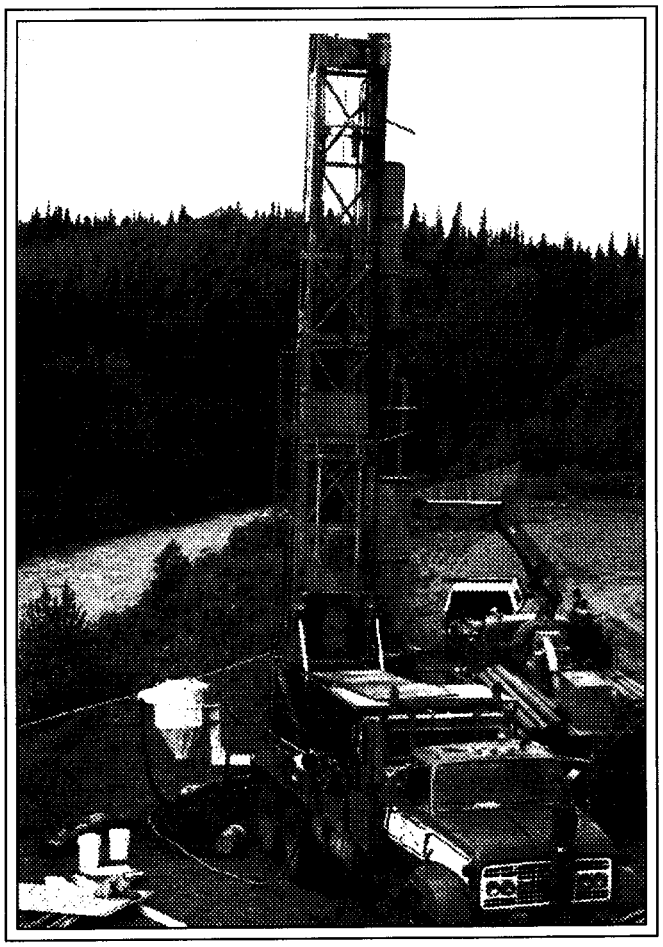
PRELIMINARY ENVIRONMENTAL ASSESSMENT HAINES- FAIRBANKS PIPELINE

DELINEATION AND CHARACTERIZATION OF METALS, ORGANOCHLORINES AND HYDROCARBONS AT MILLION DOLLAR FALLS, BLANCHARD RIVER AND BORDER STATION



Prepared for:
INDIAN AND NORTHERN AFFAIRS
ARCTIC ENVIRONMENTAL STRATEGY

Prepared by:
ROYAL ROADS UNIVERSITY
APPLIED RESEARCH DIVISION

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1. INTRODUCTION

1.1 Background

In August 1995, UMA Engineering Ltd. (UMA) in association with AMBIO Research Associates Inc. (AMBIO) submitted a report entitled "Preliminary Environmental Assessment: Haines-Fairbanks Pipeline" to Indian and Northern Affairs Canada (DIAND), Arctic Environmental Strategy (AES), Action on Waste, Whitehorse. This report was commissioned as part of the AES Action on Waste program to provide preliminary assessment information and identify additional resources required for future assessment and remediation at five sites along the Haines-Fairbanks pipeline. The five sites, shown in Figure 1-1 included:

1. **Oil Spill at Mile 207.6**: This fuel spill was located 3 km south of the Destruction Bay Pump Station. The 60 m x 500 m spill was caused by the cutting of the pipe for maintenance purposes in 1956.

2. **Junction Pump Station**: This pump station was located approximately 15 km north of Haines Junction at Mile 158 of the pipeline. Most of the buildings were intact and there were two suspected waste disposal areas.

3. **Million Dollar Falls**: This site was originally used as a used as a military camp and highway construction camp, and was later converted to a construction camp for the pipeline. There was one large disposal area and some evidence that materials were buried on site. The site is presently used as a recreational area and campsite.

4. **Blanchard River Pump Station**: This site is located at Mile 87 of the pipeline and is just on the Yukon side of the border with British Columbia. The site is presently owned by the Yukon Territorial Government (YTG) Highways Department. The portions of the original pump station were either modified or removed and there is evidence of old disposal areas at the site.

