011a, McKinney et al. 2010). Changes in water masses may also result in changes in temperature, salinity, and species composition and food web structures (Borgå et al. 2010).

Modifications in temperature may also alter partitioning of organic compounds between dissolved and particulate phases in water and air and therefore affect the bioavailability of contaminants in aquatic ecosystems (Borgå et al. 2010). Ultimately, annual changes in contaminants biomagnification could be indicative of climate change disturbance.

Among the other biological and physiological factors that are important in interpreting contaminant data of arctic wildlife are life history parameters and lipid content (Ylitalo et al. 2001). Lipid content is critical in the tissue dynamics of many lipophilic POPs, and is commonly oversimplified from a biological perspective. POPs concentrations in various tissues (blubber, liver, kidney, muscle, and brain) were similar on a lipid weight basis, except for brain, which had lower lipid-adjusted POP concentrations because the blood–brain barrier can limit contaminant transfer (Krahn et al. 2001). Alternately, delayed transfer of POPs to the brain hypothetically does not explain lower brain POP levels with respect to pseudo-equilibrium concentrations established across the blood–brain barrier. Lower brain concentrations are likely related to the higher polarity of brain lipids (e.g., phospholids) compared to adipose tissue for example. Regardless, assessing toxicokinetic distribution is important especially for target organs (e.g., brain).

Emphasis should also be put on the multiple ecological, biological, and physical (natural and anthropogenic) variables that need to be considered when analyzing contamination in species and more importantly when comparing data between studies. Researchers are beginning to orchestrate their research in order to integrate a maximum number of parameters in their analyses but more studies need to be done. In addition to all these primordial variables, the impacts of climate change will also have to be considered in analyses because changes in seasonal icing, temperature or food webs can probably have great effects on the bioaccumulation and biomagnification of contaminants. A number of important points should be included in studies in order to adequately evaluate the biomagnification and limit the variations within and between food web studies. Samples should preferentially be collected during the same season of the same year and at the same location. The most species possible should be collected and stable isotope analyses should be analyzed to get a clear idea of the trophic positions of species. Because of the fundamental differences in the bioaccumulation behavior of water- and air-breathing organisms, both groups should also be included in the analyses when possible (mammalian/birds and fish) (Gobas et al. 2009). In the case of bioaccumulative PFCAs and PFSAs, as well as protein-associated degradation products of chlorinated and brominated POPs, chemical characteristics of compounds should be considered as every structural form, including isomers, may have specific bioaccumulation potential. For example, PFOS has been strongly associated with serum protein (i.e., albumin) (Meijer et al. 2003) and therefore the protein composition of analyzed tissue may affect the calculation of BMF and TMF.

4.3. Conclusions and recommendations

4.3.1. A growing list of chemicals in biota

- PCBs, DDT related compounds, and toxaphene (chlorinated bornanes) remain the most prominent POPs in arctic fish and marine mammals, followed by chlordane-related compounds, HCH isomers and chlorobenzenes.
- PCBs remain the most prominent POPs in seabird eggs and higher trophic level seabirds generally have a larger proportion of PCBs as a percentage of total organohalogen compounds.
- Prominent, relatively new POPs are PBDEs and PFOS, which are detectable in all biota although generally at much lower concentrations than PCBs or toxaphene. An exception is PFOS, which is at the part per million level in polar bear liver and on par with several chlorinated POPs in polar bear adipose tissue.
- Many other non-PBDE BFRs have been detected at low or sub-ng concentrations in arctic biota over the past 5 years as analytical labs have turned their attention to them. The most prominent is HBCDD, which was recently added to the Stockholm Convention and has been reported in freshwater and marine fishes, beluga, seals, seabirds and polar bears.
- Other emerging BFRs are BTBPE, PBEB, HBB, BB-101 and TBECH. BB-101 and BB-153 were also found in polar bear tissues. However, concentrations of these less studied BFRs are much lower than PBDEs or HBCDD.
- Brominated chemicals with natural sources including hydroxylated and methoxylated PBDEs and brominated dimethyl bipyrroles have been shown to be present in arctic marine mammal blubber. The methoxy BDEs and HDBPs are present at similar concentrations to anthropogenic BDEs.
- Other classes of chemicals that now have substantially more data than was available for CACAR II include the C_9–C_{12} perfluorocarboxylates. ΣPFCAs exceeded concentrations of PFOS in all species except in seabird eggs and polar bear liver. PFOSA was also a prominent PFAS in beluga and narwhal liver as well as in marine fish but near detection limits in seal and polar bear liver and seabird eggs.
- PCNs remain important dioxin-like contaminants especially in beluga and in seabird eggs. Spatial coverage in ringed seals has improved. However, no information is available on PCNs in terrestrial animals.
- Only limited data are currently available for SCCPs and MCCPs (seals, beluga, seabird eggs). SCCPs were detected at low concentrations in arctic char collected near Iqaluit, suggesting that local sources could be important for this chemical group.
- Limited data on current use pesticides that are routinely detected in arctic air (endosulfan, trifluralin, dacthal, chlorpyrifos, PCNB) suggests that concentrations are low in marine and terrestrial animals and that these chemicals are not biomagnifying from prey to predator.
- Chemicals with characteristics of POPs for which there are no new measurements reported in the period 2003–2012 include chlorinated diphenyl ethers, pentachlorophenol and hydroxyheptachlorostyrene, for which very limited data were reported in CACAR II.
- Among the 27 chemicals/chemical groups in the Stockholm Convention and the additional UNECE lists (Chapter 1, Table 1.3), chlordecone, diclofol, and trifluralin remain unreported although preliminary measurements for chlordecone suggest that it may be present at sub-ng g^{-1} concentrations in ringed seal blubber.

4.3.2. Spatial and among species comparisons

- Among the seabird eggs (black-legged kittiwakes, black guillemots, glaucous gulls, ivory gull, northern fulmars, and thick-billed murres) sampled in the Canadian Arctic, glaucous gulls had the highest concentrations of PCBs, other legacy POPs and PBDEs due to their high trophic position relative to most of the other species.
- In ringed seals, average concentrations of ΣHCH, ΣCBz and toxaphene are higher in the western and central Archipelago locations than Hudson Bay and the eastern Arctic (Pangnirtung). Also β-HCH continues to be a prominent contaminant in the western and central Arctic Archipelago. This suggests the influence of Pacific waters and Asian sources on these sites.
- Perfluorinated compounds, PBDEs and HBCDD are higher in ringed seals in Hudson Bay than other locations, reflecting the closer proximity to source regions in southern Canada and northern US.
- Hudson Bay beluga also had higher ΣDDT and ΣPBDEs than other locations i.e., than southern Beaufort or eastern Baffin (Cumberland Sound) stocks. However, ΣPBDE concentrations in beluga liver from Hudson Bay were approximately 45 times lower than measured PBDE concentrations

in St. Lawrence beluga, illustrating the generally much lower concentrations of these contaminants in arctic resident species.

- Beluga and narwhal have the dubious distinction of having the highest concentrations of most POPs compared to other marine mammals (seals, polar bear, walrus). Polar bears have similar levels of PCBs (in subcutaneous fat) as beluga and narwhal blubber but much lower levels of other POPs.
- Spatial trends of POPs in polar bears are generally similar to those in ringed seals with higher ΣHCH in the western and central Archipelago and higher DDT, dieldrin and chlordane related compounds in Hudson Bay and eastern arctic animals.
- PFOS concentrations in polar bear liver are the highest of any arctic animals and southern Hudson Bay animals have the highest levels.
- PBDEs, HBCDD and BB-101 are also higher in Hudson Bay polar bears than in bears from other regions within the Canadian Arctic.
- Limited data for POPs in caribou and moose confirms the much lower levels of most chemicals compared with marine mammals. However, in caribou and moose, PFASs were the major POPs with concentrations in liver ranking ahead of PCBs and PBDEs (ΣPFCAs > PFOS > ΣPCBs > ΣPBDEs).
- PFOS and other perfluorinated compounds were higher in caribou liver than in muscle and this was found to be the case for other mammals in a study of contaminants in the traditional diet.
- POPs concentrations in the breast tissue of terrestrial game birds were low as well, similar to terrestrial herbivores.

4.3.3. Temporal trends

4.3.3.1. Overview

- Concentrations of legacy POPs are generally declining in all biota in the Canadian Arctic. However, the rates of decline vary substantially among species and locations making it challenging to summarize the overall trends.
- Annual sampling for most biota since the early-2000s has revealed some surprising trends for legacy POPs such as increasing concentrations of PCBs in burbot liver, increased toxaphene in arctic char and ringed seals, as well as increased ΣCHL and PCDD/Fs in northern fulmar eggs.
- These increases (and subsequent declines in some cases) are generally unexplained but presumably related to year-to-year differences in dietary exposure of sampled animals (percent lipid, size and sex of animals generally being similar).
- Temporal trends in biota are available for POPs recently added to the Stockholm Convention (PBDEs, HCH isomers, PFOS, HBCDD, endosulfan) as well as for other halogenated chemicals, a much larger group of chemicals, including PFCAs, PCNs, SCCPs and several novel brominated flame retardants.
- Similar to the legacy POPs, the temporal trends for the new, or recently added POPs, vary with species and region and are generally more complex because the datasets incorporate sampling periods with increasing and decreasing levels.
- Temporal trends of ΣPBDEs and PFOS are mirroring the known production or predicted global emissions for these chemicals in selected species at certain sites. Agreement is very good for PBDE and PFOS trends in seabird eggs from Prince Leopold Island.
- No temporal trends are available for chlordecone and hexabromobiphenyl.
- Statistical power of the fish, seabird egg, and marine mammal temporal trend datasets has improved relative to CACAR 2003 due to the use of annual sampling. Although not yet fully evaluated, there is evidence that some datasets are capable of detecting a 5% change in concentration at a power of 80%, which was a goal of the monitoring program (INAC 2004).

4.3.3.2. Freshwater fish

- Concentrations of legacy POPs are generally declining in Canadian arctic freshwater fishes (burbot, lake trout, landlocked arctic char) and in sea-run char with some important exceptions.
- In sea-run char, chlordane, CBz and DDT concentrations have declined substantially at Cambridge Bay since 1987 while no decline is evident at Pond Inlet and Nain. Cambridge Bay may be unique in that Cambridge Bay is a former DEW-line site and previous studies identified high and localized contamination of PCBs and other organochlorines.
- Burbot sampled at Fort Good Hope on the Mackenzie River showed increasing concentrations of PCBs, DDT, chlordanes and toxaphene over the period 2001 to 2009 compared to concentrations found in samples from the 1990s. However, as of 2010 concentrations of all four POPs had returned to levels found in the 1990s and early 2000s.

- Concentrations of PCBs and chlorobenzenes in burbot from Great Slave Lake showed no major increase or decrease over the period, however higher concentrations were seen in 2000 and 2001 compared to the period 2006–2010.
- Lake trout from Great Slave Lake showed increased concentrations of PCBs and chlorobenzenes in the period 2004–2006 while other legacy POPs declined.
- POPs in lake trout in Lake Laberge and Kusawa Lake in the Yukon show significant declines over the period 1992–2010 unlike the lake trout in Great Slave Lake.
- POPs in landlocked arctic char in Lake Hazen, Amituk Lake and Char Lake also declined significantly over the period from the early 1990s to 2010. However, in Resolute Lake the declines were significant only for ΣHCH.
- Resolute Lake char were also distinguished by increasing toxaphene over the period 2003–2011. This upward trend, along with the lack of change of PCBs, DDT, and chlordanes in this lake may be an indication of mobilization of old sources of these chemicals that could have been used at the Resolute airport and former military base which is within the lake catchment.
- The rise and fall of PCBs and chlorobenzenes in Great Slave Lake and the more striking increase of PCBs, DDT, chlordanes and toxaphene at Fort Good Hope during the 2000s remain unexplained. Climate change, however, could be a factor influencing the fish diets and migration patterns and feeding areas. Changes in the availability of PCBs from the atmosphere due to particle scavenging or from legacy sources such as river and lake sediments and soils upstream could also be a factor.
- As reported in the CACAR III mercury assessment (2013), mercury concentrations have increased in the same fish species at Fort Good Hope and in Great Slave Lake but unlike the POPs, the increasing trends are continuous with no evident decline suggesting that different pathways and sources are involved.
- The results for POPs in fish suggest that overall trends in remote sites (e.g., high arctic lakes, Kusawa Lake) are mirroring the gradual decline in atmospheric concentrations, however sites influenced by local or regional sources, which may be from local use or greater atmospheric deposition in the past, have more variable and sometimes opposite short term trends.

4.3.3.3. Seabirds

- Concentrations of most of the legacy POPs (e.g., PCBs, DDE) have decreased in Canadian Arctic seabirds since 1975 and now appear to be levelling off.
- PFCAs have been increasing since 1975 in eggs of both northern fulmars and thick-billed murres whereas PFOS levels do not show any discernible trend. The trend for PFCAs mirrors the global production and emissions of PFOA and PFCA precursors, which are known to have increased substantially in the period 1990–2005 although they likely declined after 2005 (Armitage et al. 2009).
- Concentrations of PBDEs increased in northern fulmars and thick-billed murres between 1975 and 2003, and now appear to be decreasing in both species. The trends in these species mirror the known use in North America where "penta" PBDE were phased out as of 2004.
- The annual sampling undertaken in recent years (2005 onwards) of the arctic seabird eggs has greatly improved the power of the time series.
- Trends of other BFRs, toxaphene and endosulfan are unknown for seabirds.

4.3.3.4. Marine mammals

- Significant declines have been seen in chlorinated pesticides in ringed seals with ΣDDT and α-HCH declining in all 4 regions. However declines of PCBs and chlordane-related compounds were observed only in the East Baffin and Hudson Bay regions while β-HCH increased in the Beaufort and Lancaster region samples. This regional difference may be due to the influence of Pacific Ocean waters traversing the Arctic archipelago
- The lack of decline of PCBs and OCPs in Beaufort Sea beluga also suggests the influence of different sources in the Western Canadian arctic i.e. ocean water moving through the Arctic Archipelago from the Pacific Ocean via the Bering Sea and possibly with Russian freshwater inputs.
- Overall, there are declining trends with the relative magnitude of ΣDDT >α-HCH >Σ_{10}PCB >ΣCHL. These trends are generally similar to those in arctic marine mammals in Greenland and Svalbard.
- No new temporal trend data are available for narwhal or walrus.

4.3.4. Food web modeling

- Bioaccumulation modeling has been applied to both terrestrial and marine food webs and provides insights into the understanding of pathways and processes influencing the accumulation of POPs in wildlife and humans.
- Terrestrial food web modeling of the lichen-caribou-wolf food chain predicted successive cyclical fluctuations of tissue concentrations primarily due to (i) seasonal changes in lipid content and body size and/or (ii) lactational excretion (females only).
- Better data is required on key modeling parameters in food webs including efficiencies of uptake from water, air and food, and especially on the biotransformation rates that play a key role in biomagnification.

4.3.5. Climate change-contaminants interactions

- The relatively long time series for POPs now available i.e., 15 to 18 years of sampling over the past 30–40 years for seabirds, seals and beluga are making it possible to examine probable linkages to climate change variables.
- Evidence is emerging that shifts in diet (and their food webs) has had contaminant-specific effects on spatial or temporal trends of contaminants.

Photo: Nikolaus Gantner

- The assessment of climate impacts requires the collection of much ancillary data including C and N stable isotope ratios and fatty acid profiles, as well as ice out times e.g., for examing trends in seals and fish.

4.3.6. Recommendations

- The current NCP program determines almost all the 27 POPs currently listed (as of May 2013) under the Stockholm Convention and the UNECE POPs list. However, more focus is needed on new candidate chemicals on those lists (PCNs, pentachlorophenol, hexachlorobutadiene) as well as on SCCPs, chlordecone and hexabromobiphenyl in order to fully assess their importance as contaminants in the biological environment.
- The measurements in biological samples could be better synchronized with atmospheric measurements, where a greater number of chemicals are being analyzed in air e.g., novel BFRs and organophosphate flame retardants, siloxanes, and CUPs, both in the Canadian Arctic and in other air measurement programs.
- The ever-expanding list of target analytes presents challenges for those laboratories involved in monitoring programs for legacy and emerging organic contaminants to generate new information, particularly on emerging contaminants. In many cases, this analytical burden (i.e., method development) is too great in terms of the resources that are required and the funding that is available.
- While annual sample collection has boosted the statistical power of the biological program and therefore must be continued, consideration should be given to de-emphasizing annual measurements of some legacy POPs, where statistical analysis shows that the datasets meet monitoring goals, and placing more emphasis on new candidate or emerging chemicals which may have limited datasets.
- It must be recognized that a major strength of the temporal trend programs conducted under the NCP is the availability of archived samples from specimen banks. These must be maintained to continue to have a strong program for POPs monitoring.

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CHAPTER 5

Biological Effects of Halogenated Organic Contaminants

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Photo: Sam Bentley

CHAPTER 5

Biological Effects of Halogenated Organic Contaminants

Coordinating authors: Peter Ross and Lisa Loseto
Contributors: Birgit Braune, Tanya Brown, Kelly Johnson, Robert Letcher, Lisa Loseto, Derek Muir, Ken Reimer, Peter Ross

5.1. Introduction

Anthropogenic contaminants have been a concern in the Canadian Arctic for over 30 years due to relatively high concentrations of bioaccumulating and biomagnifying persistent organic pollutants (POPs) found in some arctic biota and humans. Prior to 1997, biological effects data were minimal and insufficient at any level of biological organization. Fisk et al. (2005) had concluded that at that time few studies had addressed the potential effects of these contaminants in Canadian arctic wildlife. Examination of possible biological effects in Arctic organisms is a difficult task. There are inherent problems with any study of wildlife in the Canadian Arctic due to the difficulty and expense of travel and fieldwork. Beyond this, the linkage of biological effects to anthropogenic contaminants in an exposed organism is difficult. Biological effects can be measured at different levels of biological organization, from the molecular level to the ecosystem level. Biomarkers measurable at a molecular level respond early, but are not readily interpreted ecologically. Measures with established ecological relevance, such as population declines or reduced reproductive rates, often respond too late to have diagnostic or preventative value.

There are two basic approaches in assessing the possible biological effects of anthropogenic contaminants in wildlife. The first involves the comparison of concentrations measured in arctic species to those associated with effects observed in laboratory animal studies, semi-field studies and field-based studies. However, these types of comparisons have inherent weaknesses. Laboratory animals are most often exposed to single toxicants, or to technical products at high dosing concentrations, for short periods of time. Based on the effects observed under these controlled lab conditions, it is difficult to extrapolate the possible adverse effects at lower and chronic exposure in animals in the field. Wild animals are generally exposed to lower concentrations of POPs relative to controlled lab studies, but they are exposed to mixtures of contaminants and other stressors over their entire lifetime. Moreover, wildlife are exposed to environmentally weathered contaminant mixtures due to the change in composition of many mixtures caused by abiotic degradation, metabolism and subsequent filtering up through the food web. The sensitivity to the effects of contaminants also varies among species and the extrapolation of the effect levels developed for laboratory animals is a confounding problem.

The second approach involves measuring biological responses that are related to contaminant exposure, based on the endpoints of those responses that are often referred to as biomarkers. At present, use of biomarkers is one of the only approaches available to begin to test the hypothesis that contaminants are acting biologically on the animals, although these are correlative contaminant-biomarker linkages rather than cause-effect relationships. Almost any biological change, from molecular to ecological, can serve as a biomarker; however, the term most often refers to changes at sub-cellular levels (Peakall 1992, Huggett 1992, McCarthy and Shugart 1990). Biomarkers are typically measures of normal processes whose values abnormally change as a result of exposure to contaminants. The sensitivities of biomarkers have generally been established using laboratory animals and their applicability to arctic wildlife is little studied. It is also not possible to determine causality, only that a statistical association has been found between a biomarker and the contaminant in question. Most contaminants co-vary and thus it is not possible to state equivocally that the biomarker response has been caused by one particular contaminant. There may be other contaminants not analyzed that are just as significant.

While the Arctic is generally remote and often considered pristine, contamination of food webs generally results either from releases from a modest number of local sources, or by delivery via atmospheric and oceanic pathways (Figure 5.1; also see Figure 2.22 in Chapter 2). While localized contamination can present health risks to a number of species in certain areas (Kuzyk et al. 2003), food

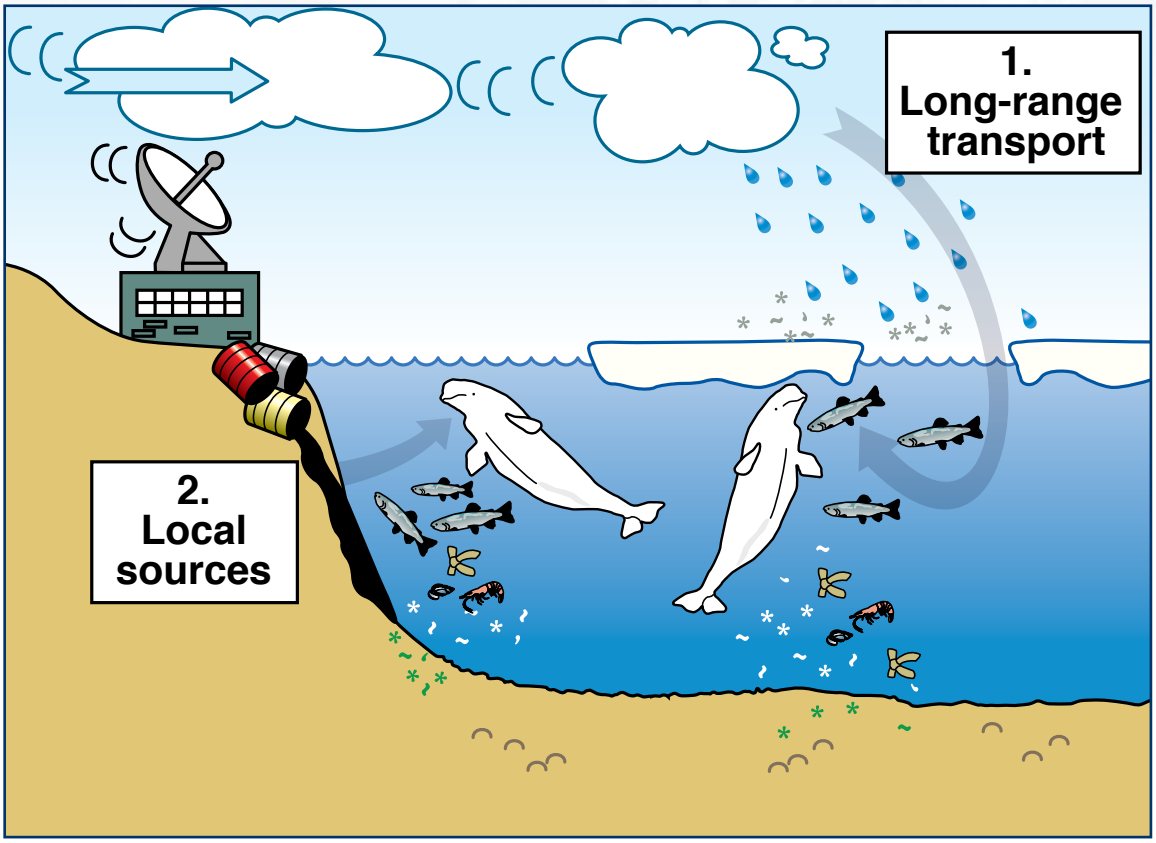

FIGURE 5.1

Beluga whales and other arctic marine mammals are exposed to both "local" and "global"sources of contaminants, although food web-based amplification of contaminants delivered via long range transport largely explains the moderately elevated levels in high trophic level biota.

web-based biomagnification leads to elevated levels of persistent contaminants such as polychlorinated biphenyl (PCBs) and dichlorodiphenyltrichloroethane (DDT) in high trophic level seabirds and marine mammals throughout the Arctic (Braune et al. 2005).

Marine mammals and seabirds inhabiting more southerly, industrialized, regions are exposed to much higher concentrations of POPs. These have been linked to adverse effects, including endocrine disruption, immunotoxicity, developmental malformations and reproductive impairment De Guise et al. 1995, Lahvis et al. 1995, Mattson et al. 1998, (Mos et al. 2006, Ross 2006, Tabuchi et al. 2006b). These observations are based on a variety of study designs, including captive feeding studies, correlative field studies, associative field studies, and more mechanistically based studies of surrogate species exposed to a range of single or multiple chemical doses. While all POPs are considered "toxic", the PCBs continue to be viewed as the major contaminant of concern at the top of the food chain in the northern hemisphere (Mos et al. 2006, Loseto and Ross 2011, Ross 2000).

Concerns about contaminants in the Canadian Arctic emanate, in part, from studies that have demonstrated possible health effects in subsistence-oriented humans, polar bears and beluga whales (Braathen et al. 2004, Dallaire et al. 2004, White et al. 1994). However, conducting research on the effects of contaminants on the health of arctic biota is constrained by a number of factors:

- logistical challenges related to Arctic environments;
- the presence of lower contaminant concentrations relative to more southerly (impacted) populations;
- the presence of complex mixtures of hundreds of different contaminants;
- access to suitable biological tissues from often large, elusive and/or dangerous wildlife species;

- access to fresh samples and timely processing by a field laboratory for many health endpoints;
- legal and ethical constraints related to often charismatic megafauna; and
- confounding influences of age, sex, condition, and/or feeding ecology on contaminant levels and patterns, as well as on the health of the study animals.

Given the inherent ethical, legal, and logistical constraints in demonstrating cause-and-effect for specific chemicals in marine mammals and other wildlife, a "weight of evidence" has been espoused, akin to the approach taken for humans (Ross 2000). In the case of arctic species, evidence of adverse effects related to contaminants is limited to species contaminated by local PCB sources (e.g., black guillemots) (Kuzyk et al. 2003) or those which have been reported in more contaminated species, such as polar bears (Letcher et al. 2010, Lie et al. 2005, Skaare et al. 2001) and glaucous gulls (Verreault et al. 2010).

The health of animals under study reflects a combination of factors, thus it is important to critically evaluate influencing factors such as feeding ecology and condition, especially with a rapidly changing ice-associated food web. By incorporating these factors into the design of studies and/or into data interpretation, contaminant-related effects may be distinguished from other stressors (Figure 5.2A). Climate change is likely to alter contaminant pathways in the Arctic (Macdonald et al. 2005, Macdonald et al. 2003) and the health of wildlife (Burek et al. 2008) as a result of changes in sea ice cover, temperature profiles, food web productivity, and feeding ecology (Chambellant 2010, Mallory et al. 2010). Climate change may therefore be considered as a stressor in its own right, but it may also change the way in which wildlife are affected by contaminants (Figure 5.2B; See section 4.3.5).

Collaborations between scientists and subsistence consumers in the Arctic have been a cornerstone of Arctic studies, effectively strengthening the impact and relevance of results. By working with hunters, samples have been collected in support of temporal and spatial trend monitoring, and effects-based research. However, while the conditions of collection, transport and storage of samples for contaminant analysis are relatively straight forward, the same cannot be said of the collection of samples for the study of health endpoints. Highly specialized protocols are often needed to accurately measure enzymes, hormones, hormone receptors, and/or the function of the immune system. In addition, variation in age, sex and condition can influence both contaminant concentrations and health endpoints, necessitating their consideration in study design and sample size.

Fisk et al. (2005) reviewed and summarized, until 2003, studies on biological effects related to contaminant exposure, and compared new tissue concentration data to threshold effects levels. Until 2005, in general very little was known about the

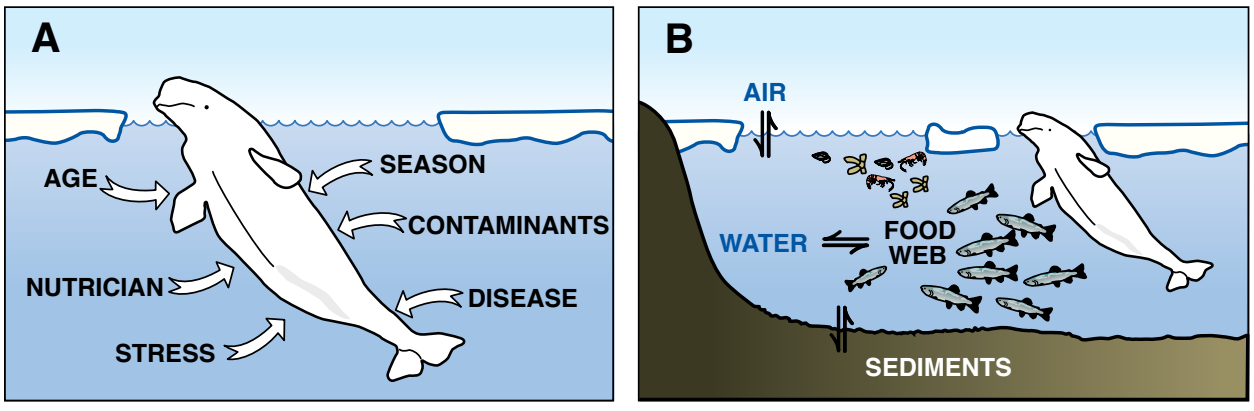

FIGURE 5.2

A. The health of beluga whales and other arctic species is influenced by a combination of biological factors, as well as anthropogenic stresses. These factors may act independently or together, underscoring the importance of multidisciplinary studies. B. Climate change may alter contaminant pathways and the health of beluga and other arctic species.While these changes create challenges for researchers as they strive to measure effects of contaminants on the health of long-lived species, it also presents opportunities to engage community members that can offer insight into the processes that are underway.

sensitivity of arctic species, particularly marine mammals, to the effects of POPs (de Wit et al. 2004). Black guillemots examined near PCB-contaminated Saglek Bay, Labrador, had enlarged livers, elevated ethoxyresorufin-*O*-deethylase (EROD) and liver lipid levels, and reduced retinol (vitamin A) and retinyl palmitate levels, which correlated to the PCB levels in the birds (Kuzyk et al. 2003). Circulating levels of thyroid hormones in polar bears were correlated to PCB and OH-PCB plasma concentrations, but the impact at the population level was unknown. High PCB and organochlorine pesticide (OCP) concentrations were found to be strongly associated with impaired humoral and cell-mediated immune responses in polar bears, implying an increased infection risk that could impact the population. In beluga whale, cytochrome P450 (phase I) and conjugating (phase II) enzymes had been extensively profiled (immunochemically and catalytically) in the liver, demonstrating the importance of contaminants in relation to enzyme induction, metabolism and potential contaminant bio-activation and fate. Concentrations of POPs in fish, seabirds, and arctic terrestrial wildlife were generally below effects thresholds, with the possible exception of PCBs in burbot in some Yukon lakes, Greenland shark, glaucous and great black-backed gulls, and Toxic Equivalents (TEQs) for dioxin-like chemicals in seabird eggs. PCB and DDT concentrations in several arctic marine mammal species exceeded apparent effects thresholds, although evidence of stress in these populations was lacking. At the time, there was little evidence that contaminants were having widespread effects on the health of Canadian arctic biota, with the possible exception of polar bears. It was concluded that further research and better understanding of exposure to POPs in arctic biota was needed considering factors such as tissue levels that exceed effects thresholds, exposure to "new" POPs of concern, contaminated regions, and climate change.

In a follow-up to the Fisk et al. (2005) review, Letcher et al. (2010) provided an updated assessment and summary regarding the exposure and effects of POPs in arctic wildlife and fish. In the context of this assessment, POPs encompass an array of anthropogenic halogenated organic substances and their degradation and metabolic by-products have been found in the tissues of exposed animals. POPs have been of concern in the circumpolar Arctic for decades. For example, as a consequence of bio-accumulation, in some cases the biomagnification of legacy POPs (e.g., PCBs, DDTs and chlordane-related compounds (CHLs) and polybrominated

Photo: Martin Fortier/ArcticNet

diphenyl ether (PBDEs), as well as perfluorinated alkyl substances (PFASs) have been found in Arctic biota and humans. Of high concern are the potential biological effects of these contaminants in exposed arctic wildlife and fish. Prior to 1997, biological effects data were minimal and insufficient at any level of biological organization. However, post-2002, new POPs effects data have been generated for several high trophic level species, including seabirds (e.g., glaucous gull, polar bears, arctic fox, and arctic char) as well as semi-captive studies on sled dogs (see reviews by Letcher et al. 2010 and Sonne 2010). Regardless, even more recently, there continues to be a dearth of data on true contaminant exposure and cause-effect relationships with respect to these contaminant exposures in arctic wildlife and fish.

Indications of adverse effects from exposure have largely been based on correlations between biomarker endpoints and tissue residue levels of POPs (e.g., PCBs, DDTs, CHLs, PBDEs and in a few cases PFASs, perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonates (PFSAs). Some exceptions include studies on the contaminant effects in control and exposed cohorts of captive Greenland sled dogs, and performance studies mimicking environmentally relevant PCB concentrations in arctic char. Recent tissue concentrations in several arctic marine mammal species and populations exceed a general threshold level of concern of 1 part-per-million (ppm; $\mu g\ g^{-1}$) (Letcher et al. 2010). Clear evidence of POPs-related stress in these populations remains to be elucidated. There remains minimal evidence that POPs are having widespread effects on the health of arctic organisms, with the possible exception of East Greenland and Svalbard polar bears and Svalbard glaucous gulls. However, the effects of POPs in arctic wildlife have to be placed in the context of other environmental, ecological and physiological stressors (both anthropogenic and natural) that create a highly complex picture. For instance, seasonal changes in food intake and corresponding cycles of fattening and emaciation seen in arctic animals can modify contaminant tissue distribution and toxicokinetics (contaminant deposition, metabolism and depuration). Also, other factors, including the impact of climate change (seasonal ice and temperature changes, and its connection to food web changes, nutrition, etc. in exposed biota), disease, species invasion and the relation to disease resistance will impact toxicant exposure. Overall, further research for a better understanding of the impact of POPs on animal performance in arctic biota is recommended.

Regardless, it was postulated by Letcher et al. (2010) that arctic wildlife and fish at the highest potential risk of POPs exposure and mediated effects are in East Greenland, Svalbard, Hudson Bay (West and South) polar bears, Alaskan and Northern Norway killer whales, several species of gulls and other seabirds from the Svalbard area, Northern Norway, East Greenland, the Kara Sea and/or the Canadian central High Arctic, East Greenland ringed seal and a few populations of arctic char and Greenland shark.

Sonne (2010), with an in depth focus on polar bears and arctic predator model species, provided an overview of the relationship between contaminant exposure, contaminant residues in various tissues and organs, and the health effect parameters. Sonne (2010) expanded on the relationships between concentrations, exposure and health effects reported in Letcher et al. (2010). Multiple scientific studies of polar bears indicate negative relationships between exposure to these contaminants and health parameters; however, these are all of a correlative nature and do not necessarily imply true cause-and-effect relationships. Therefore, information from controlled studies of farmed Norwegian arctic foxes and captive East and West Greenland sledge dogs were used as part of a "weight of evidence" in the clarification of contaminant exposure and health effects in polar bears. The review showed that hormone and vitamin concentrations, liver, kidney and thyroid gland morphology as well as reproductive and immune systems of polar bears are likely to be influenced by contaminant exposure. Furthermore, exclusively based on polar bear contaminant studies, bone density reduction, neurochemical disruption and DNA hypomethylation of the brain stem seemed to occur. The range of tissue concentration, at which these alterations were observed in polar bears, were ca. 1–70,000 ng g^{-1} lw for POPs (blood plasma concentrations of some PCB metabolites were even higher), ca. 1–1,000 ng g^{-1} lw for PBDEs and for PFASs and Hg, 114–3052 ng g^{-1} ww and 0.1–50 $\mu g\ g^{-1}$ ww, respectively. While similar concentrations were found in farmed foxes and captive sledge dogs, the lack of dose-response designs did not allow an estimation of threshold effects levels. In addition, it was not possible to identify a specific group of contaminants underlying the effects. For East Greenland polar bears the corresponding daily total PCBs + OC pesticides and ΣPBDE oral exposure was estimated to be 35 and 0.34 ng g^{-1} body weight, respectively. Furthermore, PFASs concentrations, at which population effect levels could occur, are predicted to be attained by the year

2012 for the East Greenland polar bear subpopulation, assuming current trends. Predicted effects on reproduction were supported by physiologically-based pharmacokinetic (PBPK) modeling of critical body residues (CBR) with risk quotients ≥ 1 for ΣPCB, dieldrin, ΣPFASs and total PCBs + OC pesticides. The estimated daily TEQ intake for East Greenland polar bears and East Greenland sledge dogs were 32–281-fold above WHO ΣTEQ guidelines for human exposure. East Greenland polar bears had concentrations of PCBs, dieldrin, chlordanes and ΣHCH that exceeded human tolerable daily intake (TDI) values. While such comparisons must be made with caution, along with PBPK modeling of CBRs and bone mineral density comparisons, these were the only tools available for the evaluation of contaminant-related risks for polar bears. It was concluded that polar bears seem to be susceptible to contaminant induced stress that may have an overall sub-clinical impact on their health and population status through impacts on their immune and reproductive systems.

5.2. Effects of PCB Contamination on Local Biota at Saglek Bay, Labrador

5.2.1. Marine environment

Saglek Bay, Labrador, has been the site of a military radar station (LAB-2) since the late 1950s (Kuzyk et al. 2005b). During a preliminary site investigation in 1996, extensive PCB contamination was found in soil at the site, and subsequent work found elevated PCB concentrations in local sediments, invertebrates, fish and seabirds (Kuzyk et al. 2005b). PCBs adsorbed to soil particles were eroding from a beach ravine into the marine environment and accumulating in the nearshore sediments (Brown et al. 2009).

From 1997 to 1999, in conjunction with the excavation and removal of the PCB-contaminated soil from the terrestrial environment at Saglek Bay, an extended study was undertaken to assess the contamination in both the marine sediments and biota (Brown et al. 2009, Kuzyk et al. 2005b). The results revealed that PCB-contaminated marine sediments were widely distributed between the mainland, where the radar station is situated, and Big Island, located approximately 6 km to the north (Kuzyk et al. 2005b). The PCB contamination was largely localized to the Saglek-Anchorage area and decreased exponentially with increasing distance from the source beach (Kuzyk et al. 2005b).

Average PCB concentrations in the nearshore marine sediments exceeded the Canadian sediment quality guideline (21.5 ng g^{-1} dw) by 41-fold and PCB concentrations in benthic invertebrates, shorthorn sculpin, and black guillemots were exceptionally high (Kuzyk et al. 2005b). Relatively high PCB concentrations were also measured in some great black-backed gulls and ringed seals (Kuzyk et al. 2005b).

To determine an appropriate management strategy for the PCB-contaminated sediments, an effects-based ecological risk assessment (ERA) was completed to identify the potential risks to the local biota (Brown et al. 2013, Kuzyk et al. 2005a, Kuzyk et al. 2003). Risks were evaluated for three components of the marine ecosystem: benthic invertebrates, shorthorn sculpin, and black guillemots.

Twenty-two sites within Saglek Bay were selected for the benthic invertebrate analyses based on PCB concentrations in the sediments (Figure 5.3). These included five reference sites with < 5 ng g^{-1} dw PCB anticipated in sediments, five sites with anticipated PCB concentrations from 5–250 ng g^{-1} dw, six sites with anticipated PCB concentrations between 250–2,000 ng g^{-1} dw, and six sites with PCB concentrations anticipated to exceed 2,000 ng g^{-1} dw. The exposure assessment for benthos was based on the PCB concentrations measured in the sediment samples at these 22 sampling sites. The sampling program was designed to minimize the influence of parameters, such as grain size and organic carbon content, by sampling sites where these factors would be relatively constant. Although sediment PCB concentrations exceeded the Canadian interim sediment quality guideline level; sediment toxicity testing and a benthic community survey showed no evidence of adverse effects. In contrast, results clearly showed that shorthorn sculpin and black guillemots were potentially at risk from the contaminated sediments in Saglek Bay as they existed during the assessment period 1997–1999.

Shorthorn sculpin (n=101) were collected from 13 different locations in Saglek Fjord (Figure 5.3) comprising the reference sites. Twelve (nos. 23–34) were located within 9 km of the contaminated beach, i.e., within the boundaries identified for the ERA (Brown et al. 2013), and the thirteenth location, was located between 13 km and 25 km from the beach. Measured PCB concentrations in Saglek Bay sculpin (16–72,100 ng g^{-1} ww liver) were compared to the literature, i.e., the tissue PCB concentrations at which risks to fish reproduction and survival had

Photo: Mark Mallory

been reported, and to four site-specific biological endpoints: fish body condition (condition factor), lipid content, relative liver mass (hepatosomatic index) and activity of a cytochrome P450 1A (Cyp1A) isozyme (determined via EROD) activity in sculpin liver tissue (Brown et al. 2013, Kuzyk et al. 2005a). The results showed that EROD activity in sculpin from the most contaminated beach site was 25-fold higher than the mean for the uncontaminated reference site (Rose Island) (Kuzyk et al. 2005a). Although thresholds for EROD induction occurred at PCB exposures as low as 50 ng g^{-1} (whole body minus liver ww); the minimum PCB exposures associated with risk to sculpin reproduction and survival, based on literature toxicity thresholds, appear to be in the order of 1,000 ng g^{-1} ww or more. Among sculpin, these levels of exposure (> 1,000 ng g^{-1} ww in whole fish excluding livers) occurred within 3 km of the contaminated beach area; however, they only occurred frequently in the immediate coastal area surrounding the contaminated beach, where the overall average sediment PCB concentration is approximately 750 ng g^{-1} dw (Brown et al. 2013).

PCB concentrations and thirteen site-specific biological endpoints in 31 black guillemot nestlings were measured from three PCB exposure groups (liver ww): highly exposed beach group (170-6,200 ng g^{-1}), moderately exposed Islands group located on two unnamed islands (hereafter referred to as Rocky and Little Bluebell Islands) 5–6 km from the beach (24–150 ng g^{-1}), and the reference group located on Glitsch Island and two unnamed islands (hereafter called Black and Gull Islands) 16–18 km from the beach (15–46 ng g^{-1}) (Brown et al. 2013) (Figure 5.3). Several endpoints showed no relationship to PCB exposure: malic enzyme, thyroid mass and activity, mass of the bursa, spleen, heart, and adrenal glands, chick growth, and hatching success. Malic enzymes, the thyroid, the heart and the adrenal are all direct or indirect physiological indicators of metabolic functioning, while growth is a functional endpoint strongly linked to metabolism. Therefore, the non-significant response for this set of endpoints provided quite convincing evidence that guillemot metabolism has not been significantly affected by PCB exposure at Saglek Bay.

In contrast, significant effects that were related to nestling PCB exposure were found for: liver enlargement, thymus mass, retinoid levels, steroid hormone levels, and the phytohemagglutinin (PHA) skin test immune response (Kuzyk et al. 2003 and Brown et al. 2013). These endpoints are all direct or indirect physiological indicators of immune functioning and reproductive development. Therefore, the responses measured for this set of endpoints strongly suggest that guillemot immune function and the developing reproductive system had been affected by PCB exposure at Saglek Bay. Based on the collective evidence, the minimum PCB exposure associated with risk to guillemot reproduction and survival was 1,250 ng g^{-1} ww. Among the black guillemots, only nestlings from the beach group experienced PCB exposures at concentrations likely to be associated with risk to survival or reproduction (> 1,250 ng g^{-1} ww in nestling livers). The average sediment PCB concentrations associated with these exposures are approximately 77–355 ng g^{-1} dw.

A secondary objective of this ERA, provided that the contaminated sediments represented a risk as they existed in the period 1997–1999, was to provide information that would support the development of site-specific sediment remediation objectives to ensure the protection of local wildlife. The results of this ERA suggest that the average sediment PCB concentrations in the foraging areas of shorthorn sculpin would need to be reduced to less than 750 ng g^{-1} dw to protect the local sculpin population. For black guillemots, the ERA identified a lower sediment threshold of 77–355 ng g^{-1} dw. The conservative end of this range, 77 ng g^{-1} dw, was therefore the best estimate of a PCB concentration in sediments that would be protective for the black guillemots. Since black guillemots occupy a relatively high trophic level, have a relatively small home range, and forage locally, the derived site-specific level (77 ng g^{-1} dw) is to be protective of most bird and fish species in the area.

In 2006–2007, a study was undertaken to assess ecosystem recovery over an eight-year period after cleanup of the terrestrial source. The study investigated contamination in the marine sediments and PCB concentrations and effects in two indicator species (shorthorn sculpin and black guillemots). All samples collected in 2006–2007 were taken from the same areas as in 1998–1999. Surface sediment measurements indicated decreases in both the extent and average concentrations of PCBs throughout Saglek Bay (Brown et al. 2009). Finer sediments were being transported toward the western end of the shallow Saglek Bay area and deposited under the influence of oceanic transport processes (Brown et al. 2009). In addition, the contaminated sediments that were being deposited to the north in the deep muddy basin were simultaneously diluted and buried with "clean" sediment resulting in an overall decrease to the surface sediment PCB levels in the area (Brown et al. 2009).

Significant decreases in PCB concentrations and a decline in biological effects were also measured in shorthorn sculpin and black guillemots. Within the contaminated beach area, average sculpin ΣPCB concentrations showed a 19-fold decrease between 1999 and 2006 while concentrations in guillemot nestlings from the highly exposed beach, moderately exposed Islands, and reference groups decreased 6-, 6-, and 2-fold, respectively (Brown et al. 2009). Of the eight endpoints measured in shorthorn sculpin, seven showed no relationship to PCB exposure: biotransformation enzyme activity (phase I: EROD; phase II: uridine diphosphate-glucuronyltransferase (UDP-GT)), vitamin A, organ histopathology, organ histomorphometry, body condition, liver lipid content, and hepato-somatic index. Hepatic concentrations of vitamin E in sculpin showed unexpected decreases with increasing PCB exposure, compared to the results

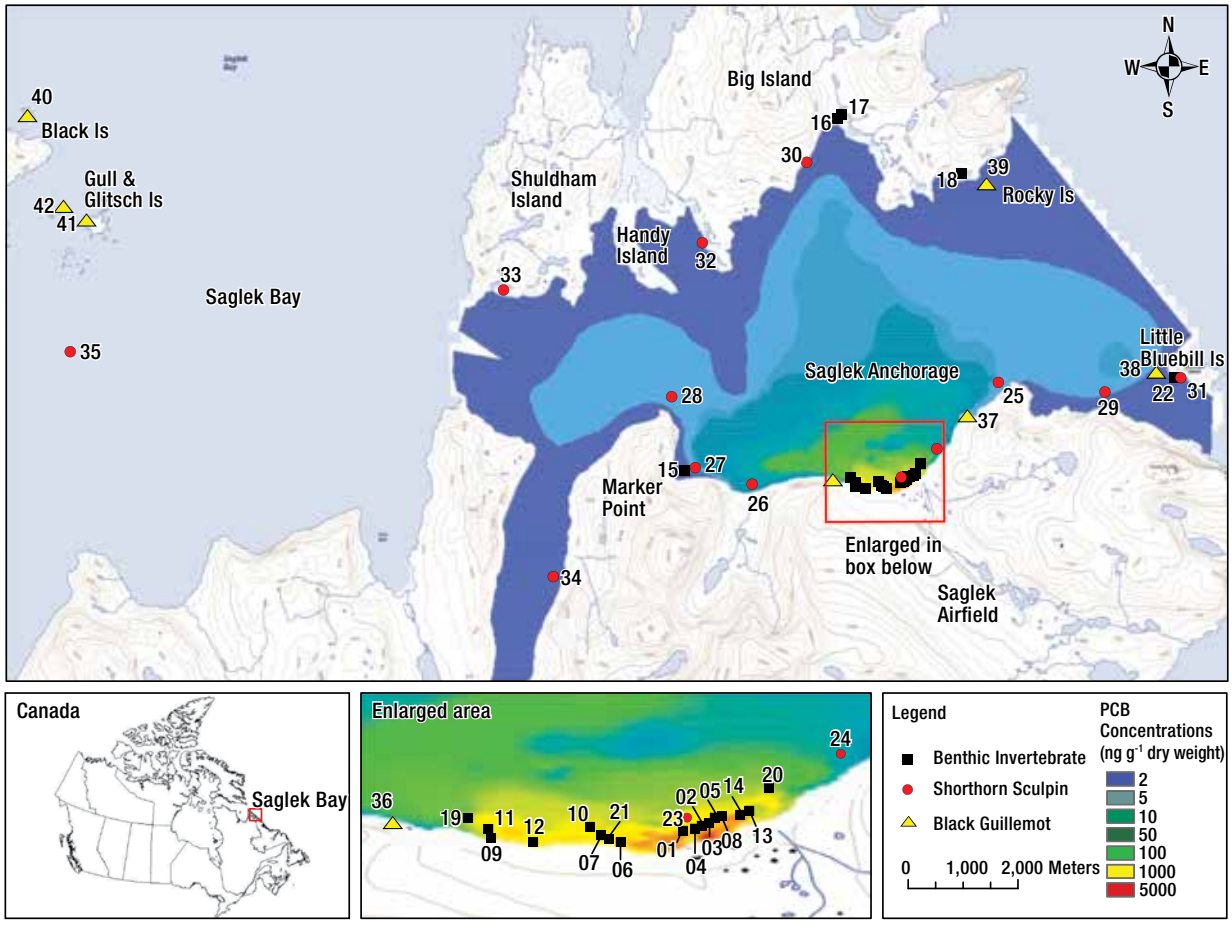

FIGURE 5.3

Distribution of PCB-contaminated sediments in Saglek Bay, Labrador, Canada during the study period (1997-1999) and location of benthic (*n*=22, squares), shorthorn sculpin (n=13, circles), and black guillemot (*n*=7, triangles) sample sites for site-specific studies of PCB exposure and effects (Brown et al. 2013).

of previous studies (Nyman et al. 2003), thus these results were considered indeterminate in terms of risk to sculpin health.

Of the ten endpoints measured in black guillemots, eight showed no relationship to PCB exposure: biotransformation enzyme activity (phase I: EROD; phase II: UDP-GT), vitamin A, thyroid hormone levels, bone mineral density, organ histopathology, organ weight, estradiol. In contrast, significant effects were measured for testosterone levels, acetylcholinesterase (AchE) activity, and PHA skin test immune response (ESG 2013). Therefore, these results suggest that guillemot immune function and the developing reproductive system were still affected by the PCB exposure at Saglek Bay. Furthermore, a significant decrease in AchE activity with increasing PCB concentrations was found in guillemot nestlings, suggesting that guillemot neurological functioning may also have been affected.

In 2007, PCB concentrations measured in shorthorn sculpin (whole body minus liver) and black guillemot nestlings (liver) were below concentrations (1,000 ng g^{-1} ww) previously associated with risks of impaired reproduction and survival (ESG 2013). These results were supported by the biological endpoints measured in the sculpin, which indicated no risk. However, biological effects were still measured in the black guillemots, which suggest that PCB-associated risk was still present for this upper-trophic level species. Physical and biological monitoring of Saglek Bay through the collection of surface sediment samples and shorthorn sculpin, conducted between 2008 and 2011, has shown that PCB levels are decreasing with time and that average sediment PCB concentrations are below the site-specific threshold (77 ng g^{-1} dw) established for probable adverse effects (ESG 2013). Sediment PCB levels have continued to decrease over time, and risks to black guillemots are also assumed to have decreased and may therefore no longer be at risk.

5.2.2. Terrestrial environment at Saglek Bay

PCBs can act as endocrine disrupting compounds (EDCs) and can therefore interact and perturb normal physiological functions. Endocrine disruption is thought to induce histological damage to the skeletal system. While the physiological mechanism is not fully understood, it's thought that because PCBs possess antiestrogenic properties, they inhibit the binding of estrogen to the estrogen receptor subsequently inhibiting estrogen induced responses (Johnson et al. 2009). In laboratory settings, PCB exposure has been reported to alter bone composition in rats (Andrews 1989, Lind et al. 2000, Yilmaz et al. 2006). As well, studies on polar bears and seal bones from East Greenland and the Baltic Sea, respectively, indicate that reduced bone mineral density is linked to organochlorine exposure (Lind et al. 2003, Sonne et al. 2004).

Thyroid hormones are critical for metabolism, growth, and development in mammals. A disruption in thyroid function could lead to adverse effects on growth and development and could also have important consequences for lipid metabolism and energetics. PCBs have been found to decrease the levels of serum thyroid hormone in laboratory rats (Craft et al. 2002, Van Birgelen et al. 1995). As well, studies on free-ranging seal species suggest contaminant-mediated thyroid disruption (Routti et al. 2008, Tabuchi et al. 2006a).

Deer mice were selected as an indicator species for the terrestrial monitoring program at Saglek Bay to assess ecosystem recovery after cleanup of the PCB source. Results from the monitoring program showed residual PCB contamination in soil, plants and deer mice at the beach area (ESG 2007). In 2007, PCB concentrations and three site-specific biological endpoints (bone mineral density, thyroid histomorphometry, and thyroid histopathology) in deer mice were measured from two PCB exposure areas: the exposed beach area and a reference area (Figure 5.4).

PCB concentrations (ΣPCB; total 91 congeners measured) in mice (whole body) from the Beach area (382 ng g^{-1} to 22,700 ng g^{-1}, ww) were significantly greater than reference area mice (15.6 ng g^{-1} to 187 ng g^{-1}, ww) (Johnson et al. 2009). Histological examinations of the mice thyroid showed no consistent modifications between the two exposure groups. As well, thyroid epithelial cell heights (i.e., histomorphometric trait) for the deer mice did not differ between exposure groups. On the other hand, deer mice at the beach group (41.9 ± 11.2 g cm^{-2}) had significantly lower bone mineral density than mice from the reference group (56.1 ± 9.8 g cm^{-2}). The T-score, a measurement of bone mineral density used in humans to define osteoporosis, was calculated for deer mice from the beach group. The T-scores ranged from -3.3 to 0.64 and the average was -1.45. Based on the World Health Organization classification scheme for humans, the average classification for these mice would be osteopenia (i.e., T-score ranging from -1.0 to -2.5) while the most extreme cases would be osteoporosis (T-score less than -2.5) (Johnson et al. 2009). Fracture risk

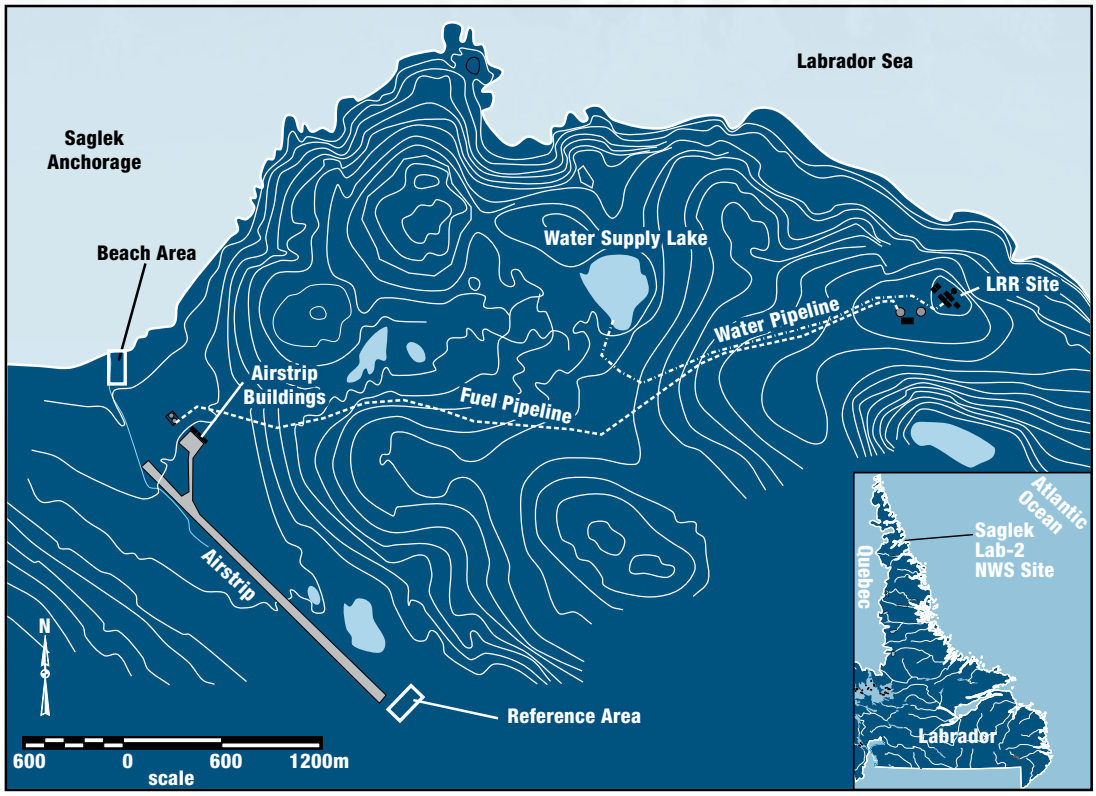

FIGURE 5.4

Sampling sites for deer mice (Beach and Reference) at Saglek, Labrador (From Johnson et al. 2009).

increases 1.5 to 3-fold for every standard deviation decrease in bone mineral density (Kanis et al. 1994). Therefore, assuming the same biomechanical forces apply and using a conservative factor of 1.5, mice at Saglek Bay were found to be up to five-fold more susceptible to fracture risk than mice at the reference area (Johnson et al. 2009). Despite these effects, the beach area appears to support a healthy and abundant population of deer mice. Considering the short life span of the deer mice (< 1 year) and given that the population continues to persist at the beach after 20 years of elevated exposure to PCBs, there is no evidence that PCB levels at the beach have affected mice at the population level (Johnson 2010).

5.3. Beluga Whales

5.3.1. Introduction

Beluga whales are the most abundant arctic cetacean with a discontinuous circumpolar distribution (Brodie 1989). Within Canada, there are thought to be seven distinct populations that are delineated based on summer habitat use and genetic profiles (COSEWIC 2004). The St. Lawrence Estuary beluga whale population is thought to be a relic arctic population that is genetically distinct from other Canadian Arctic populations (de March et al. 2002). This population also represents one that is currently exposed to several stressors ranging from local contaminant sources from industry to habitat loss in this maritime shipping corridor. These stressors have impacted their health and are thought to have hindered population growth (Béland et al. 1993, Martineau et al. 2002). While the eastern Beaufort Sea beluga whale population has not experienced such stressors, their habitat has begun to undergo change such as sea ice loss resulting from climate warming (Serreze et al. 2007) and will likely experience more industrial-related stressors as the arctic and non-renewable sources become more accessible.

Typically, belugas reach sexual maturity at seven years of age with an estimated life expectancy of 60 plus years. This odontocete is size dimorphic and females are 80% the length of males (Doidge 1990). Size was found to increase with latitude where whales from the eastern Beaufort Sea population

were larger than the eastern Hudson Bay population (Luque and Ferguson 2010). On average, males are a length of 4.5 metres and weigh approximately 1,500 kg, females are 3.5 metres long at about 1,300 kg and newborn calves are approximately 1.5 metres weighing near 70 kg. Approximately 40% of the beluga's body weight is blubber. Beluga whales are thought to be generalist mid-trophic level feeders whose diet relates to habitat. Arctic cod is thought to be an important forage species for some beluga populations (Dahl et al. 2000, Loseto et al. 2009, Seaman et al. 1982, Welch et al. 1993), however, other species such as redfish, halibut and shrimp were found in Greenlandic beluga stomach contents, whereas Pacific salmon were dominant prey items for Alaskan beluga populations (Frost and Lowry 1981). Typically, beluga whales are placed at trophic level 4, e.g. (Hobson et al. 2002, Hoekstra et al. 2003) just below top predators such as polar bears.

Thus their higher trophic level, significant blubber content and long lives render them vulnerable to contaminants such as PCBs that are lipophillic, accumulate over time and biomagnify up food webs. Long-term monitoring of beluga whales has provided valuable information on the spatial and temporal trends in both new and old compounds. One of the most successful monitoring and research sites is at Hendrickson Island in the Mackenzie Estuary. Beluga whales are increasingly being viewed as ecosystem indicators in the Arctic, reflecting their integration of food webs, their importance in Inuit culture, and their potential vulnerability to climate change.

5.3.2. Eastern Beaufort Sea beluga whales and Hendrickson Island

Every summer, the eastern Beaufort Sea beluga population arrives to the Mackenzie River estuary in the thousands, representing one of the largest summering aggregations of beluga whales (Fraker et al. 1979). The summer harvest of Beaufort Sea beluga whales by communities of the Inuvialuit Settlement Region (Northwest Territories, Canada) is an important component of the Inuvialuit subsistence lifestyle (Usher 2002). The Beaufort beluga whale population is one of Canada's largest, with a minimum estimate of 40,000 individuals (COSEWIC 2004). At present, there is no indication of population decline.

The eastern Beaufort Sea beluga population undergoes one of the longest migrations for this species, travelling to the Bering Sea in the winter and to the eastern Beaufort Sea and Amundsen Gulf in the summer (Richard et al. 2001). This large home range incorporates two different ocean bodies and their associated ecosystems, which increases the seasonal and regional complexity of diet and dietary contaminant sources. Other beluga populations, such as the Alaskan Cook Inlet, the High Arctic Cumberland Sound and the Gulf of St. Lawrence populations have small home ranges or short migration routes (Hobbs et al. 2005, Richard et al. 2001) thus, their diet and contaminant exposure can be associated within a common feeding region.

Divergent dietary fatty acid signatures, stable isotopes (C and N) and mercury (Hg) signatures in beluga whales suggest a size-dependent segregation of feeding preferences (Loseto et al. 2008). Further insight into feeding ecology and habitat use are a requisite component of evaluating source, transport, fate and effect features of persistent organic pollutants.

5.3.3. Beluga size, diet and condition in relation to concentrations of PCBs and PBDEs

Earlier evidence of a size-based segregation of Beaufort Sea beluga whales has been further supported by more recent assessments of PCB and PBDE concentrations and patterns in Beaufort Sea beluga whales. The trends, in relation to PCBs (and PBDEs), for the 2007 to 2010 length and dietary composition indicators for the beluga health project are presented. While PCBs and OCPs typically increase with age, the results did not show a significant trend with age (Figure 5.5).

Evaluating only males, the ΣPCB concentrations did not differ over the period ($p = 0.89$) ranging from 3,630 ± 450 ng g^{-1} lw in 2009 to 3,120 ± 490 ng g^{-1} lw in 2010. The ΣPBDEs were an order of magnitude lower than the PCBs, yet unlike PCB's mean concentrations, differed over the period ($p = 0.3$). The age of beluga whales did not show a significant relationship with PCB or PBDE concentrations (PCBs $r = 0.1$, $p = 0.4$; PBDEs $r = 0.03$, $p = 0.8$) (Figure 5.5). Rather, beluga length was positively related to PCBs for all years and sexes combined ($r = 0.6$, $p < 0.0001$); however, among individual years, belugas collected in 2008 did not maintain a significant length relationship with PCBs ($r = 0.4$, $p = 0.9$). Similarly, length positively related to PBDEs for all years combined ($r = 0.3$, $p = 0.04$), and in 2008 and 2009 relationships were not significant (2008 $r = 0.04$, $p = 0.8$; 2009 $r = 0.3$, $p = 0.3$).

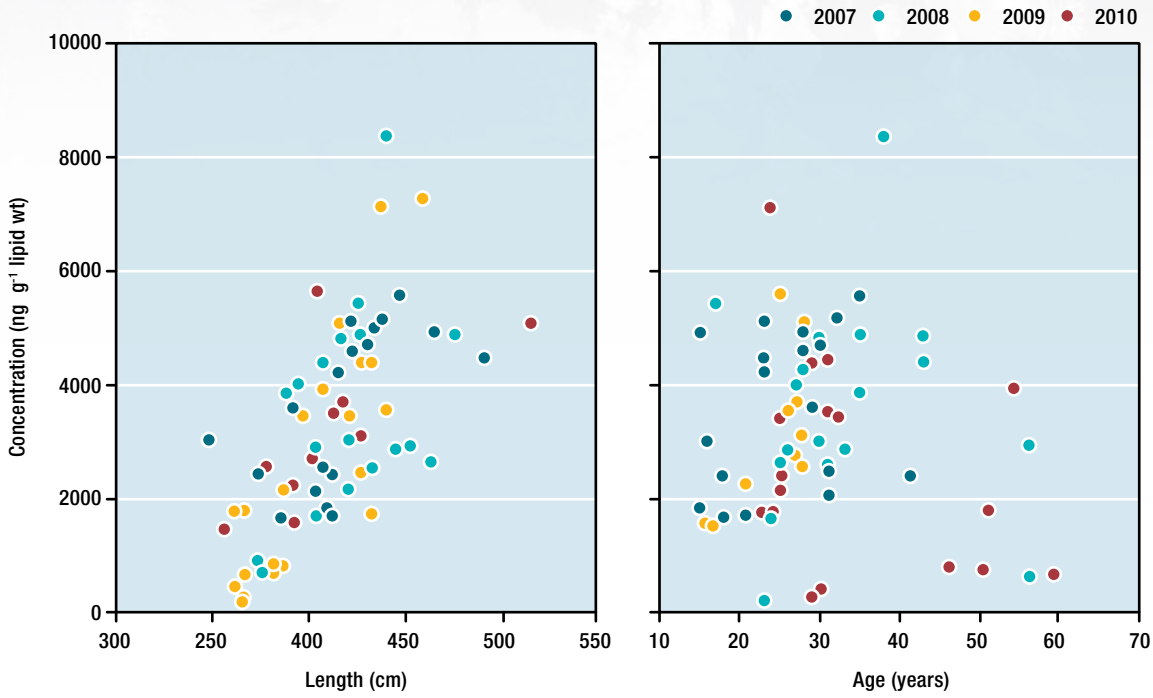

FIGURE 5.5

Total PCB concentrations in males correlated with total body length (with the exception of 2008 beluga) likely due to a combination of size, habitat use and feeding ecology. PCBs were not correlated with age. The lack of a size trend in 2008 suggests similar foraging strategies or contaminant levels in prey for all individuals sampled in that year (Loseto and Ross 2012).

TABLE 5.1. Mean carbon and nitrogen stable isotope ratios (per mil) for beluga liver and muscle samples. Correlations determined for beluga length trends for carbon and nitrogen isotopic values in beluga liver and muscle (Loseto and Ross 2012)

	$\delta^{15}N$ (‰)		$\delta^{13}C$ (‰)	
Year	muscle	liver	muscle	liver
2007	17.2 ± 0.3	18.0 ± 0.4	-18.3 ± 0.2	-19.5 ± 0.2
2008	16.9 ± 0.3	16.8 ± 0.3	-18.5 ± 0.2	-20.5 ± 0.2
2009	16.7 ± 0.3	16.1 ± 0.4	-18.3 ± 0.2	-19.2 ± 0.2
2010	17.9 ± 0.4	16.7 ± 0.5	-18.7 ± 0.3	-20.2 ± 0.3
p value	*0.24*	*0.005*	*0.516*	*< 0.0001*

The PCB concentrations among the sized-defined habitat use groups were found to be significantly different ($r = 0.6$, $p < 0.0001$). Largest males had the highest mean PCB concentrations at 4,400 ± 250 ng g^{-1} lw and smallest males had the lowest concentrations averaging 1,800 ± 480 ng g^{-1} lw. Concentrations of PBDEs did not significantly differ between the three habitat use groups ($r = 0.3$, $p = 0.1$), however the largest males had significantly higher concentrations of 24.8 ± 2 ng g^{-1} lw than the smallest whales 16.5 ± 4 ng g^{-1} lw (Figure 5.5).

5.3.4. Relationships between stable isotopes and fatty acids with PCBs and PBDEs in beluga whales

Stable isotopes of carbon and nitrogen in 2008 and 2009 had generally weak trends in relation to length relative to previous years (Table 5.1). There were no differences between male and female isotopic ratios. This stark contrast from previous years as well as the 2007 trend lends some support for changes in diet or feeding behaviour during the three study years.

Fatty acid signatures also provided insight into feeding ecology as it is related to length (Figure 5.6) and contaminant concentrations in beluga. Fatty acid data was summarized for the inner beluga blubber using a principle component analysis (PCA) with 38 dietary fatty acids. The copepod and arctic cod fatty acid marker 20:1n9 was driving scores along the first axis along with the essential FA docosahexaenoic acid (DHA). 20:1n9 was significantly higher in the larger beluga relative to the smaller beluga (7.7, 12.3% of the total, $p < 0.0001$, t-tests).

The fatty acid PCA scores were used to evaluate drivers of diet such as length, which describes habitat use and diet, as well as PCB and PBDE concentrations. With the exception of 2008, PC1 and length were significantly related (Figure 5.6). However, PC1 scores were significantly related to PCBs and PBDEs in all four years ($p < 0.01$). These results demonstrate the link between recent diet and PCB concentrations. The lack of a size trend with PCBs in 2008 suggests that beluga may not be feeding as previously found with size driven foraging behaviour, yet their diet is associated with contaminant concentrations. This may in part be due to an inter-annual change in feeding ecology, as the whales alter their foraging behaviour with changing ice conditions.

5.3.5. Transplacental transfer of PCBs and PBDEs in beluga whales

Organic pollutants are transferred from females to their offspring throughout the reproductive process, thus exposing neonates to some of the highest levels of endocrine disrupting compounds they will encounter during their lifetime. Lactational transfer of pollutants has been well described in marine mammals, but *in utero* exposure has rarely been documented because of obvious difficulties in obtaining fetal samples from healthy pregnant females. In a recent study, beluga mothers passed on approximately 11% of their ΣPCB and ΣPBDE blubber burden to their young before birth (Desforges et al. 2012). In addition to this important transfer at an early developmental stage, this transmission was not homogenous across PCB and PBDE congeners, and was highly dependent on Log $K_{OW.}$ PCB and PBDE congeners with values below 7 were more readily transferred (Figure 5.7). These results highlight the important role that the physicochemical properties of different PCBs and PBDEs play in governing transfer from mother, and hence, exposure to the fetus.

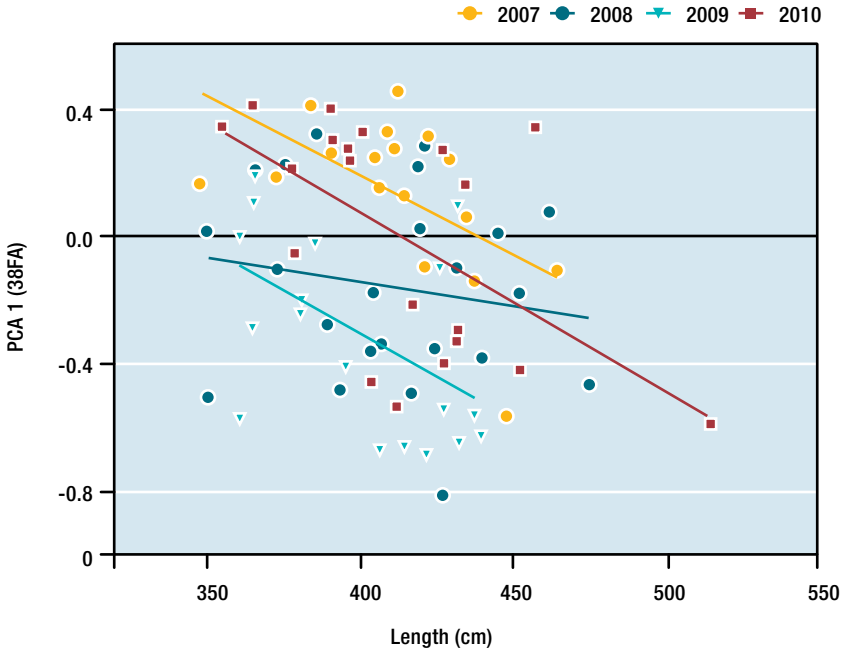

FIGURE 5.6

The first principal component of a PCA for 38 fatty acids was related to the concentrations of PCBs, the top persistent contaminant in beluga whales. This appears to provide support for the established notion that feeding ecology shapes contaminant exposure and accumulation in beluga (Loseto and Ross 2012).

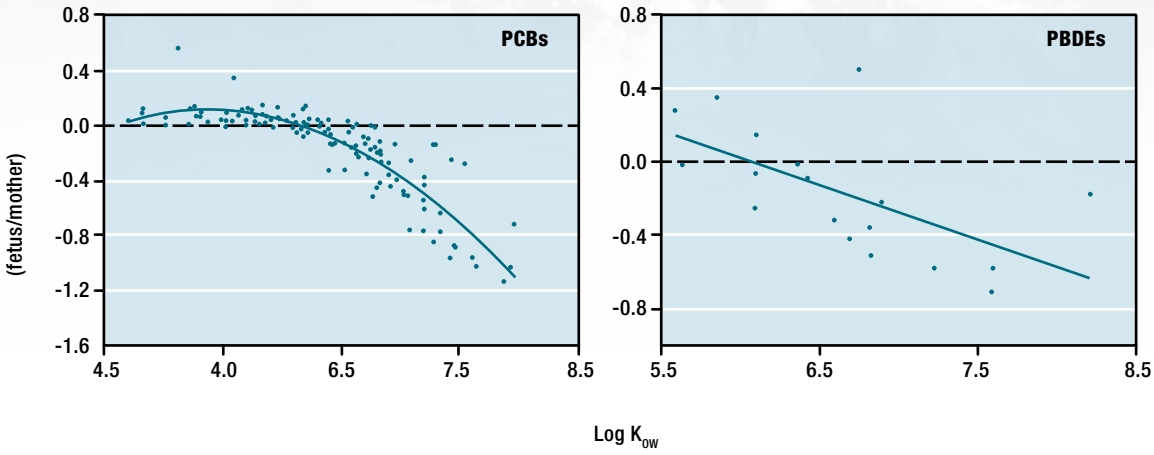

FIGURE 5.7

Average partition ratios plotted against logarithmic octanol-water partition coefficients (log K_{OW}) for PCBs and PBDEs. Partition ratios were calculated as the blubber concentration in the fetus divided by that in the mother and were logarithmically transformed. The dashed line represents partition parity (Desforges et al. 2012).

The toxicological implications of the ready placental transfer of organic contaminants in these beluga are unclear. The risk of toxic insult to neonates is enhanced during pregnancy because exposure occurs during development when hepatic metabolic pathways appear to decrease (Juchau and Faustman-Watts 1983). Experimental studies suggest severe reproductive effects including fetal malformations and mortality, decreased litter size and lower survival rate of newborns (Kihlstrom et al. 1992, Reijnders 1986, Wells et al. 2005). More research is needed to assess the risk of chemical exposure during critical stages of fetal development.

5.3.6. Effects of POPs on beluga health

Beluga whales occupy a high trophic level in the arctic food web, rendering them vulnerable to contamination by a variety of persistent environmental contaminants. While a variety of established "biomarker" approaches can be applied to studies of marine mammals, new technologies provide an opportunity to build on past efforts and shed light on an important facet of arctic contamination (Lockhart et al. 2005, Muir et al. 1999, Stern et al. 2005).

5.3.7. Endocrine endpoints: Vitamins and hormones

Vitamin A concentrations in free-ranging marine mammals are thought to be disrupted by PCBs through several modes of toxic action (Jenssen et al. 2003, Mos et al. 2007, Rolland 2000). Vitamin A is an essential dietary component required for growth, development and maintenance of endocrine, reproductive and immune systems (Simms and Ross 2000). Similar to hormones, vitamin A is distributed to target tissues via transport proteins (retinol-binding protein (RBP)), where it is esterfied for storage or converted to retinoic acid. Retinoic acid binds to nuclear receptors (RAR and RXR) to control physiological functions through gene transcription. Considering plasma levels of vitamin A were found to relate with PCB levels compared to whole blood, it is important to conduct inter-tissue comparisons (Jenssen et al. 2003).

Total vitamin A in blubber was highest in beluga studied in 2009, compared to levels measured in 2007, 2008 and 2010 (2007: 42.2 ± 4 μg g^{-1} lw; 2008: 34.2 ± 3 μg g^{-1}; 2009: 51.4 ± 3 μg g^{-1}; 2010: 43.9 ± 4 μg g^{-1}; $p = 0.004$). Total vitamin A in liver and inner blubber did not differ between sexes ($p < 0.05$), but vitamin concentrations in the outermost blubber layer were higher in females ($p = 0.03$). After accounting for the confounding influences of sex, age, condition, and length, total vitamin A ($r^2 = 0.19$, $p = 0.001$) and the retinol-retinyl ester ratio ($r^2 = 0.20$, $p = 0.008$) negatively correlated with blubber PCB concentrations (Figure 5.8). In contrast, plasma vitamin A ($r^2 = 0.24$, $p = 0.02$) and all forms of vitamin A in inner blubber (retinol: $r^2 = 0.22$, $p = 0.001$; total vitamin A: $r^2 = 0.43$, $p < 0.001$) positively related to PCBs. These results indicate a contaminant-related disruption of vitamin A homeostasis in beluga whales where vitamin A is mobilized from its primary storage site in the liver, resulting in elevated concentrations in plasma and blubber (Figure 5.8). Given the importance of vitamin A in crucial physiological functions related

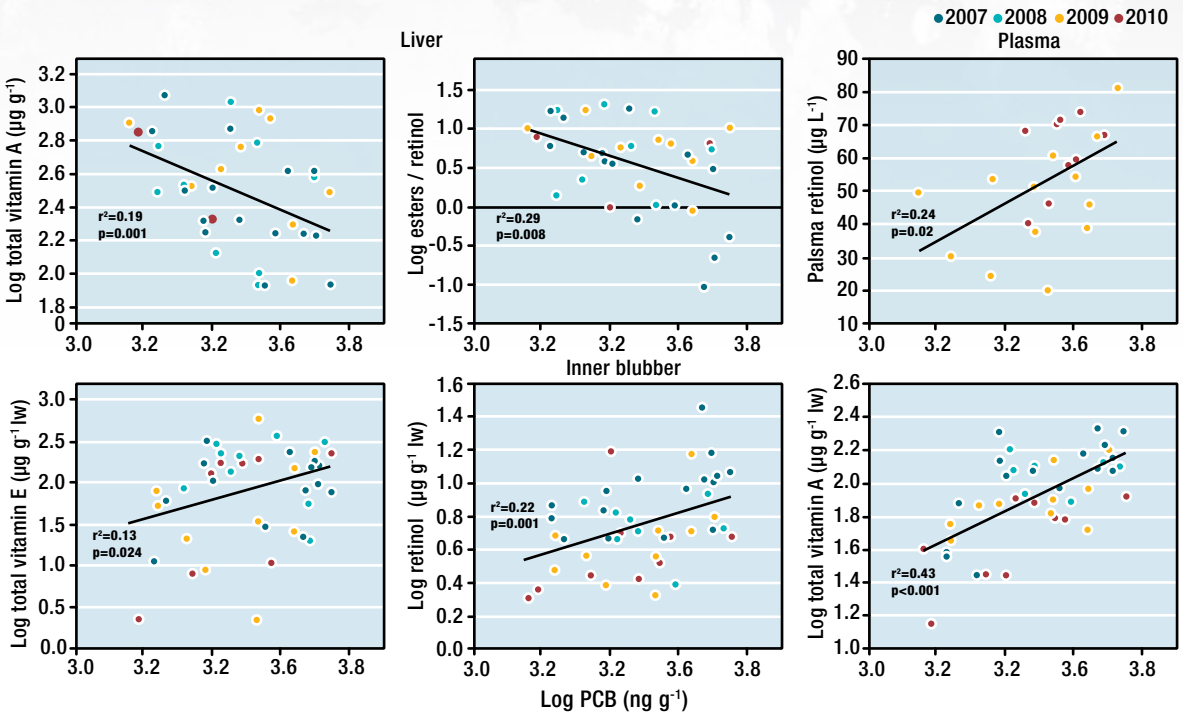

FIGURE 5.8

Vitamin A and E compounds correlate with PCB concentrations in liver, plasma, and inner blubber of Beaufort Sea beluga whales. Taken from Desforges et al. (2013).

to development, reproduction and immunological health, these results underscore the potential risk of population level effects in beluga whales.

Other, well known biomarkers for endocrine disruption are the thyroid hormones and steroid hormones (Loseto and Ross 2011). Thyroid hormones are responsible for the oversight of such key processes as growth and development, with implications for sexual development and neurological development. Altered levels of circulating hormones with increasing contaminant levels (i.e., PCBs) are thought to result from (a) steroid breakdown via PCB and/or PCB metabolite induced enzyme activity (cytochrome P450 induction) and/or (b) a competitive displacement by PCBs and/or their metabolites of hormones from their receptors. A decrease in thyroid hormone concentrations with increasing pentabromotoluene (PBT) contaminant levels has been observed in spotted seals, ribbon seals, harbour seals and polar bears (Braathen et al. 2004, Chiba et al. 2001, Sormo et al. 2005, Tabuchi et al. 2006a).

Thyroid hormones were measured in beluga serum in 2008 and 2009. Free circulating T3 and T4 were determined along with total T3 and T4 in serum samples. With the exception of T3 and T4 in 2009, all free and total T3 and T4 were significantly and positively related to one another. Samples collected in 2009 did not differ between sexes. No correlations were observed with ΣPCB or ΣPBDE concentrations. These early results might suggest that contaminant concentrations are not high enough to disrupt thyroid hormone homeostasis, but a small sample size, as well as confounding factors (age, sex, and condition) may have masked the preliminary assessment.

In 2008, several biological variables were measured to evaluate health effects. For example cholesterol, vitamin E and D were measured in serum; these have been also touted as biomarkers (e.g., Rosa et al. 2007). Vitamin E is known for its prevention of lipid oxidation and propagation of free radicals. Additionally, Thiobarbituric Acid Reactive Substances (TBARS) were measured to determine if degradation of lipids resulting from peroxidiation was taking place. TBARS are produced by lipid peroxidiation and are thus used as an oxidative stress biomarker.

There were no significant negative trends with these biomarkers and PCBs, suggesting a lack of an effect on blood lipid oxidation and vitamin circulation. Rather, positive trends were observed. For example, cholesterol in serum was positively related to PCB concentrations, suggesting that diet confounds the

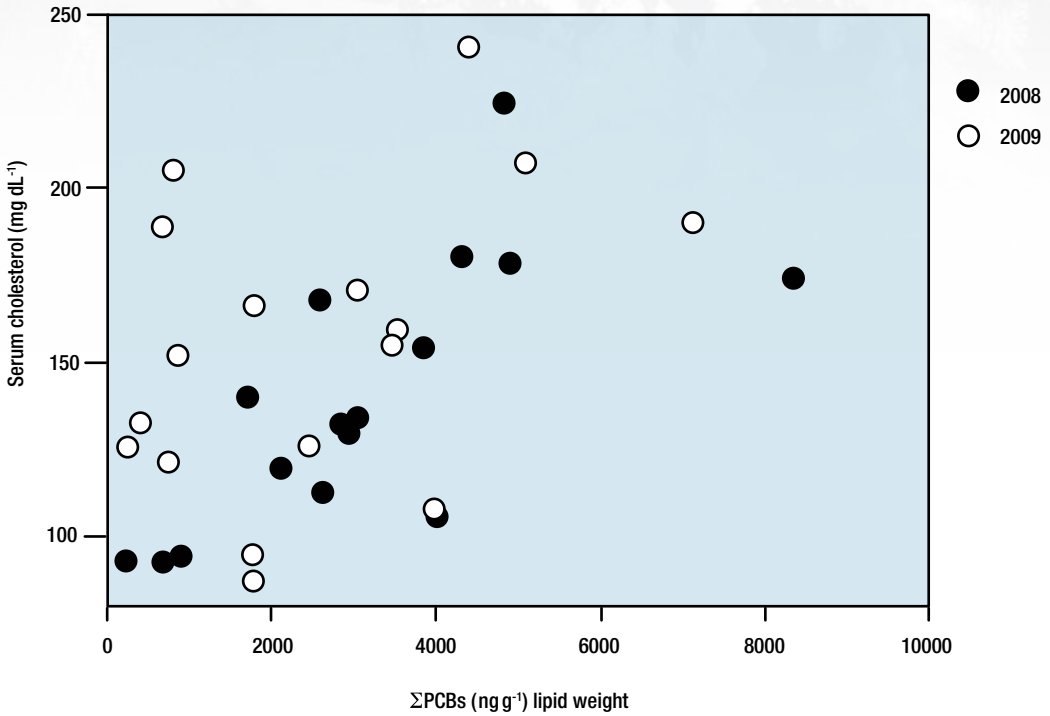

FIGURE 5.9

Relationship between cholesterol in serum and PCB concentrations in beluga (Loseto and Ross, unpublished data).

relationship with contaminants (Figure 5.9). Similarly to vitamin A, vitamin E positively correlated with PCBs in blubber (Figure 5.8). A positive relationship between cholesterol and the lipophilic vitamin E was observed in belugas and has been observed in humans (Cham et al. 1998).

5.3.8. The development and application of new genomics-based tools to assess beluga health

Beluga whales may be affected by contaminants at the population, individual, and/or cellular-molecular level. While population level consequences are of significant concern, demonstrating such impacts is fraught with difficulty and rarely possible. New genomics techniques, like quantitative polymerase chain reaction (qPCR), may offer important opportunities to detect changes of specific targeted gene mRNA transcripts (Veldhoen et al. 2009). Previous studies have reported PCB-related increase in thyroid hormone receptor expression in harbour seals from British Columbia, Canada, and ringed seals from Svalbard and the Baltic Sea (Routti et al. 2008, Tabuchi et al. 2006a). Recently, in killer whales from the Northeast Pacific, Buckman et al. (2011) found PCB-related increases in the expression of five target genes including the aryl hydrocarbon receptor, thyroid hormone receptor alpha, estrogen receptor alpha, interleukin-10, and metallothionein-1.

New beluga-specific tools to investigate the impacts of PCBs and PBDEs on gene expression have been developed (Noël et al. 2013). Blubber, skin, liver, and muscle samples were taken from the 54 Hendrickson Island belugas (24 from 2008, 20 from 2009, and 10 from 2010). Samples were later preserved in RNA and stored at -20°C until total RNA isolation. Blubber samples were divided into inner, middle, and outer blubber in order to investigate any possible variations in gene expression within the blubber layer.

Briefly, total RNA was isolated using the single-step RNA isolation method based on guanidine isothiocyanate/phenol/chloroform extraction with Trizol as a reagent. Total cDNA was produced using Superscript II RNase H- reverse transcriptase. RNA from all the 44 samples of blubber, skin, liver and muscle and 20 samples of kidney was successfully extracted.

Beluga-specific primers to evaluate were developed for 15 genes based on their potential sensitivity to persistent organic pollutants, or their role in

TABLE 5.2. Fifteen beluga whale-specific primers developed for qRT-PCR application to tissue samples collected from belugas from the Beaufort Sea (Noel et al. 2013).

Ribosomal protein L8 (L8)	Adiponectin
Glyceraldehyde-3-phosphate Dehydrogenase (GAPDH)	Leptin
Cytoplasmic Beta Actin (CBA)	Insulin-Like Growth Factor 1 (ILGF1)
Thyroid Receptor Alpha (TR-a)	Vitamin D Receptor (VDR)
Thyroid Receptor Beta (TR-b)	Metallothionein 1 (MT1)
Estrogen Receptor Alpha (ER-a)	Heat Shock Protein 70-1 (HSP70-1)
Peroxisome Proliferator-Activated Receptor Gamma (PPAR-g)	Glucocorticoid Receptor (GR)
Retinoid X Receptor Alpha (RXR-a)	Aryl Hydrocarbon Receptor (AhR)

nutrition and metabolism (5.2). Included were three housekeeping genes (ribosomal protein L8, Glyceraldehyde-3- phosphate dehydrogenase (GAPDH) and cytoplasmic B-actin). Quantitative real-time polymerase chain reaction (qRT-PCR) was used to provide a relative quantification of results.

Housekeeping genes are used to evaluate the quality of the data. Bustin et al. (2010) recommended that normalisation should be performed against multiple housekeeping genes. In the present study, the geometric mean for the expression of three housekeeping genes was used. Preliminary results for two important toxicology-related genes, aryl hydrocarbon receptor (AhR) and cytochrome P450 (Cyp1A), are available (Noël et al. 2013). AhR and Cyp1A expression were quantified in liver, the main organ for the metabolism of contaminants. Dioxin-like compounds such as certain PCB congeners exert their toxicity in part via the aryl hydrocarbon receptor (AhR), a soluble, ligand-activated transcription factor. The activation of AhR induces the transcription of multiple target genes including cytochrome P450 (Cyp 1A), a metabolizing enzyme. The expression of AhR and Cyp1A increased significantly with age. Beluga collected in 2010 had significantly lower AhR and Cyp1A expression, probably reflecting their younger age, although the potential influence of feeding ecology, contaminant exposure, environmental conditions cannot be ruled out and are currently under investigation. Generally, the expression of AhR and Cyp1A increased with PCB concentrations (Figure 5.10), although the relationship was not significant for AhR in the 2010 whales likely reflecting the small sample size for that particular year.

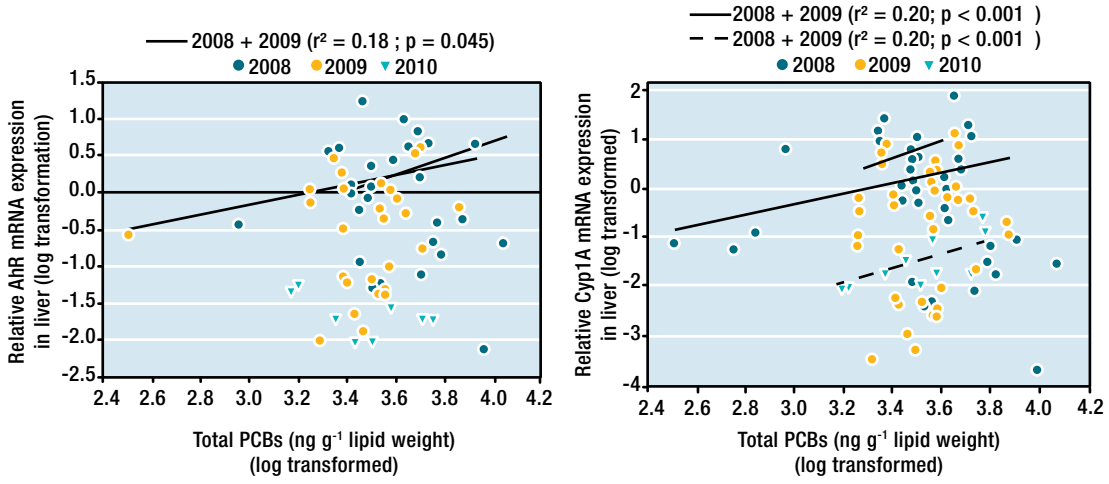

FIGURE 5.10

AhR and Cyp1A expression in liver of beluga males increased with PCB concentrations in blubber. Fold change expression is relative to the geometric mean of the three housekeeping gene expression (Noël et al. 2013).

Other studies have reported an increase in AhR expression with exposure to dioxin-like contaminants (see section 5.2.1) (Braune et al. 2011, Verreault et al. 2013). Jensen and Hahn (2001) also reported that the beluga AhR is a high affinity AhR, suggesting that this species might be particularly sensitive to dioxin-like compounds.

These preliminary results reveal that an important toxicology-related gene is up-regulated in Beaufort Sea beluga whales, despite their exposure to only moderate levels of PCBs. This indicates that individual whales are exposed to levels of contaminants that elicit physiological responses. The extent to which these responses may affect this population is currently unclear.

5.4. Polar Bears

An extensive review of the health effects of long-range atmospheric transport (LRAT) contaminants in arctic top predators, including polar bears, was done by Sonne (2010). Polar bears inhabit a cold environment and therefore rely on energy-rich fatty and waxy tissues as their main energy source. Since the 1940s, large amounts of fat-soluble atmospheric and marine long-range transported persistent and toxic chemicals have biomagnified in the arctic marine food webs. The review by Sonne (2010) showed that hormone and vitamin concentrations, liver, kidney and thyroid gland morphology as well as reproductive and immune systems of polar bears are likely to be influenced by contaminant exposure. Bone density reduction, neurochemical disruption and DNA hypomethylation of the brain stem were also observed health effects of contaminants on polar bears. The range of tissue concentration, at which these alterations were observed in polar bears, were ca. 1–70,000 ng g^{-1} lw for POPs (blood plasma concentrations of some PCB metabolites were even higher), ca. 1–1,000 ng g^{-1} lw and 114–3,052 ng g^{-1} ww for PBDEs and PFASs, respectively.

Lie et al. (2004) investigated the humoral immunity vs. POPs in blood plasma of polar bears from Svalbard, Greenland and from Churchill, Canada between 1998 and 1999. The Canadian polar bears were considered as a reference group which were thought to be subject to lower contamination levels. The polar bears were captured/recaptured during 1998–1999 and were immunized with inactivated influenza virus, reovirus, herpes virus and tetanus toxoid at the time of capture. At the time of immunization and recapture (32–40 days following immunization), blood plasma levels of PCBs, OCPs, serum IgG concentrations and specific antibodies against influenza virus, reovirus, herpes virus, tetanus toxoid and Mannheimia haemolytica were analysed. The statistical analyses showed that tetanus toxoid was positively correlated with ΣPCB while IgG and influenza/reovirus titres were negatively correlated with blood plasma ΣPCB concentrations. The authors concluded, as in the previous AMAP assessment (de Wit et al. 2004), that POPs exposure may impair the humoral immune response toward micro pathogens which, in the most ultimate cases, may affect the individuals' chances of survival. Interestingly, the authors found that PCB concentrations were significantly higher in blood plasma from bears with a low body condition index (score 1 [very lean] to score 5 [very fat]).

A recent trans-Arctic study of temporal (pre- vs. post-industrial) and spatial (Canadian High Arctic,

Photo: André Rochon/ArcticNet

Svalbard and East Greenland) trend study was carried out to compare polar bear reproductive organ size from 55 male and 44 female East Greenland polar bears sampled in 1999–2002 and the results were compared with those previously reported from Canada sampled in 1994–1997 (Sonne et al. 2007). It was reported that the size of baculum and uterus of Canadian polar bears were significantly higher compared to those of East Greenland polar bears. Researchers concluded that this could be due to exposure of polar bears in East Greenland to higher concentrations of anthropogenic long-range transported POPs or due to climate fluctations.

5.5. Seabirds

5.5.1. Biomarker responses associated with halogenated organic contaminants in northern fulmars and black guillemots

Northern fulmars breeding in the Canadian Arctic share the same relative trophic level with other seabird species throughout this region (Fisk et al. 2001, Hobson 1993). However, organochlorine concentrations in fulmars are higher than expected based on calculated POP-trophic level relationships (Buckman et al. 2004, Fisk et al. 2001). EROD activity and retinoid (vitamin A) concentrations in livers, as well as thyroid hormone (total triiodothyronine (TT_3), total thyroxine (TT_4) levels in blood plasma were measured in adult northern fulmars at two breeding colonies in the Canadian High Arctic; Prince Leopold Island Migratory Bird Sanctuary in Lancaster Sound and Cape Vera on northern Devon Island. Biomarker levels or responses did not differ significantly between males and females at either colony, nor was there any significant difference between colonies (Braune et al. 2011). No significant relationships were found between retinoid or thyroid hormone levels and any of the contaminants or TEQs measured in the northern fulmars suggesting that, either contaminant exposure in the Canadian fulmars was not of sufficient magnitude to significantly affect those biochemical markers, or that they are not a sensitive indicator of contaminant exposure in the fulmars (Braune et al. 2011). However, there was a significant positive correlation between EROD activity and hepatic TEQs (Figure 5.11), which suggests that EROD induction occurs in northern fulmars at environmentally-relevant contaminant concentrations. Hepatic EROD activity is catalyzed by isoenzymes from the Cyp1A subfamily which are induced by coplanar halogenated hydrocarbons (e.g., dioxin-like compounds) with high affinity for the AhR receptor (Peakall 1992, Poland and Knutson 1982). Other avian studies have also reported positive correlations between TEQ concentrations and EROD activity (Bosveld et al. 2000, Elliott et al. 1996, Letcher et al. 2010).

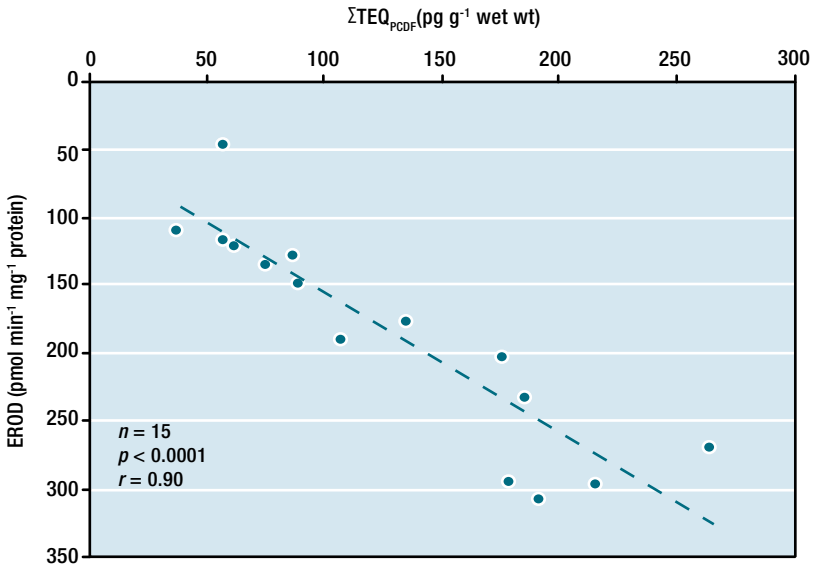

FIGURE 5.11

Relationship between toxic equivalents of polychlorinated dibenzofurans (TEQ- PCDF) and hepatic EROD in adult fulmars from Prince Leopold Island. TEQ-PCDF constituted 78% of the total TEQ (Braune et al. 2011).

Photo: Martin Fortier/ArcticNet

Helgason et al. (2010), Kubota et al. (2005), and Kuzyk et al. (2003) showed that liver biomarkers respond to relatively low PCB exposures in black guillemot nestlings at Saglek Bay, Labrador. As expected, based on circumpolar patterns of organochlorines, adult northern fulmars from Bjørnøja in the Barents Sea had a higher mean ΣTEQ (7.3 ± 8.7 ng g^{-1} lw (Knudsen et al. 2007)) than the Prince Leopold Island fulmars (3.8 ± 2.0 ng g^{-1} lw, Braune et al. 2010). The fulmars from Bjørnøya also showed a positive correlation between EROD activity and hepatic TEQs based on concentrations of PCDD/Fs and non-ortho and mono-ortho PCBs (Helgason et al. 2010). Further, a meta-analysis of contaminants and health-related physiological variables in fulmars from the Canadian and Norwegian Arctic as well as the Faroe Islands demonstrated that exposure to PCBs, dioxins and furans may be associated with modulation of thyroid and retinoid homeostasis on a large geographical scale (Verreault et al. 2013).

Studies in 1999 at Saglek Bay, Labrador, found adverse effects on the immune and endocrine systems, and on organ development in black guillemot chicks in nests within 6 km of a point source of marine PCB pollution (Kuzyk et al. 2003). In 2007, the study was repeated to assess any ecological improvements following the cleanup of PCB-contaminated soil at Saglek Bay. Significant declines in PCB concentrations in the livers of guillemot chicks between 1999–2000 and 2007 indicate that the remediation of PCB-contaminated soil at Saglek Bay has been effective in reducing PCB levels in the marine ecosystem (Burgess 2009). Increased plasma testosterone and estradiol concentrations, increased liver EROD activity, and decreased liver retinol and retinyl palmitate concentrations suggest that PCB concentrations in the guillemots have declined below the levels associated with adverse effects. However, elevated hepatic PCB levels (geometric mean of 116 ng g^{-1} wet wt) in guillemot chicks closest to the originally-contaminated Saglek Bay beach area are still associated with lower than normal thyroid hormone levels (thyroxine) in the blood and elevated levels of two neurotransmitter enzymes (cholinesterase, monoamine oxidase) in the brain suggesting that, although there have been major improvements since 1999, there has not yet been a full return to normal conditions (Burgess 2009).

5.5.2. Contaminant-related oxidative stress in glaucous gulls

A recent study looked at the relationships between levels of legacy POPs and indicators of oxidative stress in nestling glaucous gulls at two Canadian Arctic sites (Karrak Lake in Queen Maud Gulf Bird Sanctuary and Devil Island, both in Nunavut) (Wayland et al. 2010). The study found that, although hepatic contaminant levels were relatively low in the glaucous gull chicks, oxidized glutathione (GSSG) concentrations rose with increasing organochlorine/PCB concentrations whereas thiols, including glutathione (GSH), were negatively correlated. However, the evidence for a shift to a more oxidized state, measured as decreased GSH, increased GSSG, or an elevated GSSG:GSH ratio, was weak leading to the conclusion that the glaucous gull nestlings at the two colonies were exposed to lower levels of oxidative stress than birds in more contaminated environments.

5.6. Risk Assessments of Marine Mammals and Seabirds

5.6.1. Understanding risks associated with complex mixtures in arctic marine mammals

While the accumulation of POPs has been well documented in arctic marine mammals, an understanding of the related health risks remains largely elusive. The highly complex nature of contaminant mixtures found in arctic marine mammals presents a major

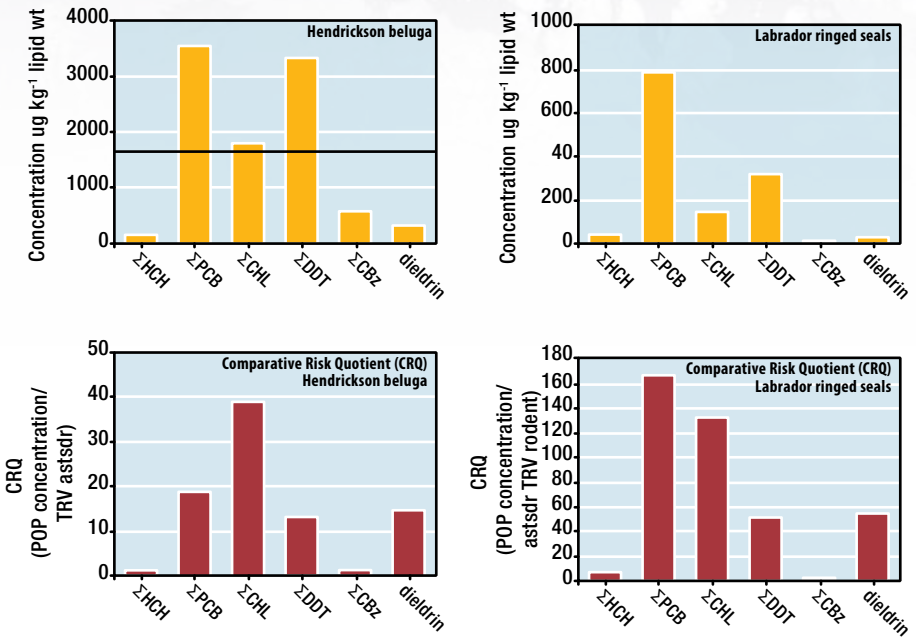

FIGURE 5.12

Comparative Risk Quotients (CRQs; red bars) are derived from the combination of concentrations measured (yellow bars) in free-ranging marine mammals (beluga whales, left; ringed seals, right) and Toxicity Reference Values (TRVs) collated from the U.S. Agency of Toxic Substances and Disease Registry(ATSDR 2012): CRQ = [POP in marine mammal] / TRV in rodents. (Ross, Unpublished data, Dept of Fisheries and Oceans, 2012).

impediment to documenting "causality" associated with a specific contaminant. Given the "conserved nature" of many physiological endpoints among mammals, rodents are typically used to evaluate chemical safety in humans. Such an approach has rarely been used in wildlife toxicology studies, the existence of an extensive database of toxicological profiles for rodents provides one promising means of prioritizing POPs of concern in the Arctic. POP-related health risks were characterized in two arctic marine mammals—ringed seals and beluga whales by deriving Corrected Risk Quotients (CRQ) using [POP in marine mammal]/[Toxic Reference Value (TRV) in rodents] (ATSDR 2012). The collective results (Figure 5.12) suggest that the health risks to marine mammals inhabiting remote regions can be attributed to several POPs, while risks to marine mammals inhabiting contaminated sites are more likely to reflect locally used chemicals (e.g., PCBs at Saglek Bay).

5.6.2. Observed concentrations vs. thresholds for biological effects

Previous assessments of POPs in Canadian and circumpolar arctic wildlife have included comparisons with No Observed Adverse Effects Levels (NOAELs) and Lowest Observable Adverse Effects Levels (LOAELs) or other effects thresholds based on laboratory and captive animal studies, or on field observations (de Wit et al. 2004, Fisk et al. 2005). The effects assessment is updated here using mean concentrations of PCBs, PFOS and PBDEs in marine mammals and seabirds for the period 2003–2010. Maximum annual means over the period 2003–2010 (Annex Tables 1, 4, 6 and 11) were used for the assessment. It should be noted that this cross species comparison provides only a general assessment of the possible effects or biochemical responses, because pharmacodynamic and pharmacokinetic characteristics are species-specific and can influence sensitivity in a species (Schwacke et al. 2002).

Mean ΣPCB concentrations in marine mammal blubber are compared with reported thresholds for effects for free-ranging bottlenose dolphins and for harbour seals from Hall et al. (2006) and Ross et al. (1996) (Figure 5.13). Mean concentrations for all 3 species are below these values although some individuals, especially polar bears in western Hudson Bay, may exceed them. However, ΣPCB concentrations in beluga and polar bears exceed the toxicity reference value for immunotoxicity and

endocrine disruption of 1.3 µg g^{-1} lw in harbor seals (Mos et al. 2010). Also, liver detoxification enzyme systems may be elevated based on the results for expression of AhR and Cyp1A in beluga (Noël et al. 2013).

Mean ΣPCB concentrations in Canadian arctic seabird eggs are compared with reported thresholds for effects for egg mortality and hatching success in fish eating birds in Figure 5.14. Concentrations are well below these thresholds except for glaucous gull where some individual eggs may exceed the threshold. However, where liver EROD was elevated in northern fulmars (Braune et al. 2011) eggs in the same population had ΣPCB averaging about 170 ng g^{-1} ww. The elevated EROD was likely due to combined effects of PCDFs, PCDDs and non-ortho-PCBs which were 128 pg g^{-1} ww, 10 pg g^{-1} ww and 22 pg g^{-1} ww, respectively (Braune et al. 2010). As noted for marine mammals, it is likely that liver detoxification enzyme systems are elevated as a result of PCB exposure although for the seabirds the co-occurring PCDFs and non-ortho PCBs were responsible for the responses.

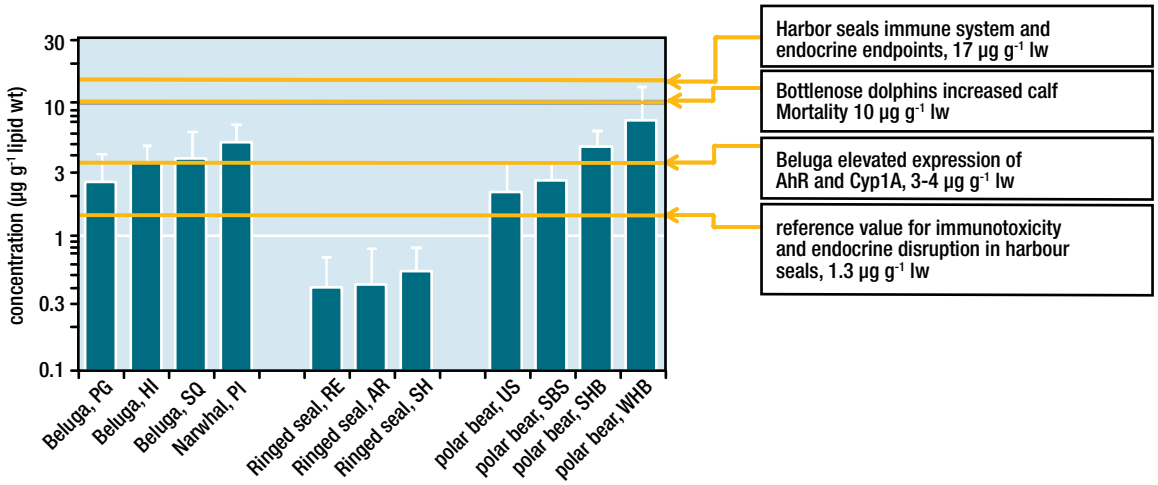

FIGURE 5.13

Mean concentrations (+1 SD) for ΣPCBs in blubber of beluga and narwhal (PG=Pangnirtung, HI-Hendrickson Is.,SQ=Sanikiluaq, PI=Pond Inlet), ringed seals (SH=Sachs Harbour, AR= Arviat, RE=Resolute), and polar bears (LJS=Lancaster/Jones Sound, SBS=Southern Beaufort Sea, SHB=Southern Hudson Bay, WHB=Western Hudson Bay). Effects values for free-ranging bottlenose dolphins and for harbour seals are from Hall et al. (2006) and Ross et al. (1996): Data from Annex Table A4-1 and A4-13. The approximate concentration in blubber associated with elevated expression of AhR and Cyp1A is from Noël et al. (2013).

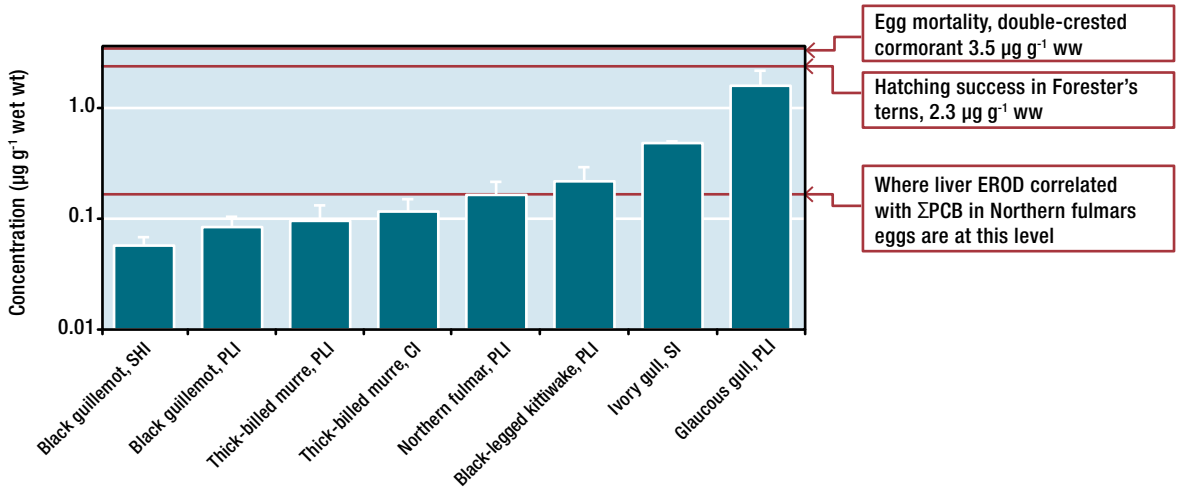

FIGURE 5.14

Mean ΣPCB concentrations in Canadian arctic seabird eggs compared with reported thresholds for effects for egg mortality and hatching success in fish eating birds. Data are taken from Annex Table A4-8.

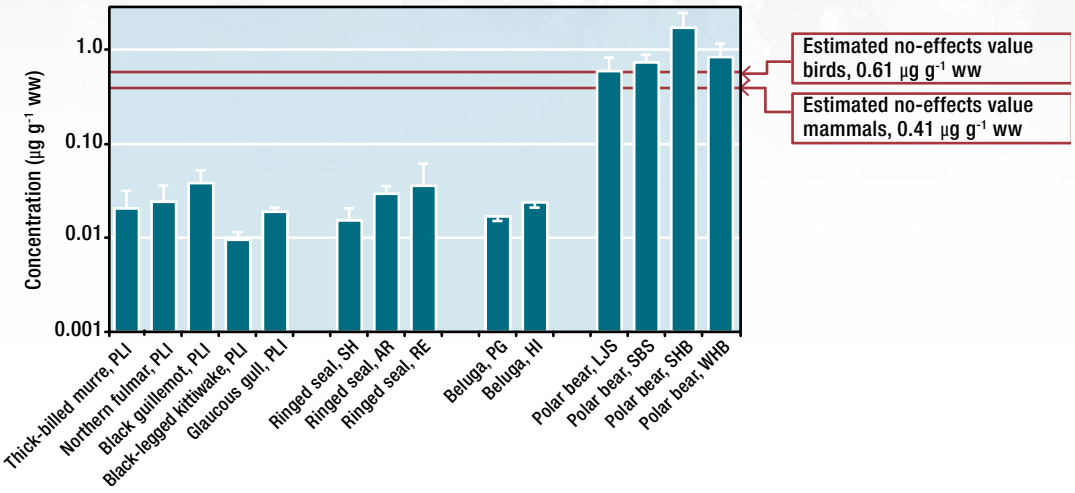

FIGURE 5.15

Mean concentrations (+1 SD) for PFOS in liver of seabirds (PLI=Prince Leopold Is), ringed seals (SH=Sachs Harbour, AR= Arviat, RE=Resolute) beluga (PG=Pangnirtung, HI-Hendrickson Is.), and polar bears (LJS=Lancaster/Jones Sound, SBS=Southern Beaufort Sea, SHB=Southern Hudson Bay, WHB=Western Hudson Bay). Data are from Annex Tables A4-1, A4-11 and A4-13. Estimated no-effects values are from Environment Canada (Environment Canada 2006a).

In Figure 5.15, mean concentrations of PFOS (including PFOSA) in livers of seabirds, ringed seals, beluga whale and polar bears are compared with estimated no-effects values (ENEVs) for birds and mammals (Environment Canada 2006a). These ENEVs are conservative because they are based on a lowest observed effects concentration divided by an application factor of 100. Concentrations of PFOS in polar bear livers exceed the ENEVs. However, the seabirds have PFOS concentrations well below the ENEV for birds, which is based on studies of effects in mallard ducks (Environment Canada 2006a). PFOS concentrations in seabird eggs were also well below toxicity threshold levels found in the literature (Braune and Letcher 2013).

In the case of PBDEs, no ENEVs or effects thresholds expressed as tissue concentrations are available which preclude the assessment presented above for PCBs and PFOS. Risk assessments for PBDEs in mammals have instead focussed on doses (mg kg^{-1} d^{-1}) which are difficult to estimate for arctic wildlife. However, ENEVs for ΣPBDEs in the diets of wildlife consumers have been developed (Environment Canada 2006b). The ENEV for pentaBDE is 8.4 ng g^{-1}, which is generally higher than concentrations in Canadian arctic fish or seabird eggs (that could be scavenged by other birds or polar bears).

5.7. Assessment

5.7.1. Conclusions

- Assessing the effects of POPs on the health of Canadian arctic biota is very challenging due to a variety of factors. These include low contaminant exposures compared to biota from industrialized regions, limited access to fresh samples, difficulties in processing samples in a way that suits the needs of health endpoints in the field, and a limited knowledge of life history and feeding ecology of many species.
- While toxicological studies of arctic wildlife remain challenging, recent investment in research under the NCP is increasing the understanding of the effects of persistent contaminants on high trophic level biota.
- The effects of POPs on arctic wildlife have to be placed in the context of other environmental, ecological and physiological stressors (both anthropogenic and natural) that create a highly complex picture.
- There remains minimal evidence that POPs have widespread effects on the health of Canadian arctic animals. The best evidence for effects in top predators are from studies of East Greenland and Svalbard polar bears and Svalbard glaucous gulls, which have much higher exposures to most POPs than in the Canadian Arctic.

- Studies at the PCB contaminated site at Saglek Bay have demonstrated declines in the concentrations of PCBs in sediment, in biota, and in biological effects in the marine environment over time. PCB concentrations in shorthorn sculpin and black guillemot nestlings at Saglek Bay are below concentrations (1,000 ng g^{-1} ww) previously associated with risks of impaired reproduction and survival.
- While biological studies of shorthorn sculpin in 2007 corroborate these results, immune function and the developing reproductive system of black guillemots continued to be affected by PCBs (as initially reported in 1999).
- Surface sediment PCB concentrations in Saglek Bay have remained below the site-specific threshold (77 ng g^{-1} dw) established for probable adverse effects since 2010, suggesting reduced risk for black guillemot nestlings over time.
- Deer mice from the beach area at Saglek Bay exhibited no adverse effects to thyroid histomorphometry or histopathology (in 2007), but reduced bone mineral density suggested lingering effects associated with residual PCB contamination in the terrestrial environment.
- In beluga from the southern and eastern Beaufort Sea population, weak relationships were found between PCB concentrations and serum vitamin A levels, but not with cholesterol, vitamin E and D or Thiobarbituric Acid Reactive Substances.
- In the same animals, no relationship was found between thyroid hormones and contaminant concentrations suggesting exposure is not high enough to disrupt thyroid hormone homeostasis.
- The expression of AhR and Cyp1A in beluga increased with PCB concentrations but more work is needed to understand the influence of feeding ecology, contaminant exposure, and environmental conditions on these measurements.
- No significant relationships were found between retinoid or thyroid hormone levels and any of the contaminants or TEQs measured in the northern fulmars. However, liver EROD was elevated in northern fulmars which were likely due to the combined effects of PCDFs, PCDDs and non-ortho PCBs.
- While hepatic contaminant levels were relatively low in the glaucous gull chicks, oxidized glutathione (GSSG) concentrations rose with increasing organochlorine/PCB concentrations, suggesting the gull chicks were responding physiologically to contaminant exposure.
- ΣPCB concentrations in beluga and polar bears exceed the toxicity reference value for immunotoxicity and endocrine disruption of 1.3 μg g^{-1} lw in harbor seals.
- Mean ΣPCB concentrations in Canadian arctic seabird eggs are well below reported thresholds for egg mortality and hatching success in fish-eating birds (except for glaucous gulls).
- Concentrations of PFOS in polar bear livers exceed the ENEVs but PFOS levels in liver of birds and seals were an order of magnitude below no effects values.

5.7.2. Recommendations

- The development, validation and application of new genomics methods provides a powerful means of examining the relationship between physiological endpoints and persistent contaminants and should be applied to examine subtle effects on higher trophic level arctic animals.
- In future, emphasis should placed on the multiple ecological, biological, and physical (natural and anthropogenic) variables that need to be considered when analyzing contamination in species and when comparing data between studies.

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CHAPTER 6

Interlaboratory Quality Assurance for the Northern Contaminants Program

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Photo: Adam Socha

CHAPTER 6

Interlaboratory Quality Assurance for the Northern Contaminants Program

Coordinating authors: Victoria Tkatcheva and Eric Reiner
Contributors: Mehran Alaee, Barry Ali, Rita Dawood, Cathy Doehler, Rania Farag, Sathi Selliah, Ed Sverko, Dan Toner

6.1. Introduction

Between 2005 and 2012, six rounds of interlaboratory studies (ILS) were conducted to evaluate the analytical data provided to the Northern Contaminants Program (NCP). From 2007, laboratories that participated in the Arctic Monitoring and Assessment Programme (AMAP) were included and also evaluated to ensure that the pre-established NCP data quality objectives were met (Selliah et al. 2008). These studies involved "legacy and emerging contaminants" of concern. This summary report focuses on a broad range of organic contaminants. Presented in the body of this report is a summary of the study design, evaluation and statistical treatment of the results covering the period from 2005–2012 of NCP-III Phase 1 to Phase 6 (NCP-III 1-6) study. It presents the performance of NCP laboratories compared to the AMAP and all other laboratories that participated in the ILS. From its inception, the NCP-III 1-6 study has shown an increase in the number of participating laboratories and the addition of analytes.

Thirty-four organizations with forty-three laboratories from thirteen countries participated in NCP-III 1-6 for persistent organic pollutant (POPs) studies. Many laboratories have participated from the inception of the program whilst others joined during the later rounds. To keep current with the ever-increasing pollutant list, the NCP-III 1-6 program has steadily increased the number and type of organic pollutants included in the studies.

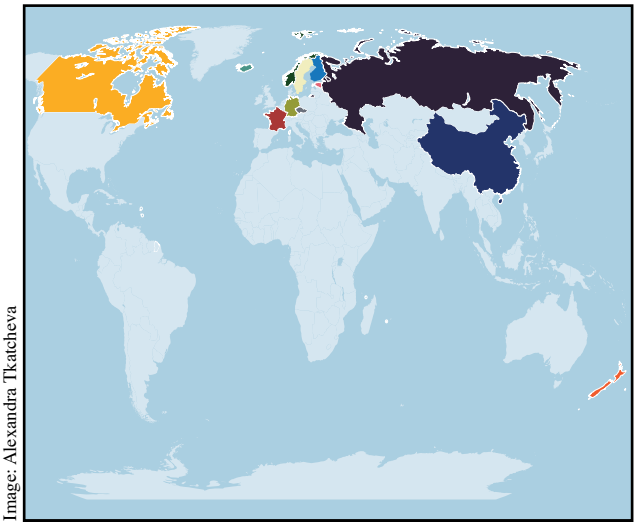


Image: Alexandra Tkatcheva

The samples submitted consisted of injection ready standards (IRS), certified reference materials (CRM) including biota material at varying concentration levels, and other samples, like seal, for which a reference material was not available.

6.2. Background

The NCP was established in 1991 under the management and jurisdiction of the Department of Indian Affairs and Northern Development, the federal departments of Health, Environment, and Fisheries and Oceans, the Yukon, Northwest Territories and Nunavut territorial governments, and Northern Aboriginal organizations—Council of Yukon First Nations, Dene Nation, Inuit Circumpolar Conference, Inuit Tapirisat of Canada, and Métis Nation of the Northwest Territories.

The first of the studies NCP-I QA Program focused on determining the types of contaminants present with particular interest as to the source and location of the contaminants. NCP-II 1-8 studies examined the effects of the contaminants on human health and assessed the Northern community involvement in developing a global agreement to control contaminant release. The eight rounds of NCP-II accommodated forty-seven participants from four countries per ILS, and on average, 60% of these participants performed persistent organic pollutants (POPs) analysis. These forty-seven laboratories participated in all subsequent ILS studies. The previous report (Stokker 2003) concluded for POPs that:

- Some losses for organochlorines (OCPs) and polychlorinated biphenyl (PCBs) in biotic samples were observed compared to the certify values.

TABLE 6.1 NCP III Phase 1 to Phase 6 participating laboratories performed for POPs

Company Name	Country	NCP/ AMAP	1	2	3	4	5	6
ALS Laboratory Group, Environmental Division *	Canada	NCP	x	x			x	x
Aquatic Ecosystem Protection Research Division, S&T Branch, Environment Canada, Burlington	Canada	NCP	x	x	x			
AsureQuality Limited – Wellington Laboratory	New Zealand			x	x	x	x	x
AXYS Analytical Services Ltd., Sidney, BC	Canada	NCP	x	x	x	x	x	x
Cantest Ltd., Burnaby	Canada					x	x	
Centre de toxicologie du Québec/INSPQ, Laboratoire de Toxicologie	Canada	NCP	x	x	x	x	x	x
Centre d'expertise en analyse environnementale du Québec (CEAEQ), Direction du laboratoire des pollutions in ous trielles	Canada			x	x	x	x	x
Centre for Environmental Chemistry of SPA "Typhoon" *	Russia	AMAP				x	x	x
Wildlife Toxicology Research, National Wildlife Research Centre, Environment Canada, Ottawa	Canada	NCP				x	x	x
Department of Applied Environmental Science, Stockholm University	Sweden					x	x	
Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Manitoba*	Canada	NCP	x	x		x		x
Department of Pharmacology and Toxicology, University of Iceland	Iceland	AMAP			x			
Estonian Environmental Centre	Estonia	AMAP					x	x
Finnish Environment Institute (SYKE)	Finland	AMAP				x	x	x
Food Research Division, Health Canada, Ottawa *	Canada	NCP		x	x	x	x	x
Great Lakes Institute for Environmental Research, University of Windsor*	Canada	NCP			x	x	x	x
International Joint Research Center for Persistent Tox Subst (IJRC-PTS), Dalian Maritime University, Dalian	China						x	
International Joint Research Center for Persistent Tox Subst (IJRC-PTS), Harbin Institute of Technology	China						x	
Laboratoire d'Etude des Résidus et contaminants dans les Aliments (LABERCA), Ecole Nationale Vétérinaire, Agroalimentaire et de l'Alimentation Nantes Atlantique (ONIRIS)	France						x	x
Laboratory of Expertise in Aquatic Chemical Analysis (LEACA)/Fisheries and Oceans Canada, Institute of Ocean Science, Sidney, BC	Canada	NCP	x	x	x	x	x	x
Laboratory Services Branch, Ontario Ministry of Environment*	Canada		x	x	x	x	x	x
Laboratory Services, Ecotoxicology and Wildlife Heath Division, Environment Canada, Ottawa*	Canada	NCP	x	x	x	x	x	x
Maxxam Analytics Inc.*	Canada		x	x	x	x	x	
National Laboratory for Environmental Testing (NLET), Laboratory and Field Service Division, Environment Canada	Canada	NCP	x	x	x	x		x
Norwegian School of Veterinary Science, Department of Food Safety and Infection Biology, Laboratory of Environmental Toxicology, Oslo	Norway	AMAP				x	x	x
Organic Analytical Services, Research and Productivity Council, Fredericton, New Brunswick	Canada	NCP					x	x
Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Masaryk University	Czech Republic	AMAP					x	
Russian Academy of Sciences, Saint-Petersburg Scientific-Research Centre for Ecological Safety RAS (SRCES RAS), St-Petersburg	Russia							x
Umweltbundesamt, Federal Environment Agency, Air Pollution Monitoring Network, Langen	Germany						x	x
Analysis and Air Quality Section, Air Quality Research Division, Environment Canada, Ottawa	Canada							x
Institut des Sciences de la Mer de Rimouski (ISMER), Laboratoire de chimic marine et spectroscopic de masse (LCM-S)	Canada		x	x		x		x
Institut Maurice Lamontagne, Peches et Oceans Canada, Mont-Joli (Qc)	Canada							x
Wellington Laboratories Inc., Guelph	Canada		x	x	x	x	x	x

Note: * number of lab participants for an organization that is more than one. Lab codes are confidential and are not associated with the alphabetic order.

- OCPs and PCBs results are more accurate and comparable at analyte concentrations greater than 1 ng g^{-1}
- Future studies should continue to ensure that reliable levels of precision and accuracy are generated for measurements of pollutants such as OCPs, PCBs, and Toxaphene.

Phase III studies of the Northern Contaminants Program (NCP-III) focused on performance evaluation of the analytical laboratories providing data to the NCP and AMAP.

6.3. Interlaboratory Comparison Studies

6.3.1. Participant profile

A formal invitation for participation in the ILS was distributed to a wide range of Canadian and international laboratories. This included past participants of the NCP as well as laboratories that participated in other known proficiency testing or evaluation studies. In addition, invitations were forwarded to laboratories currently participating in the Arctic Monitoring and Assessment Programme (www.amap.no). The participating laboratories were provided with a study identification code to maintain their confidentiality throughout the studies.

In this report, laboratories are identified as those that provide services to NCP. Table 6.1 lists only laboratories that have participated in POPs analysis for the NCP-III QA/QC Program.

In the six rounds of NCP-III, thirty-three organizations with forty-three laboratories from thirteen countries participated in ILS for POPs. Twenty of laboratories participated for three or more rounds. Laboratory participation is presented in Figure 6.1 and broken down for each contaminant level as follows:

- total number of labs that participated in six rounds
- number of non-NCP-related labs that participated in 3–6 rounds,
- total number for NCP related labs,
- number of NCP-related 3–6 rounds participants.

The ILS conducted from 2005–2012 during NCP-III for persistent organic pollutants' analyses were given the designation "NCP-III Phase 1" for the first round of studies, "NCP-III Phase 2" for the second round, and so on. Phase 1 of the studies commenced in 2005, with one year dedicated to the completion of each study round.

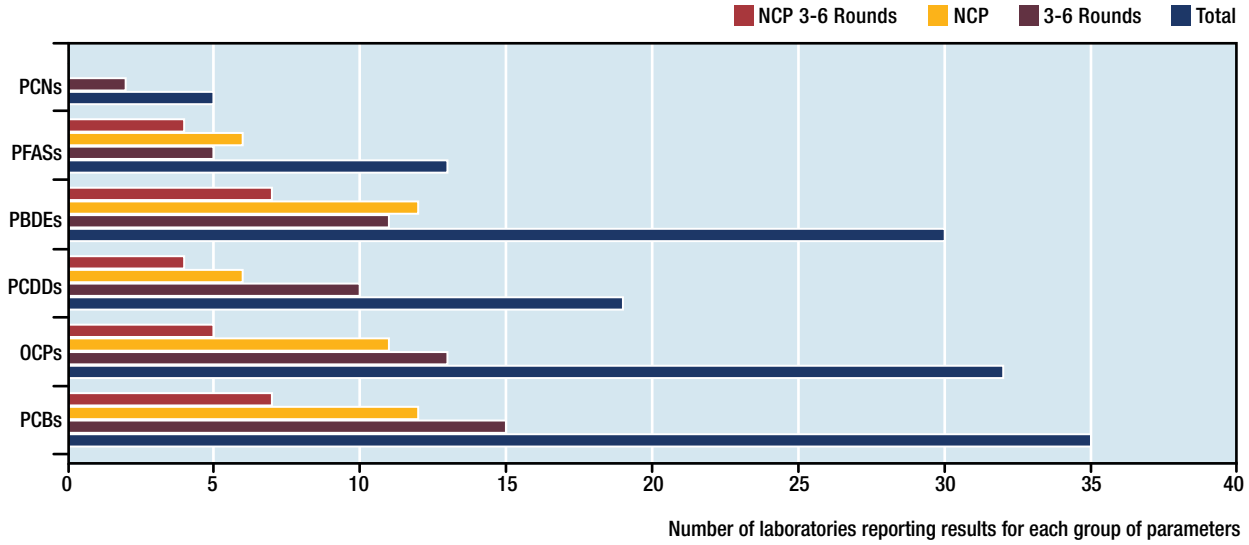


FIGURE 6.1

Laboratories contibuting to each group of POPs, NCP-III Phase 1 to Phase 6.

The evolution of the NCP-III Phase 1 to Phase 6 clearly shows:

1. an increase in the total numbers of participating laboratories (see Table 6.2),
2. more compounds analyzed in each major class of analytes (for example see Annex Figure A6-1.2H),
3. an additional class of analytes added to the program (see PFASs, PCNs, SCCPs, Table 6.2),
4. the addition of natural-matrix certified material and uncharacterized biomaterial (see Table 6.3), and
5. steady performance for NCP laboratories and for 3–6 round participants (see Figure 6.2).

6.3.2. Study design

In the first round of studies, the participating laboratories performed analyses on only IRS for POPs, primarily to assess calibration and instrument performance (Table 6.3). Subsequently, each test round of the studies involved analyses of natural-matrix certified reference materials (CRM) and uncharacterized biomaterial (UM) used for arctic POPs measurements in addition to the injection-ready standards.

Characterized materials obtained from various sources are described in Table 6.4. The CRM providers included the National Research Council (NRC) Canada, National Institute of Standards and Technology (NIST), Cambridge Isotope Laboratories (CIL), Wellington Laboratories (WL) Inc. and the Ontario Ministry of the Environment (MOE). In addition, samples of uncharacterized material used for arctic research (arctic char, lake trout and seal) were obtained from Environment Canada (EC). Wellington Laboratories (WL) Inc. and MOE prepared the injection-ready analytical standards.

TABLE 6.2 Participant profile for Interlaboratory studies conducted during NCP III 1–6

Analytes	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6
PFASs	n/a	7	4	7	10	10
PBDEs/BFRs	10	14	8	16	19	19
PCDDs/PCDFs/DL-PCBs	7	10	6	10	14	13
OCPs	12	9	11	18	20	22
PCBs	12	13	12	21	25	22
PCNs	n/a	n/a	n/a	n/a	n/a	5
SCCP	n/a	n/a	n/a	n/a	n/a	1
Total Participants	19	25	23	29	30	32

TABLE 6.3 Schedule and Target analytes for NCP III Interlaboratory Studies

Year	2005/2006	2006/2007	2007/2008	2008/2009	2010/2011	2011/2012
Target/Study code	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6
PFASs		IRS1,CRM2	IRS,CRM,UM3	IRS,CRM	IRS,CRM,UM	IRS,CRM,UM
PBDEs/BFRs	IRS1	IRS,CRM	IRS,CRM,UM	IRS,CRM	IRS,CRM,UM	IRS,CRM,UM
PCDDs/PCDFs/DL-PCBs	IRS	IRS,CRM	IRS,CRM,UM	IRS,CRM	IRS,CRM,UM	IRS,CRM,UM
OCPs	IRS	IRS,CRM	IRS,CRM,UM	IRS,CRM	IRS,CRM,UM	IRS,CRM,UM
PCBs	IRS	IRS,CRM	IRS,CRM,UM	IRS,CRM	IRS,CRM,UM	IRS,CRM,UM
PCNs						IRS,UM
SCCPs						IRS,UM

[1] IRS – injection ready standards

[2] CRMs – biological tissue certified reference material

[3] UM – uncharacterized biomaterial

TABLE 6.4 Origin and nature of samples

Samples	Sample distribution	Source	NCP III Phase					
			1	2	3	4	5	6
CARP-2 *(SRM, Ground Whole Carp)*[1]	One ampoule, 9g	NRC		x		x		
SRM 1589a *(Human Serum)*[2]	One sample, 10ml freeze dried	NIST		x				
SRM 1946 *(Fish Tissue)*[3]	One sample, 8g	NIST		x	x			
SRM 1947 *(Lake Michigan Fish Tissue)*[4]	One sample, 8g	NIST				x	x	x
WMF-01 *(SRM, Fish Tissue)*[5]	Two samples, 10g each Freeze Dried	MOE		x				
EDF-2524 *(Clean Fish Reference Material)*[6]	One sample, 10g	CIL					x	
EDF-2525 *(Contaminated Fish Reference Material)*[7]	One sample, 10g	CIL						x
Lake Trout *fish tissue*[8]	Two samples, 5 g each	MOE						x
Lake Trout *fish extracts*[8]	Two samples, 2 ml each	MOE					x	x
Arctic char[8]	One sample (Ph3 12g, Ph5 10g)	EC			x		x	
Ringed seal muscle[8]	One sample, 12 g	EC			x			
Injection ready/spiking standard (IRS)								
PBDEs/BFRs (Nonane)	1.2 ml ampouled	WL&MOE	x	x	x	x	x	x
PCDDs/PCDFs/DL-PCBs (Nonane)	1.2 ml ampouled	WL&MOE	x	x	x	x	x	x
PCBs *(Nonane)*	1.2 ml ampouled	WL&MOE	x	x	x	x	x	x
PFASs *(Methanol)*	1.2 ml ampouled	WL&MOE		x	x	x	x	x
OCPs *(Iso-octane)*	1.2 ml ampouled	WL&MOE	x	x	x	x	x	x
SCCPs *(Iso-octane)*	1.2 ml bottled	MOE						x
PCNs *(Nonane)*	1.2 ml ampouled	WL						x

1. Certified Reference Material (2001) *CARP-2, Ground Whole Carp Reference Material for Organochlorine Compounds*, National Research Council Canada, Ottawa, Canada.
2. Certificate of Analysis (2000) *SRM 1589a, PCBs, Pesticides, and Dioxins/Furans in Human Serum*, National Institute of Standards and Technology, Gaithersburg, MD.
3. Certificate of Analysis (2004) *SRM 1946, Lake Superior Fish Tissue*, National Institute of Standards and Technology, Gaithersburg, MD.
4. Certificate of Analysis (2007) *SRM 1947, Lake Michigan Fish Tissue*, National Institute of Standards and Technology, Gaithersburg, MD.
5. Certified Reference Material (2002) *WMF-01, Reference Fish Tissue for Organic Contaminant Analysis*, Laboratory Services Branch, Ontario Ministry of the Environment (MOE).
6. Certificate of Analysis (2006) EDF-2524, *Clean Fish Reference Material*, Cambridge Isotope Laboratories and Cerilliant Corporation, Round Rock, TX.
7. Certificate of Analysis (2006) EDF-2525, *Contaminated Fish Reference Material*, Cambridge Isotope Laboratories and Cerilliant Corporation, Round Rock, TX.
8. Natural-matrix sample, a non-characterised material obtained from NCP project participants

6.3.3. Data evaluation methods

Statistical analysis was performed for analytes with a number of data points greater than or equal to three. Any data reported as "0" or with a qualifier (e.g., < 0.08) were omitted from the statistical analysis. In some cases, laboratories reported a single concentration for two or more co-eluting analytes (e.g., PCB 28 and PCB 31). In these instances, the reported values were also omitted from the statistical analysis. The results were evaluated using the statistical method "Robust Statistics: a method of coping with outliers" as described in Analytical Methods Committee (2001). With this procedure, median values were used to estimate the "true" value, and the standard deviation was estimated as 1.5 x Median Absolute Difference (MAD). MAD was determined by first calculating the absolute values of the differences between each result and the median value, and then taking the median of these absolute values. Thus, the estimation of the study average and standard deviation were considered as follows: Study Average = Median and Standard Deviation = 1.5 x Median Absolute Deviation.

Each laboratory's success rate (score performance) was defined as the percentage value of the median, reported by "all laboratories", divided by the total number of reported results from that laboratory, per contaminant group. Certified values for IRS and CRMs were used to show the data recovery in each group of contaminants and have no effect on score performance. Score performance was rated using the following levels:

- 80–100% – excellent
- 60–80% – satisfactory
- 50–60% – marginal performance
- <50% – needs improvement

At the end of each phase, a preliminary annual report of the submitted results from all laboratories was distributed to the participants for verification of their reported data and for the submission of any corrections. Data correction was implemented before the final data compilation. The distribution of results from individual laboratories were represented graphically for each sample to allow participants to compare their performance relative to that of their peers. Upon completion of each study round, a final report containing the detailed data analysis and graphical presentations of results, was provided to all participating laboratories and NCP management (NCP-III Phase 1, Phase 2, Phase 3, Phase 4, Phase 5, Phase 6—six reports in total). Yearly results were presented at the NCP annual workshops. Annual reports are available upon request.

6.4. Study Results and Discussion

This summary highlights the following:

- total laboratories historical performance —"all laboratories";
- laboratories participating for three to six rounds, "3–6 round NCP" and "3–6 round non-NCP"; and
- NCP laboratories.

6.4.1. All laboratories performance for standards and certified reference materials

Laboratories were instructed to use their routine analytical methods for the sample analyses. The majority of the laboratories that participated in more than one study round showed acceptable performance in the analysis for POPs standards and CRM (Annex Table A6-1, A6-2, A6-3, A6-4, A6-5). The "all laboratories" performance result for each group of POPs is presented separately for the three sample groups, IRS, CRM and UM, and as a Total Performance result since Phase 1 has standards only (Figure 6.2a and b). The laboratories performances were:

- Highest for IRS (72–90%), except PFASs for 3–6 non-NCP labs (58%).
- PCBs and PCDDs performances for CRM samples were satisfactory for those labs who participated three to six rounds NCP and non-NCP (67–74%). NCP labs performed better than others for OCPs (65%).
- UM performances were satisfactory (PCDDs) or marginal (PCBs, OCPs, PFASs) for NCP labs in all groups, except PBDEs (46%). "All laboratories" historic performance for UM need improvement (44–52%).

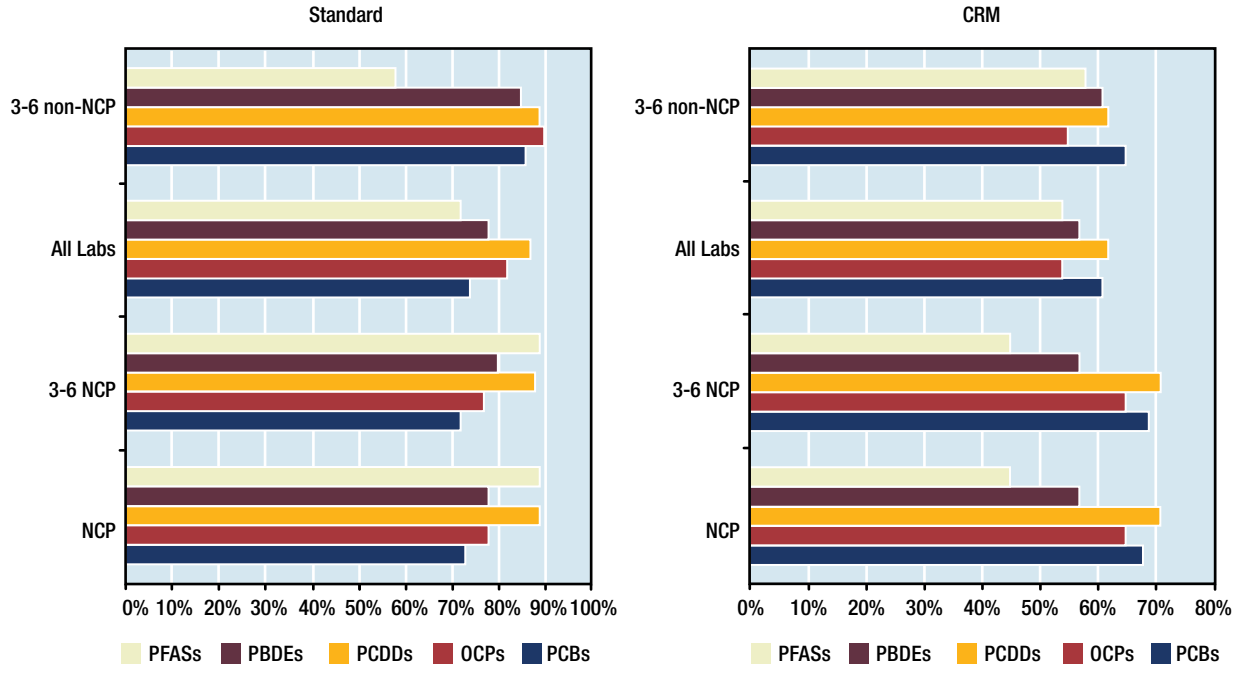


FIGURE 6.2a

Laboratories percent success in ILS, NCP-III, Phase 1–6

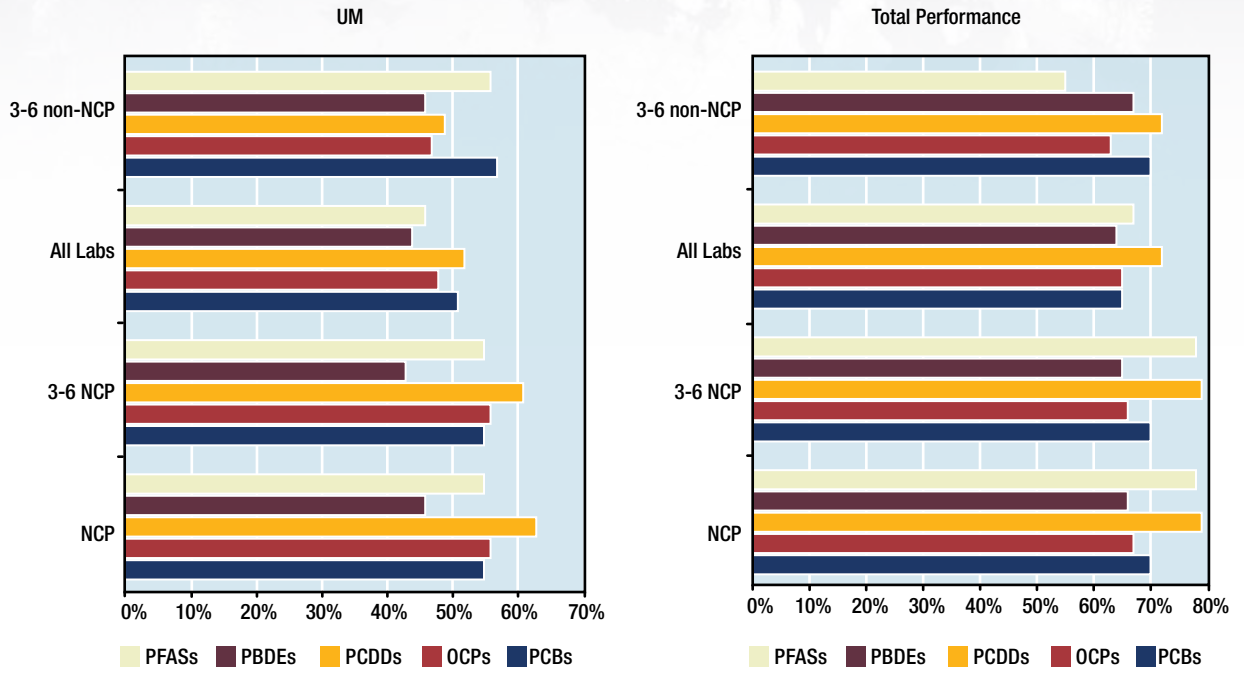


FIGURE 6.2b

Laboratories total percent success and UM performance in ILS, NCP-III, Phase 1–6

Total Performances were satisfactory in each of the five parameter groups, except for PFASs for 3–6 non-NCP labs (55%) (Figure 6.2b, second graphic, and Annex Table A6-6). Laboratories identification codes are presented in the Annex Table A6-7.

Reference values were not available for uncharacterized material for the arctic Char, ringed seal, and lake trout samples. Nevertheless, laboratories reported results for the majority of the analytes (Figure 6.2b) and the results for each parameter are discussed below.

6.4.1.1. Polychlorinated biphenyls (PCBs)

Since the PCB congener list is vast, thirty PCB congeners were recommended for NCP work and used for NCP labs in NCP-II. At the same time, the PCB congener list for AMAP labs included thirty-nine congeners (Stokker 2003). In NCP-III the total number of PCB congeners analysed in Phases 1 and 2 was sixty-one, and increased to seventy-five for Phase 6.

Thirty-five laboratories submitted data for PCBs; twelve of them were NCP laboratories. Of the fifteen laboratories that participated for three or more rounds, seven were NCP laboratories (Figure 6.1). The statistical data of each laboratory performance is presented in Annex Table A6-1.

The "all laboratories" success for PCBs analyses was satisfactory (65%) in NCP-III Phases 1–6 (Figure 6.3). Performance for IRS and CRM was also satisfactory (74% and 61% respectively) for "all laboratories" (Figure 6.3). NCP laboratories show satisfactory performance for IRS (72%) and for CRM (69%) (Figure 6.2a.). NCP-III Phase 1–6 performance summarized for each phase is presented in Figure 6.3 and in Annex Table A6-1.

The performance for PCBs shows that most of the labs demonstrated good comparability of PCB measurements (Annex Table A6-1). However, the individual performance for the majority of laboratories that participated in the NCP-III program for three to six years was higher for standards and CRM (Figure 6.2a and Annex Table A6-1). Almost half of them were NCP laboratories (Figure 6.1).

Since comparability is of particular importance for performance evaluation and to assess each laboratory's progress, the Lake Michigan fish tissue certified material (SRM 1947) was chosen to demonstrate the correlative data provided by project participants in NCP-III Phase 4–6. SRM 1947 provided a certified concentration value for thirty-two and reference concentration number for thirteen PCBs congeners

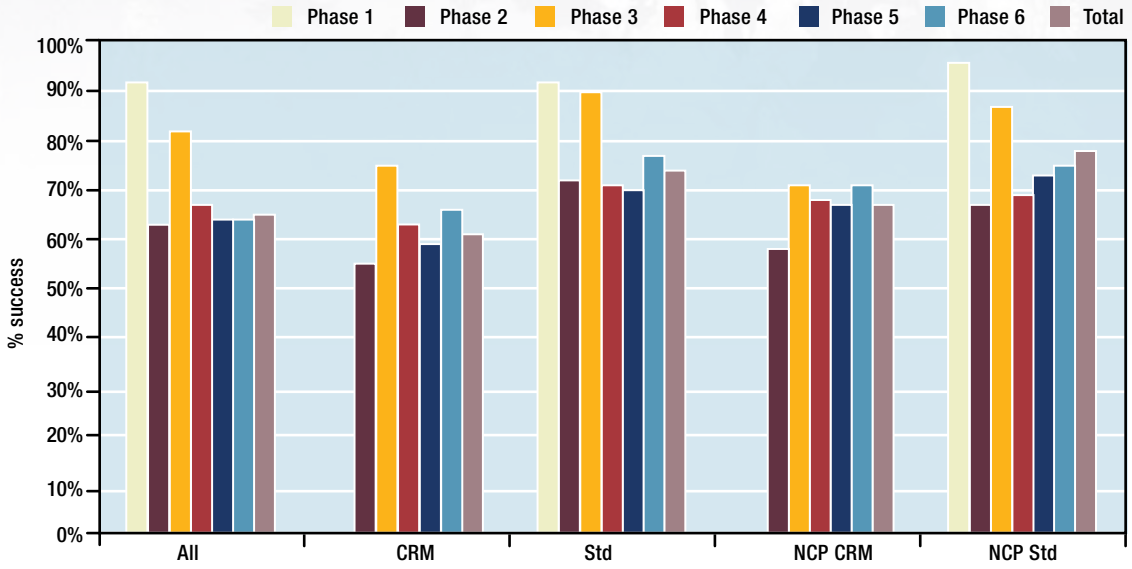


FIGURE 6.3

All laboratories combined performance for PCBs, NCP III, Phase 1–6.

respectively, and that includes twenty-nine PCBs congeners out of the thirty recommended by NCP-II (Selliah et al. 2008).

Participating labs demonstrated improvement in PCB analysis in Phase 4 and 5 as shown by SRM 1947 results (Figure 6.4). Recovery for PCB congeners 52, 82, 91, 99, 158,193 and 197 dramatically improved in Phase 5 compared to Phase 4. High bias was observed in PCB 82 and 201 in both phases, PCB 52, 63, 158, and 197 in Phase 4, and PCB 91 and 193 in Phase 5.

Other CRMs samples, such as CARP-2 used in Phase 2 and 4, contained less of the PCB congener certified concentration values. However, the same tendency of recovery closer to reference value was shown for CARP-2 (Figure 6.5).

PCB interlaboratory variability was assessed using Relative Standard Deviation (RSD) for IRS, CRM and UM values shown in the Annex (Figure A6-1.1 A to F). NCP-III Phase 3 and 5 standards were within a 20% limit for most of the PCB congeners, except for the following PCBs 4, 15, 16, 56, 123, 141, 149, 174, 196, 201, and 207. PCB 18, 28, 31, 81, and 104 had RSD values between 20% and 40%. The data shows consistency (below 40%) between samples for about 50 PCB congeners. The difference in the UM, namely ringed seal muscle and arctic char (less often), is likely related to the high oil content in ringed seal muscle.

A few exceptions were observed for seal and char. The greatest similarity was for PCB 18 (except lake trout fish extract S4), 19, 31, 37, 44, 49, 52, 63, 66, 70, 74, 77 (except lake trout fish extract S4), 82, 87, 92, 95, 99, 105, 107, 110, 114, 118, 128, 132, 135, 137, 138, 141 (except standard), 153, 155 (except EDF 2524), 156, 158, 163 (except EDF 2524), 167, 170, 172, 174, 177, 178, 180, 183, 187, 188, 189, 194, 195, 202, 203, 205, 208, 209. The difference was greater in a second group of 18 PCB congeners: PCB 1, 3, 4, 6, 22, 28, 33, 56, 81, 104, 123, 126, 146, 157, 196, 199, 200, 201. Data from all labs was not provided for PCB 15, 16, 17, 41, 45, 54, 60, 119, 207 and 209.

The uncharacterised material ringed seal muscle was analysed in Phase 3 and arctic char in Phase 3 and 5 (Annex Figure A6-1.2). Laboratories participating in Phase 3 analysed forty-seven PCB congeners in ringed seal muscle (Annex Figure A6-1.2 and C) and thirty-nine PCB congeners in arctic char. Sixty PCB congeners were analysed in Phase 5 for the char (Annex Figure A6-1.2 E and G). Three labs analyzed PCB in Phase 3 and six in Phase 5. PCB 28, 101, 105, 118, 138, 153, 180 were analysed in Phase 3 by eight to twelve participants and by sixteen to twenty in Phase 5 for UM (Annex Figure A6-1.2 F and H).

6.4.1.2. Organochlorine pesticides (OCPs)

Thirty-two laboratories submitted data for OC analysis, eleven of which were NCP laboratories. The total "all laboratories" performance was

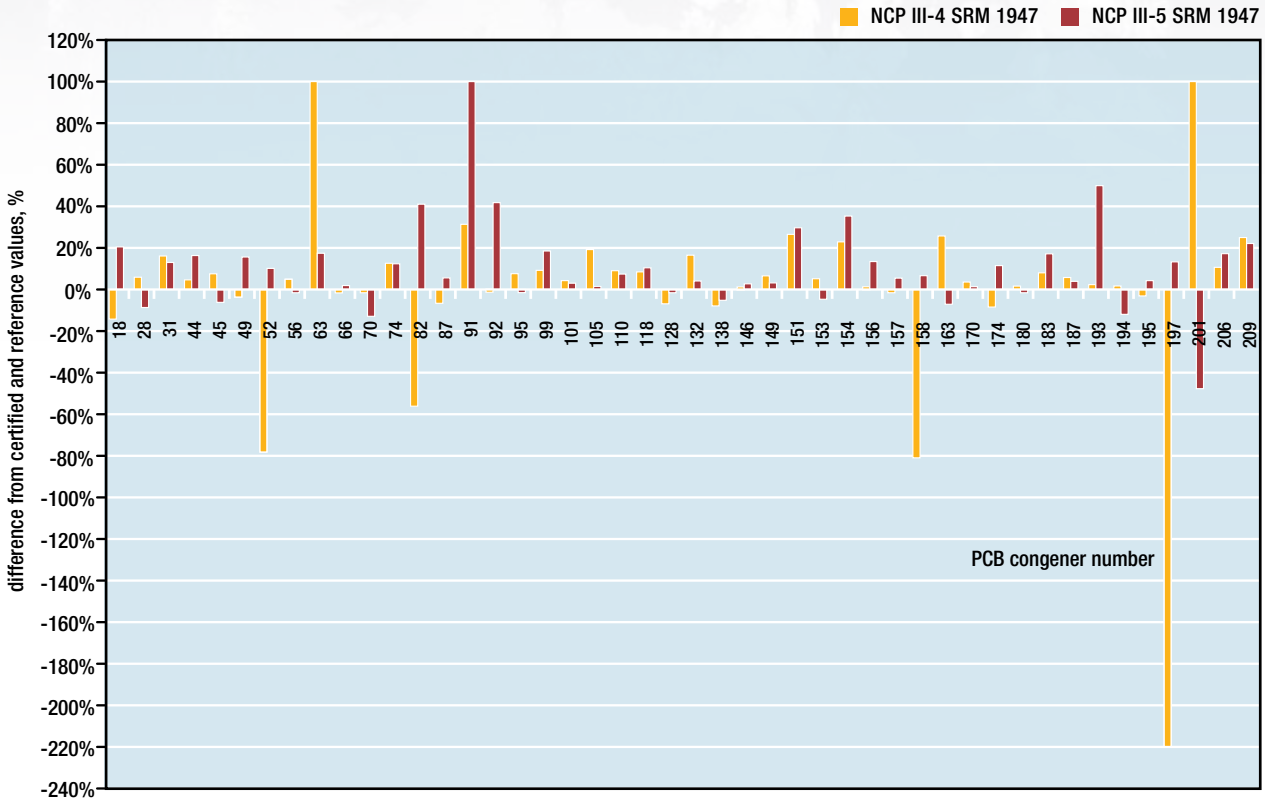


FIGURE 6.4

Improvement in PCB congener data recovered from SRM 1947, NCP III, Phase 4 versus Phase 5.

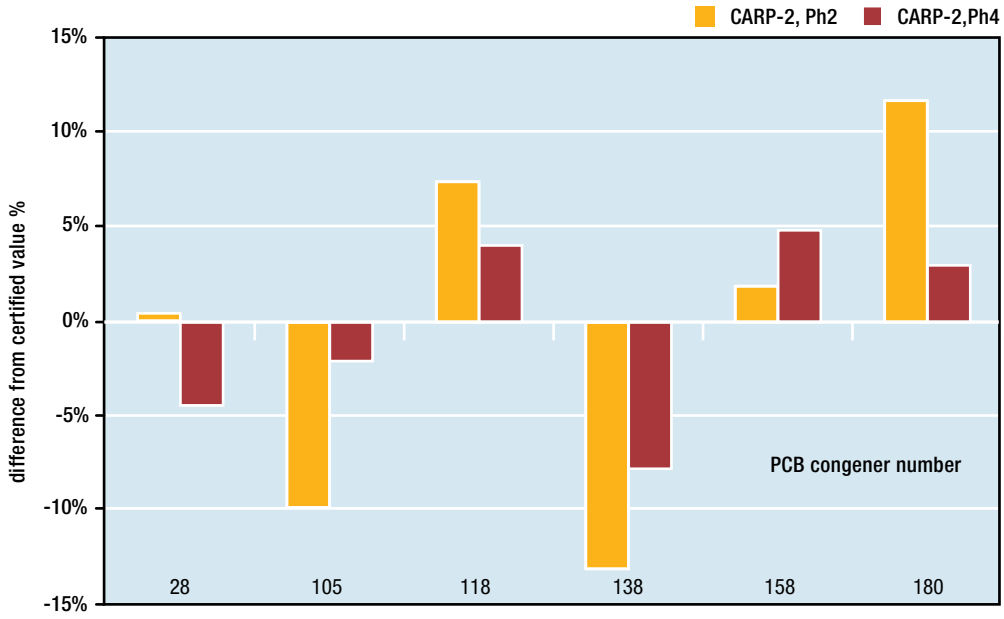


FIGURE 6.5

Improvement in PCB congener data recovered from CARP-2, NCP III, Phase 2 versus Phase 4.

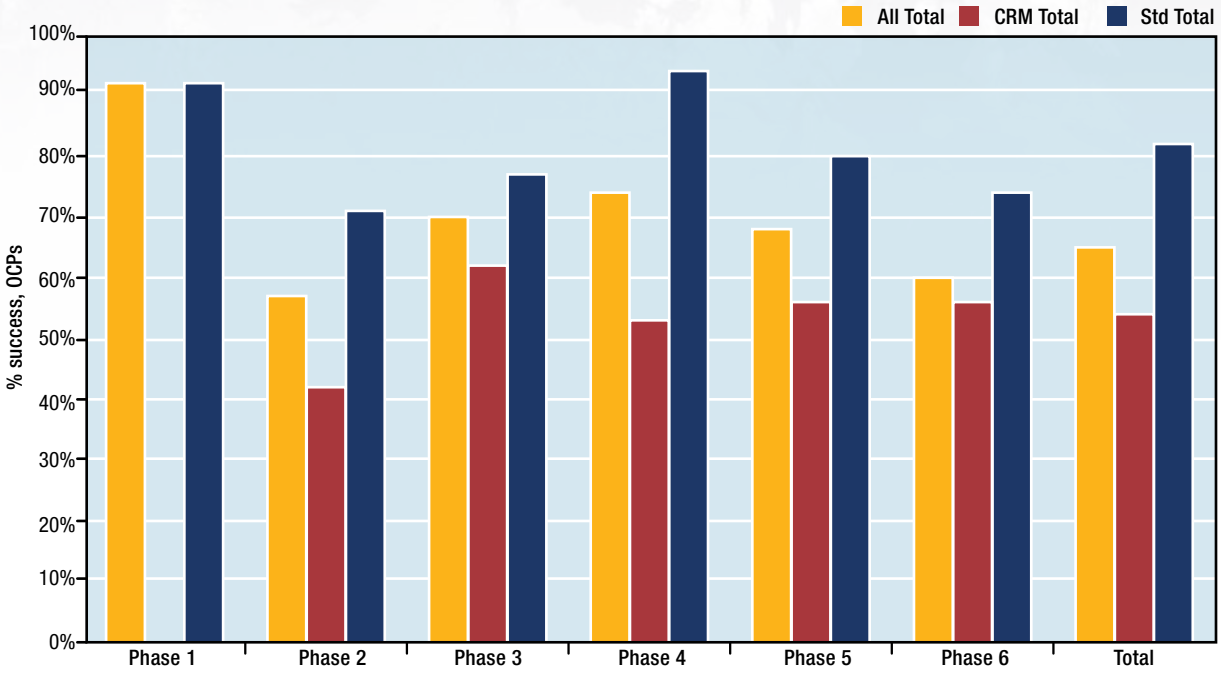


FIGURE 6.6

All laboratories combined performance for OCPs, NCP III Phase 1 – 6.

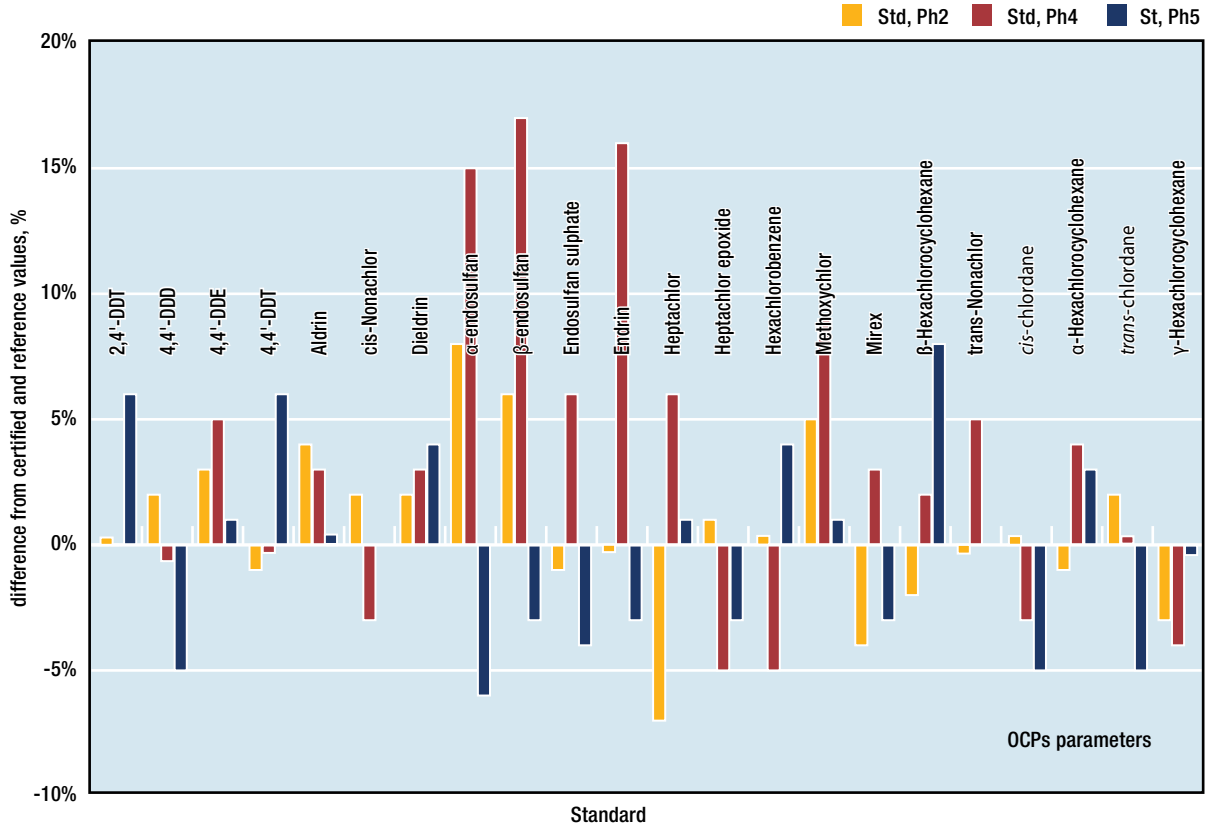


FIGURE 6.7

Accuracy and comparability of the all laboratories performance for OCPs standard, NCP III, Phase 2-5.

excellent for standards (82%) but showed marginal performance (54%) for the CRMs (Figure 6.6). The NCP laboratories performed at the satisfactory level (65%) for the CRM (Figure 6.2a).

The "all laboratories" performance was higher than 90% in Phase 1 since only injection-ready standards were analysed. Phase 2 shows a performance level close to 71% (lowest in six rounds). However, the overall success rate for standards was about 82% (Figure 6.6).

Individual lab performances for standards were much more variable for OCPs. The analysis shows that for labs participating in three or more rounds, only six out of ten participants performed adequately for OCPs, and four of those were NCP laboratories. Some lab performance was unsatisfactory for CRM, yet good for standards (Annex Table A6-2).

The analyses of OCPs in the IRS were within the 20% tolerance range of the difference between the certified and reference values (Figure 6.7, Phases 2, 4 and 5). The analyses of the parameters in biotic tissue samples were less comparable. However, the relevant SRM 1947 data in Phase 5 compared to Phase 4 analyses show comparable performance for the certified material (Figure 6.8).

For sample NCP-III-3 (SRM 1946), a low bias was observed for some of the analytes, namely for 2,4'-DDD, 2,4'-DDT, 4,4'-DDD, and Heptachlor epoxide. These findings were similar to those observed for previous results reported in NCP-III Phase 2 (Stokker 2003). To enhance and enrich the data, it would be prudent to introduce new material in future NCP-III studies.

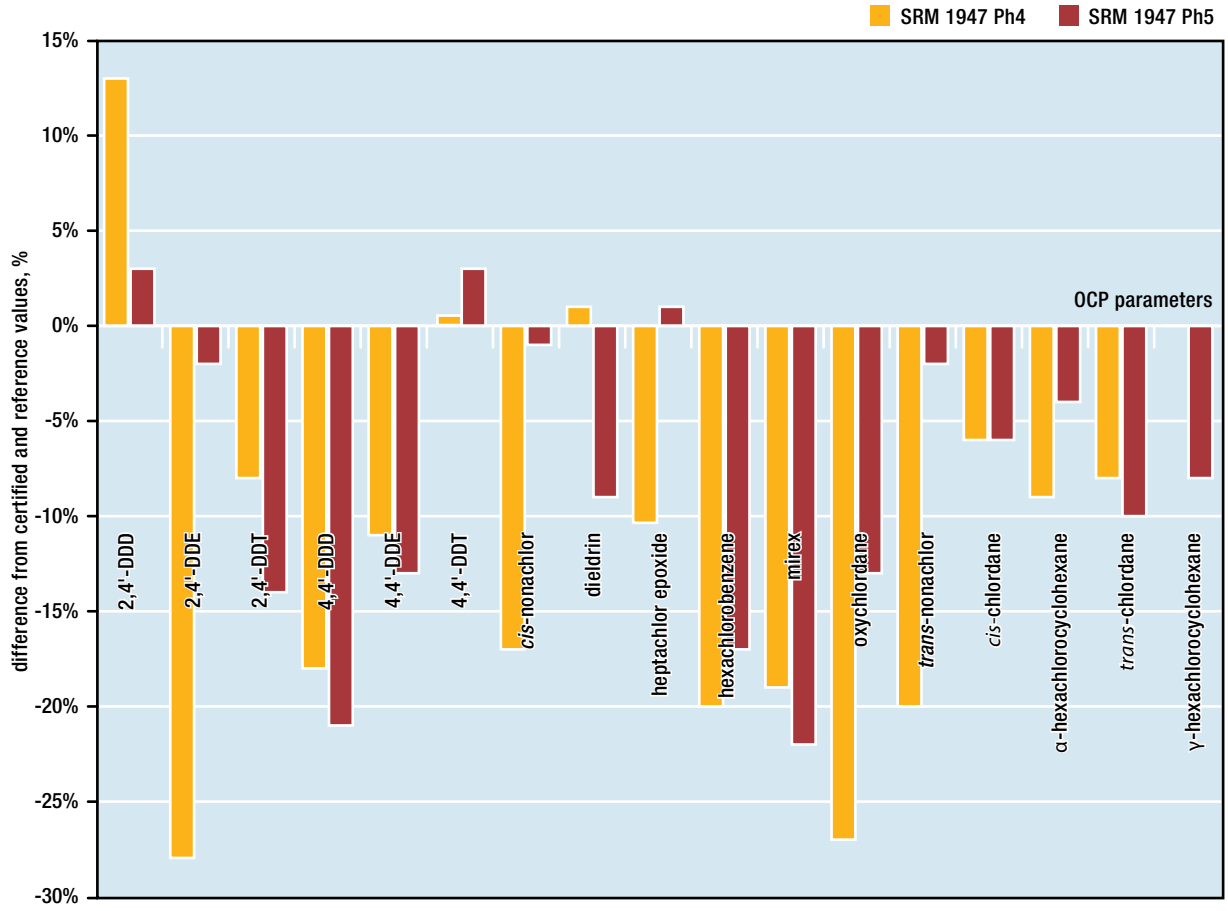


FIGURE 6.8

Accuracy and comparability of the all laboratories performance for OCPs in SRM 1947, NCP III Phase 4-5 (Study average vs. the reference value)

Results were reported for the uncharacterised material ringed seal muscle, arctic char and lake trout extract samples by most of the laboratories. There were no reference values available for the analytes. Concentration values for the uncharacterized material are presented in Annex Figure A6-2.1 (A and C). For 4, 4'-DDE, eight labs performed analyses for ringed seal muscle and seven for arctic char in Phase 3, and fourteen labs performed analyses in Phase 5 for arctic char. The 4, 4'-DDT "parent" to DDE was analyzed in ringed seal muscle by seven labs and in arctic char by three labs only for Phase 3 whereas in Phase 5, participation increased to fourteen and nine labs, respectively. In Phase 3, *trans*-Chlordane was analysed by three labs for ringed seal muscle, five labs for arctic char and heptachlor was analyzed by four labs. In Phase 5, two more labs analyzed the same compounds in arctic char. These and other results for OCPs in UM are presented in Annex Figure A6-2.1 (B and D).

Interlaboratory variability for IRS, CRM and UM OC samples used in Phase 3 compared to Phase 5 are presented in Annex Figure A6-2.2 (A and B). Seven out of twenty-five laboratories analyzing OCPs show some similar trends between samples in the following analytes: *cis*-chlordane, 4, 4'–DDE, dieldrin, hexachlorobenzene, α-hexachlorocyclohexane (except EDF-2524), *trans*-nonachlor and oxychlordane (except Phase 3 arctic char and ringed seal muscle).

6.4.1.3. Polybrominated diphenyl ethers/ brominated flame retardants (PBDEs/BFRs)

Stokker (2003) reported that PBDEs and BFR were carried out in only a few laboratories. In the NCP-III 1–6 study, thirty laboratories submitted data for BFRs/ PBDEs, twelve of which were NCP laboratories. Eleven laboratories participated for three or more years and seven of those were NCP laboratories.

Study statistics for PBDEs are summarized in Annex Table A6-3. Most of the laboratories reported results for PBDEs. A few results were reported for additional BFRs (α- and γ-HBCD).

Again, the "all laboratories" total performance over the years was much higher for the standards compared to the CRMs (Figure 6.9). Among the three or more year participants, nine labs analyzed standards while only seven considered the CRMs.

SRM 1947 data for Phase 4 and 5 (Figure 6.10) shows that most PBDEs congeners were within 20% of the certified concentration value. The performance for this biotic material improved in the second round compared to that demonstrated for PCBs and OCPs in SRM 1947 in two previous sections.

Reference values were available for WMF-01 (Phase 2) and the median result ranged between 67% and 105% of the certified and reference value. PBDEs results were reported for the majority of analytes listed in the report form, however, certified values were not available for SRM 1946, CARP-2 and SRM 1589a samples. The interlaboratory variability for the IRS was within the 20% limit for all analyzed PBDE congeners except for PBDE 183, which was in the 30% limit in Phase 3. PBDE 209, the most difficult to analyze, was in a range from 10% to 20% except for ringed seal muscle, arctic char (Phase 5) and SRM 1946. PBDEs variability for SRM 1946 was between 15% and 35% except for PBDE 17 and 28.

Arctic char, as a natural-matrix material, was analysed in Phase 3 and 5 (Annex Figure A6-3.1 A, B). Sample masses used were 12 g in Phase 3 and 10 g in Phase 5,

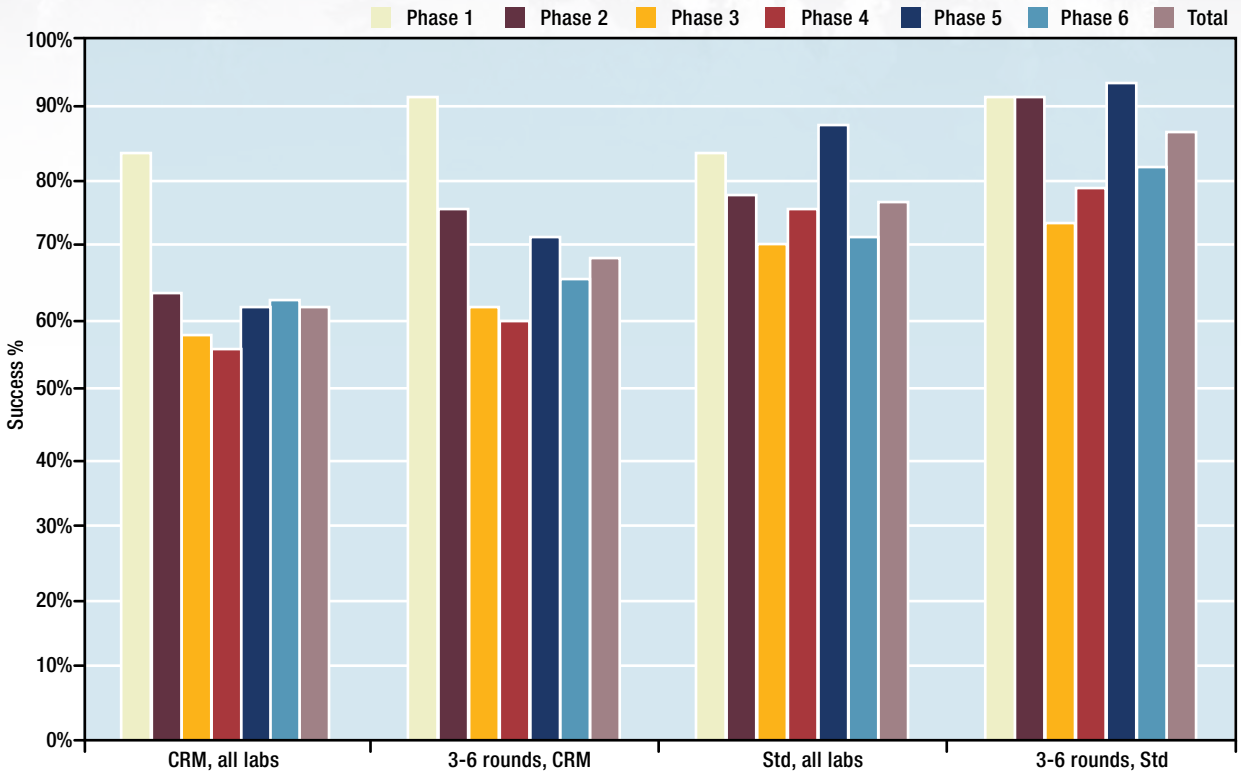


FIGURE 6.9

All laboratories combined performance for PBDEs, NCP III Phase 1-6.

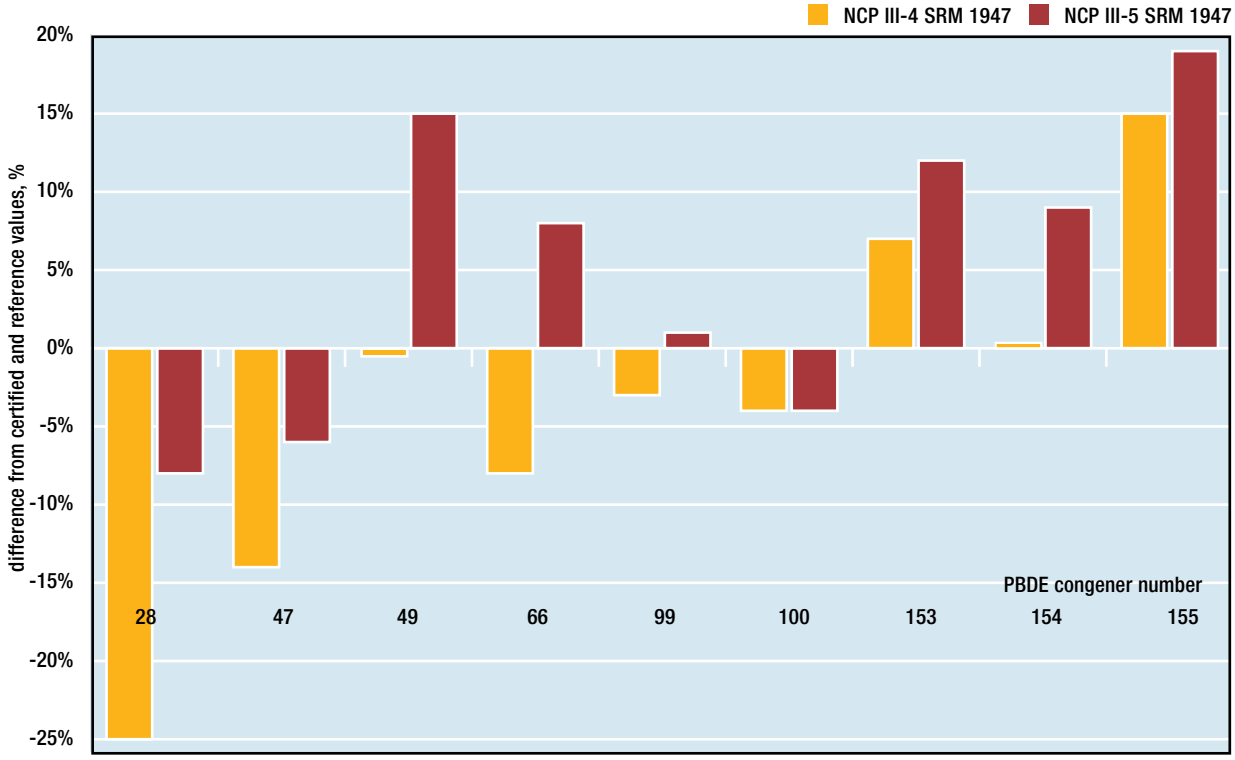


FIGURE 6.10

SRM 1947 comparable data between Phase 4 and 5 presented for PBDEs congeners with certified and reference values.

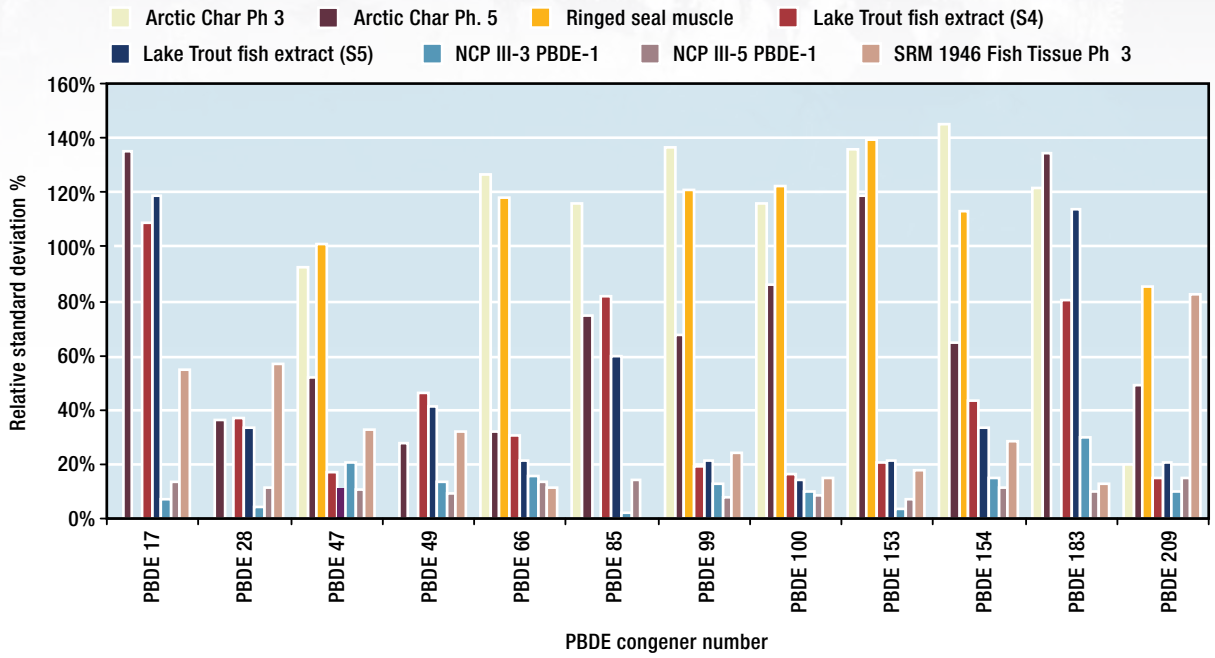


FIGURE 6.11

Inter laboratory variability for PBDEs in IRS, CRM and UM, Phase 3 versus Phase 5, NCP III.

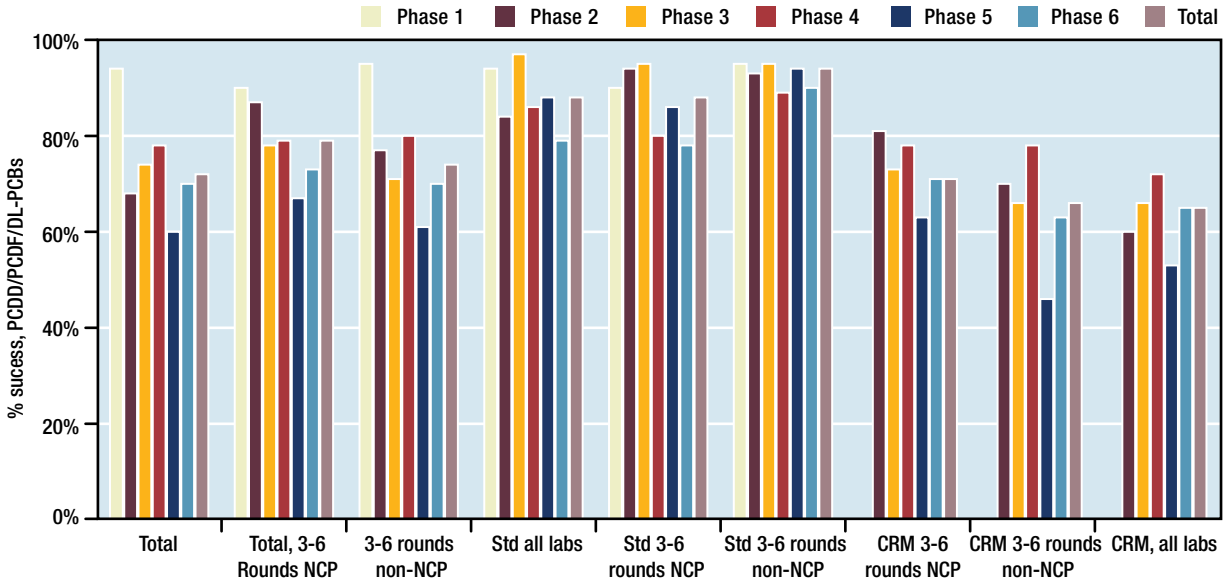


FIGURE 6.12

The combined performance of all participating laboratories for PCDDs/PCDFs/DL-PCBs. "All participants" performance versus three or more round participants, NCP and non-NCP laboratories, NCP III Phase 1-6.

however, the same contaminants were reported. High interlaboratory variability for PBDE congeners 17, 28, 47, 66, 99, 100, 154, 183 is consistent with other uncharacterized materials such as the ringed seal muscle (Annex Figure A6-3.1 C, D) and lake trout extract (Figure 6.11).

Physical and chemical properties of natural materials are reflected in higher variability and the different concentrations were analyzed for PBDEs. This fluctuation demonstrates a challenge for ILS studies using uncharacterized material.

6.4.1.4. Dioxins/furans/dioxin-like polychlorinated biphenyls (PCDDs/PCDFs/DL-PCBs)

Nineteen laboratories submitted data for PCDDs/PCDFs/DL-PCBs analysis, six of which were NCP laboratories. Ten laboratories participated for three or more rounds and four of them were NCP laboratories.

The statistical analyses performed on the results are summarized in Annex Table A6-4. The "all laboratories" total performance for the dioxin group of compounds was rated "excellent" for standards in all groups of participants (Figure 6.12).

Performance for CRM was satisfactory for NCP laboratories and the three or more round participants. However, the overall laboratory performance data for CRM in Phase 5 (three or more rounds and all participants) demonstrates that some of participating laboratories need to improve their performance in biotic material (see CRM in Figure 6.12 and Annex Table A6-4). Phase 6 results demonstrated that most of the laboratories achieved better performance for the dioxin group of parameters in biotic material (Figure 6.12).

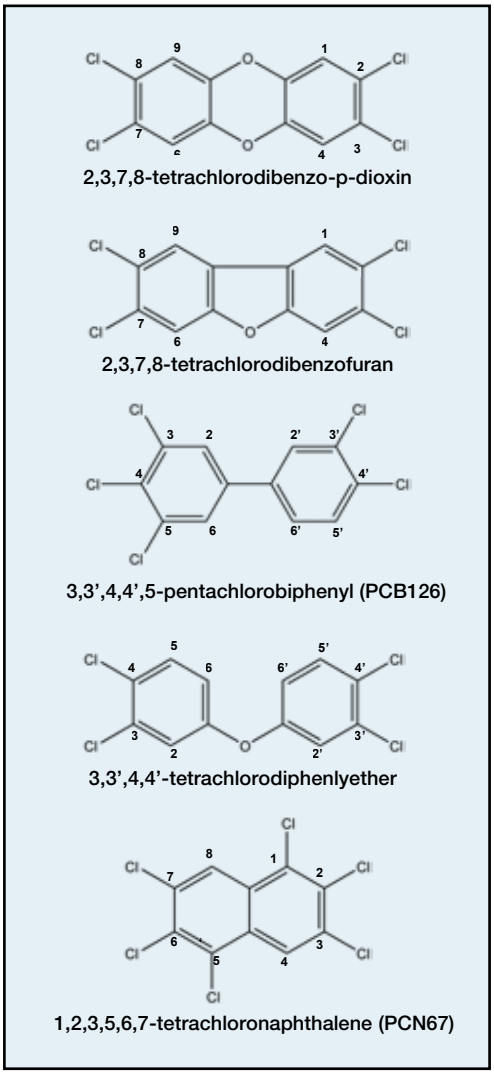
For the NCP-III-3 (SRM 1946) sample, certified values were available for only six of the DL-PCBs. The robust average values compared well with the reference values for this sample; all the robust averages were within 8% of the reference values. Laboratories showed no significant bias for the DL-PCBs in SRM 1946 and a similar trend was observed for SRM 1946 in NCP-III Phase 2, with the exception of PCB 169. The relative standard deviation values were less than 17% for the majority of the analytes.

Dioxins/furans/dioxin-like-PCBs group interlaboratory variability with RSD for IRS, CRM and UM, are presented for NCP-III Phase 3 and 5 in Annex Figure A6-4.1 (A-C). For seven PCDD congeners, the variability was within 20% for all IRS samples. 2,3,7,8-T_4CDD (most toxic) showed less variability for all analysed samples (the highest RSD was 40%, EDF-2524). PCDDs 1,2,3,6,7,8-H_6CDD showed variability close to 20% (except for arctic char). In the CRM, sample variability was high for only two dioxins: 1,2,3,4,6,7,8-H CDD and OCDD. The other six analyzed PCDDs show the highest variability in arctic char (Annex Figure A6-4.1 A).

The IRS interlaboratory variability for the dibenzofurans was within the 20% limit for all analyzed congeners in Phase 3 and 5. The CRM behaved differently: RSD for EDF-2524 was higher than 50% (except for two congeners). SRM 1947 showed only three congeners with high variability (75–120%). SRM 1946 showed one congener of 83% (Annex Figure A6-4.1 B).

Uncharacterized material samples, ringed seal muscles, arctic char and lake trout fish extract, showed the widest variability. Almost twice as many PCDDs/PCDFs/DL-PCBs compounds were analyzed for arctic Char in Phase 5: 15 compounds (Phase 3) compared to 29 (Phase 5). Taking into account that in Phase 1 (standards only analysed), seven laboratories were able to report 29 contaminants in this group may have at least two explanations:

- the number of laboratories increased from six in Phase 3 to fourteen in Phase 5, and
- there was an improvement in biological sample preparation and separation.



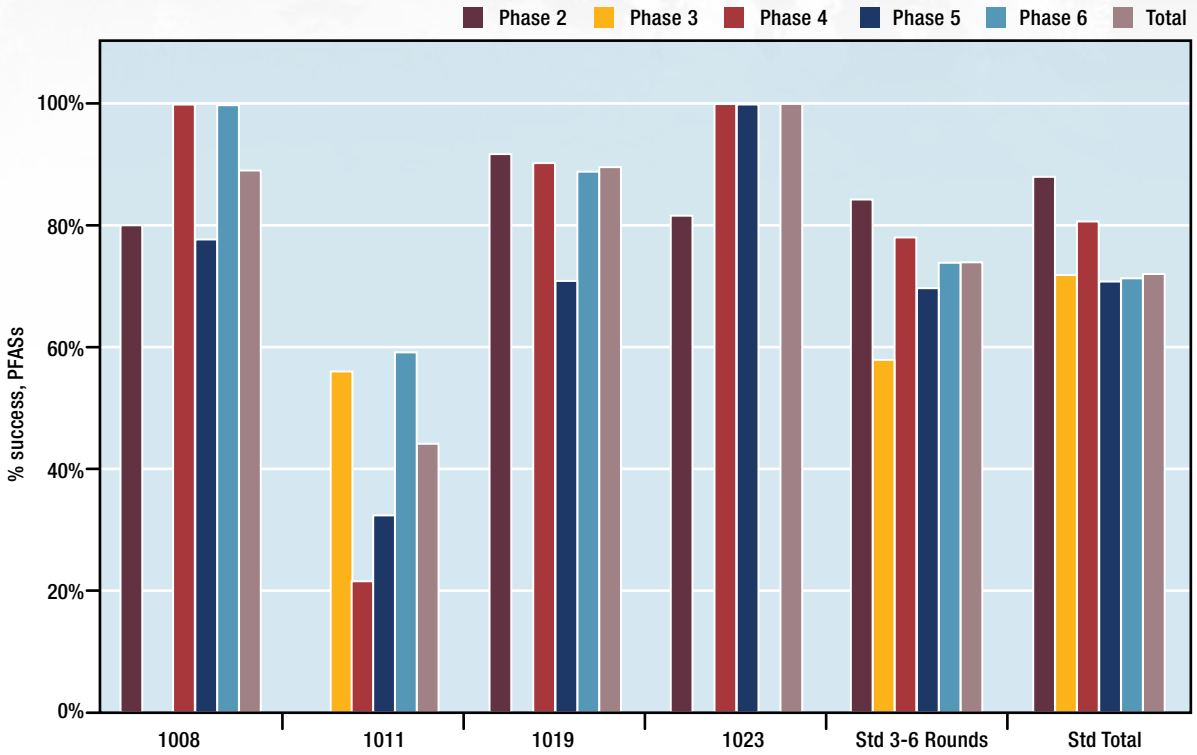


FIGURE 6.13

Combined and Individual lab performance for PFASs standards, NCP III Phase 2-6.

The dioxin-like PCBs interlaboratory variability was within 20% for all IRS. Consistent variability (within, or less than, 40%) was observed for PCB 105, 114, 118, 126 (one of the two most toxic compounds), 156, 157, 167, 169 and 189. Arctic char and ringed seal values were higher than 40% for PCB 77, 81, 123, 169, 189 (Annex Figure A6-4.1 C).

Results were reported for UM samples but reference values are not available for the analytes. In NCP-III Phase 3, three analytes for dioxins in arctic char were reported (analysed by at least three labs). Sixteen analytes were considered by at least three labs (maximum nine labs) for arctic char in Phase 5 (Annex Figure A6-4.2 A and B). Most laboratories reported results mainly for the DL-PCBs (Annex Figure A6-4.2 C and D). As discussed above, there was a larger variability observed in UM samples of arctic char and ringed seal muscle (Annex Figure A6-4.2 E and F).

6.4.1.5. Perfluorinated alkyl substances

The PFASs were not analyzed in the NCP-III Phase 1 study and were not as widely analysed by laboratories compared to other analytes in NCP-III Phase 2–6 studies. In the five rounds, thirteen laboratories submitted data for PFASs analysis, four of which were NCP laboratories. Five out of thirteen laboratories participated for three or more rounds for standards (Figure 6.13, and Annex Table A6-5).

Results were submitted mainly for the injection-ready standards and a majority of the laboratories showed good performance for PFASs analyses. Certified values were not available for PFASs in the majority of the CRM, but laboratories reported results for the analytes PFNA, PFUdA, and linear-PFOS.

Perfluorinated chemicals were not reported for arctic char, lake trout fish extract and EDF-2524 (clean fish reference material) and only sodium perfluoro-1-heptanesulfonate was identified in SRM 1946 (Figure 6.14).

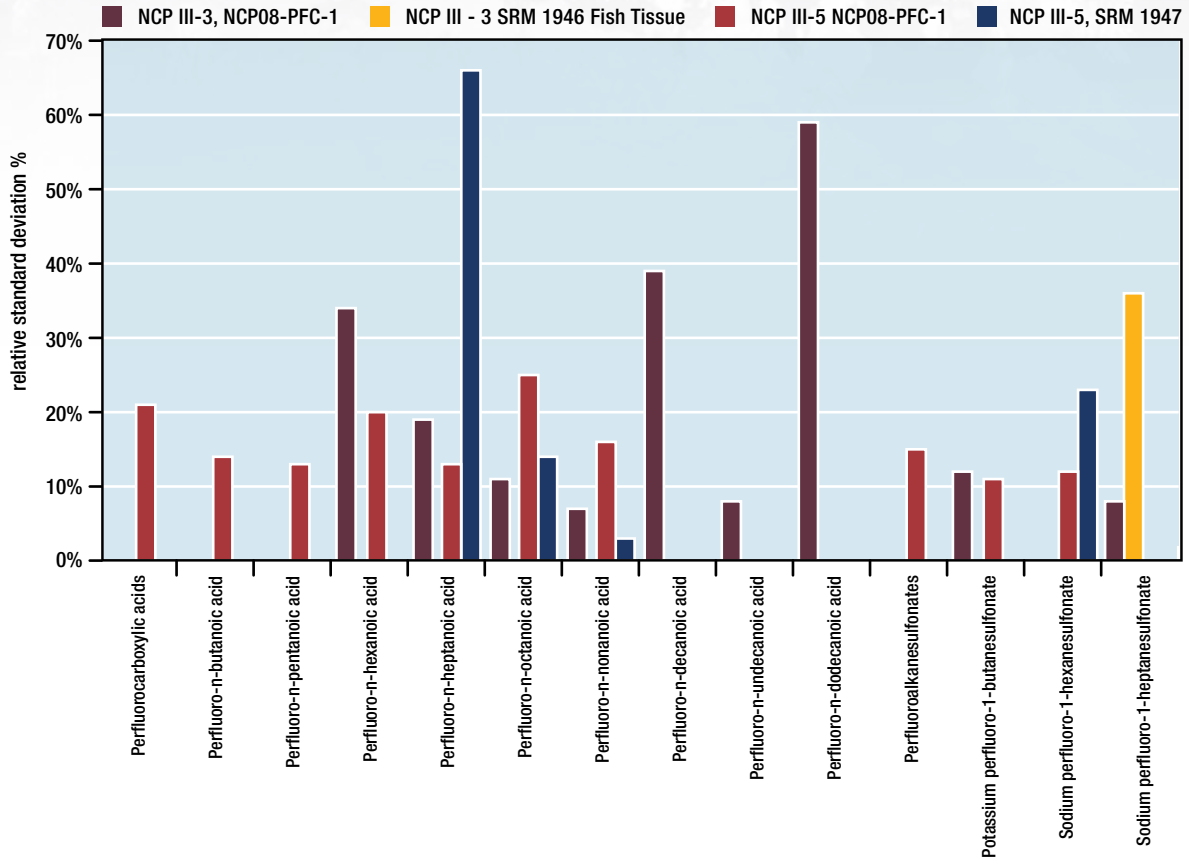


FIGURE 6.14

Interlaboratory variation NCP III Phase 3 versus Phase 5.

Photo: Guenter Koeck

6.5. Summary and Recommendations

The NCP provides funding for research and monitoring studies involving the analysis of a wide variety of different contaminants in various matrices. Data comparability is a crucial factor for results delivered by different laboratories and between different projects.

The NCP-III interlaboratory studies reported results from six rounds that involved the analysis of POPs in standards, biotic certified matrices and biotic uncharacterized matrices—specifically fish tissue material as it is extensively analysed by the majority of laboratories. The interlaboratory studies demonstrated that the NCP laboratories are capable of producing excellent and satisfactory results for POPS analysis in the standards (72–89%) and satisfactory results for PCBs, OCPs, PCDDs analysis in certified natural-matrix materials (65–71%).

The laboratories that are non-NCP and have participated for three or more rounds performed excellent for most of the standards (except PFASs, which was close to satisfactory at 58%), and satisfactory for PCBs, PCDDs and PBDEs groups of pollutants in the CRM. "All laboratories" show excellent performance for OCPs and PCDDs standards, and satisfactory for PCBs, PBDEs, and PFASs. Performance of "all laboratories" for PCBs and the dioxin group in CRM was satisfactory. However, for the other three groups of parameters, the performance of laboratories for the biotic material was at the marginal performance level, which shows that some laboratories need to improve.

For future NCP QA/QC studies the following recommendations should be considered:

1. Survey NCP labs to determine which compounds should be included in the NCP ILS Phase IV.
2. Survey NCP labs to determine which matrices should be included in the NCP ILS Phase IV, with a focus on matrices that have not yet been studied.
3. Include CRMs in NCP ILS Phase IV that have been previously studied to monitor the potential improvement of laboratories.
4. Increase the number of participating laboratories to obtain more data and possibly determine reference values for candidate reference materials.

6.6. Acknowledgements

We wish to acknowledge the Ontario Ministry of the Environment, Laboratory Services Branch. For their dedication throughout the years of study, we especially recognize the work performed by each of the participating laboratories.

6.7. References

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Glossary of chemical nomenclature

Chemical abbreviation	Common name or group
ATE (or TBPAE)	Allyl 2,4,6-tribromophenyl ether
BATE	2-bromoallyl-2,4,6-tri-bromophenyl ether
BB-101, BB-153	2,2',4,5,5'-pentabromobiphenyl, 2,2',4,4',5,5'-hexabromobiphenyl
BC	Black carbon
BFR	Brominated flame retardant
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane
ΣCBz	Sum of chlorobenzenes (tetra-, penta-, hexachlorobenzene)
CC	Cis-chlordane (α-chlordane)
CPs	Chlorinated paraffins
CPY	Chlorpyrifos, organophosphate pesticide,
Chlorothalonil	Chlorinated fungicide
ΣCHL	Sum of chlordane-related compounds, see also CC, TC, TN
CHBs	Chlorobornanes, toxaphene
Cl_{10}DP, Cl_{11}DP	Dechlorinated Dechlorane Plus related compounds
ΣCyclodienes	Sum of dieldrin, endrin and aldrin (cyclodiene pesticides)
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
DAC	Dacthal, DCPA, Chlorinated fungicide
DBA	Dibromoanisole
DBDPE	Decabromodiphenylethane
ΣDDT	Sum of DDT related compounds: p,p'-DDD, p,p'-DDE, p,p'-DDT and o,p'-DDT
p,p'-DDD	Dichlorodiphenyldichloroethane (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane)
p,p'-DDE	Dichlorodiphenylethylene (1,1-dichloro-2,2-bis(p-dichlorodiphenyl)ethylene)
p,p'-DDT and o,p'-DDT	4,4-dichloro-diphenyltrichloroethane and 2,4-dichloro-diphenyltrichloroethane
deca-BDE (BDE-209)	Decabromodiphenyl ether
dieldrin	Chlorinated cyclodiene pesticide
DL-PCBs	Dioxin-like PCBs (e.g. non-ortho substituted PCBs 77, 81, 126, 169)
DP	Dechlorane plus, anti-DP, syn-DP isomers
DPTE	2,3,-dibromopropyl-2,4,6-tribromophenyl ether
Endo	Endosulfan , α-endosulfan, β-endosulfan, endosulfan sulfate
EHTeBB (or TBB)	2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate
EtFBSE	Ethyl perfluorobutane sulfonamidoethanol
EtFOSA	Ethylperfluorooctanesulfonamide
EtFOSAA	Ethylperfluorooctane sulfonamidoacetic acid
EtFOSE	Ethyl perfluorosulfamidoethanol
FOSA	Perfluorooctane sulfonamide
FOSE	Sulfonamidoethanol
FTOH	Fluorotelomer alcohol
FTolefin	Fluorotelomer olefin
FTUCA	Fluorotelomer unsaturated carboxylates
HBBz	Hexabromobenzene
HBB	Hexabromobiphenyl (e.g. BB-153)

Chemical abbreviation	Common name or group
HBCDD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
ΣHCH	Sum of hexachlorocyclohexane (α, β, δ, and γ isomers)
γ-HCH	γ-hexachlorocyclohexane (lindane)
HDBP	Halogenated dimethyl bipyrroles
HEPX	Heptachlor exo-epoxide
L3	Octamethyltrisiloxane
L4	Decamethyltetrasiloxane
L5	Dodecamethylpentasiloxane
MCCPs	Medium chain chlorinated paraffins
MeFBSE	Methyl perfluorobutane sulfonamidoethanol
MeFOSA	Methylfluorooctanesulfonamide
MeFOSE	Methyl perfluorosulfamidoethanol
MeFOSEA	Perfluorooctane sulfonamidethylacrylate
MeFOSEA	Perfluorosulfamidoethylacrylate
MeO-PBDE	Methoxylated polybrominated diphenyl ether
Mirex	Organochlorine pesticide
Musks	Galaxolide (HHCB) and Tonalide (AHTN)
Nonachlor	*Cis*-nonachlor (CN), *trans*-nonachlor (TN)
OC pesticides	Organochlorine pesticides
OCPs	Organochlorine pesticides (e.g. DDT, CHL, HCH, dieldrin)
OCS	Octachlorostyrene
octa-BDE	Octabromodiphenyl ether
OH-PBDE	Hydroxylated polybrominated diphenyl ether
Oxychlordane	Chlordane metabolite
PAH	Polycyclic aromatic hydrocarbons
PBB	Polybrominated biphenyl (e.g. BB-101, BB-153)
PBBA	Pentabromobenzyl acrylate
PBBz	Pentabromobenzene
ΣPBDE	Sum of polybrominated diphenyl ethers
PBEB	Pentabromoethylbenzene
PBT, PBTo	Pentabromotoluene
PCA	Pentachloroanisole
PCAs	Polychlorinated n-alkanes, chlorinated paraffins, SCCPs, MCCPs
ΣPCB	Sum of polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzo-*p*-dioxin
PCDF	Polychlorinated dibenzofuran
PCDE	Polychlorinated diphenyl ether
PCN	Polychlorinated naphthalenes
PCP	Pentachlorophenol
PDMS	Polydimethylsiloxane
PeCBz	Pentachlorobenzene
penta-BDE	Pentabromodiphenyl ether (BDE 99, 100)
PCNB	Pentachloronitrobenzene, quintozene

Chemical abbreviation	Common name or group
PFA	Perfluoroalkyl acids
PFASs	Poly- and perfluorinated alkyl substances
PFBS	Perfluorobutanesulfonic acid, perfluorobutane sulfonate
PFSA	Perfluorinated alkyl sulfonate
PFCA	Perfluoroalkyl carboxylate
PFDA	Perfluorodecanoic acid, perfluorodecanoate
PFDoA	Perfluorododecanoic acid, perfluorododecanoate
PFHpA	Perfluoroheptanoic acid, perfluoroheptanoate
PFHxA	Perfluorohexanoic acid, perfluorohexanoate
PFHxS	Perfluorohexane sulfonic acid, perfluorohexane sulfonate
PFNA	Perfluorononanoic acid, perfluorononanoate
PFOA	Perfluorooctanoic acid, perfluorooctanoate
PFOS	Perfluorooctane sulfonate
PFPA	Perfluoropropionic anhydride
PFTeA	Perfluorotetradecanoic acid, perfluorotetradecanoate
PFTriA	Perfluorotridecanoic acid, perfluorotridecanoate
PFUnA	Perfluoroundecanoic acid, perfluoroundecanoate
Phthalates	Dimethyl phthalate (DMP), diethyl phthalate (DEP), di-i-butyl phthalate (DiBP), di-n-butyl phthalate (DnBP), butylbenzyl phthalate (BBP), diethylhexyl phthalate (DEHP)
POSF	Perfluorooctane sulfonyl fluoride
pTBX	2,3,5,6-tetrabromo-p-xylene
PTFE	Polytetrafluoroethylene
SCCPs,sPCA	Short-chain chlorinated paraffins
Siloxanes	D3, D4, D5, D6, L3, L4, L5
TBA	Tribromoanisole
TBBPA	Tetrabromobisphenol A
TBCT	Tetrabromo-o-chlorotoluene
TBECH	Tetrabromoethylcyclohexane
TBPH (or BEHTBP)	Bis(2-ethyl-1-hexyl)tetrabromophthalate
TC	Trans-chlordane (γ-chlordane)
TCDD	Tetrachlorodibenzo-*p*-dioxin
tetra-BDE	Tetrabromodiphenyl ether (BDE 47)
TeCV	Tetrachloroveratrole
ΣTEQ	Sum of dioxin (TCDD) toxic equivalents (PCDDs, PCDFs, DL-PCBs)
TFA	Trifluoroacetate
tri-BDE	Tribromodiphenyl ether (BDE 28/31)
Tefluthrin	Pyrethroid insecticide with a tetrafluoro-methyl benzene ring
Trifluralin	Dinitroaniline herbicide

Individual chemical nomenclature			
PBDEs	**Isomer#**	**Component (BFRs)**	**Acronym**
4-Bromodiphenyl ether	BDE 3	**Hexabromocyclododecane**	HBCDD
2,4-Dibromodiphenyl ether	BDE 7	**α-Hexabromocyclododecane**	α-HBCDD
4,4'-Dibromodiphenyl ether	BDE 15	**ß-Hexabromocyclododecane**	ß-HBCDD
2,2',4- Tribromodiphenyl ether	BDE 17	**γ-Hexabromocyclododecane**	γ-HBCDD
2,4,4'-Tribromodiphenyl ether	BDE 28	**Decabromodiphenylethane**	DBDPE
2,2',4,4'-Tetrabromodiphenyl ether	BDE 47	**1,2-Bis(2,4,6-tribromophenoxy)ethane**	BTBPE
2,2',4,5'-Tetrabromodiphenyl ether	BDE 49	**2,2',5,5'- Tetrabromobiphenyl**	PBB 52
2,3',4,4'-Tetrabromodiphenyl ether	BDE 66	**2,2',4,5,5'- Pentabromobiphenyl**	PBB 101
2,3',4',6-Tetrabromodiphenyl ether	BDE 71	**2,2',4,4',5,5'- Hexabromobiphenyl**	PBB 153
3,3',4,4'-Tetrabromodiphenyl ether	BDE 77		
2,2',3,4,4'-Pentabromodiphenyl ether	BDE 85		
2,2',4,4',5-Pentabromodiphenyl ether	BDE 99		
2,2',4,4',6-Pentabromodiphenyl ether	BDE 100		
2,3',4,4',6-Pentabromodiphenyl ether	BDE 119		
3,3',4,4',5-Pentabromodiphenyl ether	BDE 126		
2,2',3,4,4',5'-Hexabromodiphenyl ether	BDE 138		
2,2',4,4',5,5'- Hexabromodiphenyl ether	BDE 153		
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE 154		
2,2',4,4',6,6'-Hexabromodiphenyl ether	BDE 155		
2,3,3',4,4',5-Hexabromodiphenyl ether	BDE 156		
2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE 183		
2,2',3,4,4',6,6'-Heptabromodiphenyl ether	BDE 184		
2,3,3',4,4',5',6-Heptabromodiphenyl ether	BDE 191		
2,2',3,3',4,4',5,6'-Octabromodiphenyl ether	BDE 196		
2,2',3,3',4,4',6,6'-Octabromodiphenyl ether	BDE 197		
2,2',3,4,4',5,5',6- Octabromodiphenyl ether	BDE 203		
2,3,3',4,4',5,5',6- Octabromodiphenyl ether	BDE 205		
2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether	BDE 206		
2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl ether	BDE 207		
2,2',3,3',4,5,5',6,6'-Nonabromodiphenyl ether	BDE 208		
Decabromodiphenyl ether	BDE 209		
2-methoxy-2',3,4',5-tetrabromodiphenyl ether	2'-MeO-BDE68		
6-methoxy-2,2',4,4'-tetrabromodiphenyl ether	6-MeO-BDE47		

Individual chemical nomenclature

Polychlorinated biphenyls (PCBs)

	IUPAC#		IUPAC#		IUPAC#
2-Chlorobiphenyl	PCB 1	2,2',3,3',4-Pentachlorobiphenyl	PCB 82	2,3,3',4,4',6-Hexachlorobiphenyl	PCB 158
4-Chlorobiphenyl	PCB 3	2,2',3,3',6-Pentachlorobiphenyl	PCB 84	2,3,3',4',5,6-Hexachlorobiphenyl	PCB 163
2,2'-Dichlorobiphenyl	PCB 4	2,2',3,4,4'-Pentachlorobiphenyl	PCB 85	2,3,3',4',5',6-Hexachlorobiphenyl	PCB 164
2,3'-Dichlorobiphenyl	PCB 6	2,2',3,4,5'-Pentachlorobiphenyl	PCB 87	2,3',4,4',5,5'-Hexachlorobiphenyl	PCB 167
2,4'-Dichlorobiphenyl	PCB 8	2,2',3,4',6-Pentachlorobiphenyl	PCB 91	2,3',4,4',5',6-Hexachlorobiphenyl	PCB 168
2,6-Dichlorobiphenyl	PCB 10	2,2',3,4',5-Pentachlorobiphenyl	PCB 90	3,3',4,4',5,5'-Hexachlorobiphenyl	PCB 169
4,4'-Dichlorobiphenyl	PCB 15	2,2',3,5,5'-Pentachlorobiphenyl	PCB 92	2,2',3,3',4,4',5-Heptachlorobiphenyl	PCB 170
2,2',3-Trichlorobiphenyl	PCB 16	2,2',3,5',6-Pentachlorobiphenyl	PCB 95	2,2',3,3',4,4',6-Heptachlorobiphenyl	PCB 171
2,2',4-Trichlorobiphenyl	PCB 17	2,2',3',4,5-Pentachlorobiphenyl	PCB 97	2,2',3,3',4,5,5'-Heptachlorobiphenyl	PCB 172
2,2',5-Trichlorobiphenyl	PCB 18	2,2',4,4',5-Pentachlorobiphenyl	PCB 99	2,2',3,3',4,5,6'-Heptachlorobiphenyl	PCB 174
2,2',6-Trichlorobiphenyl	PCB 19	2,2',4,5,5'-Pentachlorobiphenyl	PCB 101	2,2',3,3',4,6,6'-Heptachlorobiphenyl	PCB 176
2,3,4'-Trichlorobiphenyl	PCB 22	2,2',4,6,6'-Pentachlorobiphenyl	PCB 105	2,2',3,3',5,5',6-Heptachlorobiphenyl	PCB 178
2,4,4'-Trichlorobiphenyl	PCB 28	2,3,3',4,5'-Pentachlorobiphenyl	PCB 107	2,2',3,3',5,6,6'-Heptachlorobiphenyl	PCB 179
2,4',5-Trichlorobiphenyl	PCB 31	2,3,3',4',6-Pentachlorobiphenyl	PCB 110	2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB 180
2',3,4-Trichlorobiphenyl	PCB 33	2,3,4,4',5-Pentachlorobiphenyl	PCB 114	2,2',3,4,4',5,6'-Heptachlorobiphenyl	PCB 182
3,4,4'-Trichlorobiphenyl	PCB 37	2,3',4,4',5-Pentachlorobiphenyl	PCB 118	2,2',3,4,4',5',6-Heptachlorobiphenyl	PCB 183
2,2',3,3'-Tetrachlorobiphenyl	PCB 40	2,3',4,4',6-Pentachlorobiphenyl	PCB 119	2,2',3,4',5,5',6-Heptachlorobiphenyl	PCB 187
2,2',3,4-Tetrachlorobiphenyl	PCB 41	2',3,4,4',5-Pentachlorobiphenyl	PCB 123	2,2',3,4',5,6,6'-Heptachlorobiphenyl	PCB 188
2,2',3,4'-Tetrachlorobiphenyl	PCB 42	3,3',4,4',5-Pentachlorobiphenyl	PCB 126	2,3,3',4,4',5,5'-Heptachlorobiphenyl	PCB 189
2,2',3,5'-Tetrachlorobiphenyl	PCB 44	2,2',3,3',4,4'-Hexachlorobiphenyl	PCB 128	2,3,3',4,4',5,6-Heptachlorobiphenyl	PCB 190
2,2',3,6-Tetrachlorobiphenyl	PCB 45	2,2',3,3',4,5-Hexachlorobiphenyl	PCB 129	2,3,3',4,4',5',6-Heptachlorobiphenyl	PCB 191
2,2',4,4'-Tetrachlorobiphenyl	PCB 47	2,2',3,3',4,5'-Hexachlorobiphenyl	PCB 130	2,3,3',4',5,5',6-Heptachlorobiphenyl	PCB 193
2,2',4,5-Tetrachlorobiphenyl	PCB 48	2,2',3,3',4,6-Hexachlorobiphenyl	PCB 131	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	PCB 194
2,2',4,5'-Tetrachlorobiphenyl	PCB 49	2,2',3,3',4,6'-Hexachlorobiphenyl	PCB 132	2,2',3,3',4,4',5,6-Octachlorobiphenyl	PCB 195
2,2',5,5'-Tetrachlorobiphenyl	PCB 52	2,2',3,3',5,6'-Hexachlorobiphenyl	PCB 135	2,2',3,3',4,4',5,6'-Octachlorobiphenyl	PCB 196
2,2',5,6'-Tetrachlorobiphenyl	PCB 53	2,2',3,4,4',5-Hexachlorobiphenyl	PCB 137	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	PCB 196
2,2',6,6'-Tetrachlorobiphenyl	PCB 54	2,2',3,4,4',5'-Hexachlorobiphenyl	PCB 138	2,2',3,3',4,5,6,6'-Octachlorobiphenyl	PCB 200
2,3,3',4'-Tetrachlorobiphenyl	PCB 56	2,2',3,4,5,5'-Hexachlorobiphenyl	PCB 141	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	PCB 201
2,3,4,4'-Tetrachlorobiphenyl	PCB 60	2,2',3,4',5,5'-Hexachlorobiphenyl	PCB 146	2,2',3,3',5,5',6,6'-Octachlorobiphenyl	PCB 202
2,3,4',5-Tetrachlorobiphenyl	PCB 63	2,2',3,4',5',6-Hexachlorobiphenyl	PCB 149	2,2',3,4,4',5,5',6-Octachlorobiphenyl	PCB 203
2,3,4',6-Tetrachlorobiphenyl	PCB 64	2,2',3,5,5',6-Hexachlorobiphenyl	PCB 151	2,3,3',4,4',5,5',6-Octachlorobiphenyl	PCB 205
2,3',4,4'-Tetrachlorobiphenyl	PCB 66	2,2',4,4',5,5'-Hexachlorobiphenyl	PCB 153	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	PCB 206
2,3',4',5-Tetrachlorobiphenyl	PCB 70	2,2',4,4',5,6'-Hexachlorobiphenyl	PCB 154	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	PCB 207
2,4,4',5-Tetrachlorobiphenyl	PCB 74	2,2',4,4',6,6'-Hexachlorobiphenyl	PCB 155	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	PCB 208
3,3',4,4'-Tetrachlorobiphenyl	PCB 77	2,3,3',4,4',5-Hexachlorobiphenyl	PCB 156	Decachlorobiphenyl	PCB 209
3,4,4',5-Tetrachlorobiphenyl	PCB 81	2,3,3',4,4',5'-Hexachlorobiphenyl	PCB 157		

Species names		
Group	**Common name of the Species**	**Systematic name**
Freshwater fish	lake trout	*Salvelinus namaycush*
	burbot	*Lota lota*
	Dolly Varden	*Salvelinus malma*
	Arctic char	*Salvelinus alpinus*
Terrestrial plants	crinkled snow lichen (Fla)	*Flavocetraria nivalis/cucullata*
	reindeer lichen (Cla)	*Cladonia mitis/rangiferina*
	green lichen	*Cladonia mitis*
	jewel lichen	*Xanthoria elegans*
	worm lichen	*Thamnolia vermicularis*
	willow	*Salix pulchra; Salix glauca*
	cottongrass	*Eriophorum vaginatum*
	water sedge	*Carex pulchra; Carex aquatilis*
	moss	*Rhytidium rugosum*
Terrestrial birds	ptarmigan, rock ptarmigan	*Lagopus mutus*
	willow ptarmigan	*Lagopus lagopus*
	snow goose	*Chen caerulescens*
	snow bunting	*Plectrophenax nivalis*
	ruffed grouse	*Bonasa umbellus*
	spruce grouse	*Dendragapus canadensis*
	sharp tailed grouse	*Tympanuchus phasianellus*
	northern pintails	*Ana acuta*
	mallard ducks	*Anas platyrhynchos*
	Canada geese	*Branta canadensis interior*
	lesser snow geese	*Chen caerulescens caerulescens*
Terrestrial mammals	arctic fox	*Vulpes lagopus*
	deer mice	*Peromyscus maniculatus*
	sled dogs	*Canis familiaris*
	mink	*Mustela vision*
	marten	*Martes americana*
	ermine	*Mustela erminea arctica*
	arctic hare	*Lepus arcticus*
	northern collared lemming	*Dicrostonyx groenlandicus*
	caribou	*Rangifer tarandus groenlandicus*
	moose	*Alces alces*
	wolf	*Canis lupus*
amphipods	Themisto libellula	*Themisto libellula*
scavenging amphipods	Eurythenes	*Eurythenes gryllus*
Marine zooplankton	zooplankton	*Calanus hyperboreus*
Marine fish	capelin	*Mallotus villosus*
	sandlance	*Ammodytes spp.*
	arctic cod	*Boreogadus saida*
	polar cod	*Arctogadus glacialis*
	redfish	*Sebastes mentella*
	turbot or Greenland halibut	*Reinhardtius hippoglossoides*
	Greenland shark	*Somniosus microcephalus*

Species names		
Group	**Common name of the Species**	**Systematic name**
seabirds	black guillemot	*Cepphus grylle*
	glaucous gull	*Larus hyperboreus*
	great skua	*Stercorarius skua*
	great black-backed gull	*Larus marinus*
	common eider	*Somateria mollissima borealis*
	glaucous gull	*Larus hyperboreus*
	ivory gull	*Pagophila eburnea*
	northern fulmar	*Fulmarus glacialis*
	black-legged kittiwake	*Rissa tridactyla*
	thickbilled murres	*Uria lomvia*
	common murre	*Uria aalge*
	white winged scoters	*Melanitta fusca*
	cormorant	*Phalacrocorax carbo*
Marine mammals	ringed seals	*Phoca hispida*
	spotted seals	*Phoca largha*
	ribbon seals	*Phoca fasciata*
	harp seals	*Pagophilus groenlandicus*
	harbor seals	*Phoca vitulina*
	northern fur seals	*Callorhinus ursinus*
	narwhal	*Monodon monoceros*
	beluga whale	*Delphinapterus leucas*
	polar bears	*Ursus maritimus*

Photo: David Gaspard/ArcticNet

Annex Tables and Figures

(Tables and figures are presented as supporting information and are available in electronic format only as a separate file. To receive a copy please send your request to PLCN-NCP@aadnc-aandc.gc.ca)

Chapter 2

Chapter 3

Chapter 4

Chapter 6

Notes

Notes

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Aboriginal Affairs and Northern Development Canada
10 Wellington Street,
Gatineau, Quebec K1A 0H4