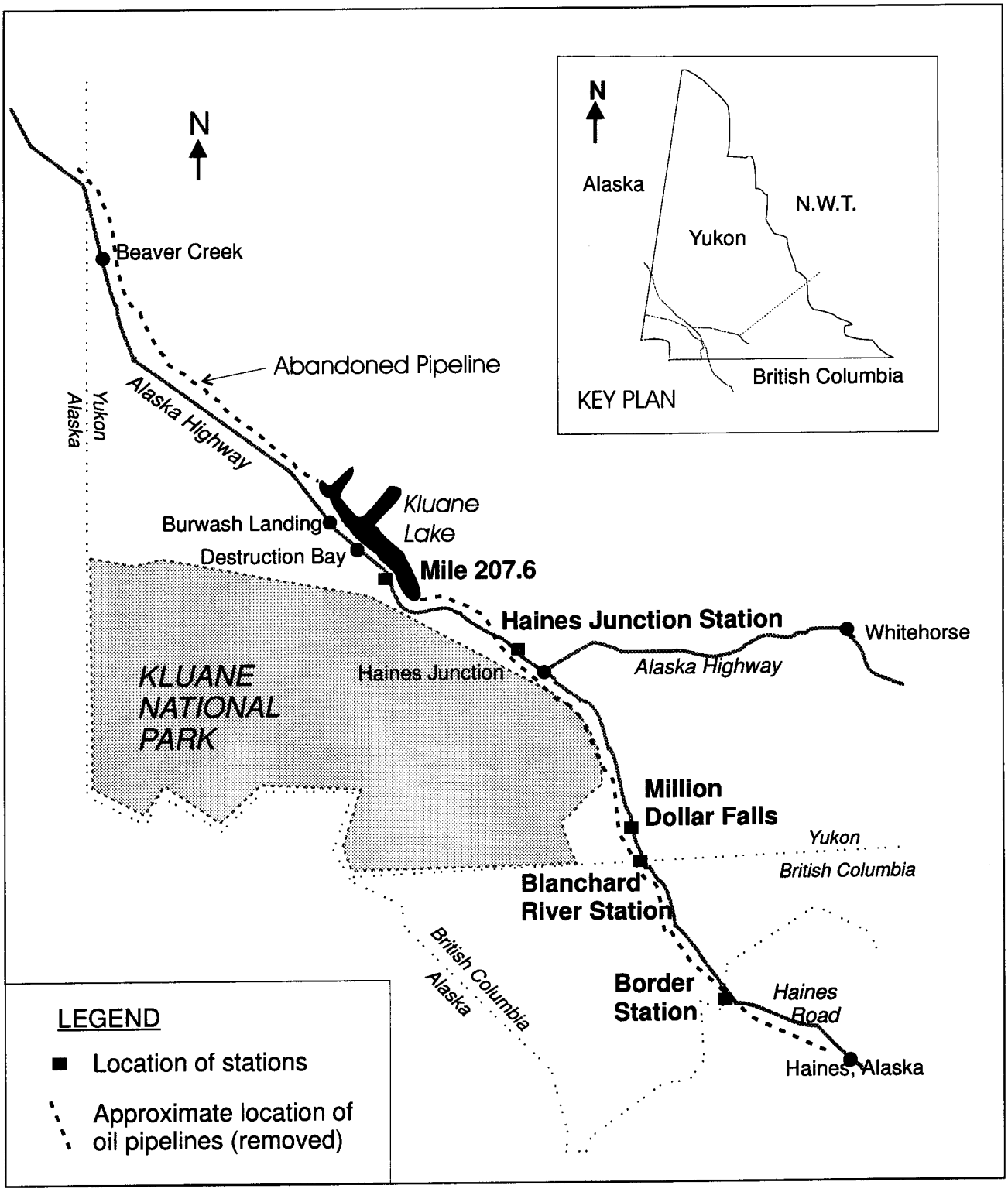
5. **Border Pump Station**: This site, located at Mile 47 on the pipeline, was demolished and buried on site. This initial assessment program was focused solely on the Border Station Site and excluded the associated airstrip (Rainy Hollow) and dump areas.

After a review of existing knowledge and site reconnaissance, field investigations were carried out in July 1995. The field programs incorporated electromagnetic surveys to detect buried metallic debris and sampling of both surface and subsurface soil and water. Plant specimens were also collected at Blanchard River. Subsurface sampling was achieved using test pits, drill holes and monitoring wells. The analytical program consisted of two components; (i) field analyses utilizing immunoassay based test kits for PAHs, TPH, BTEX and PCBs and soil vapour surveys using a photoionization detector; and (ii) detailed laboratory analyses for a broad suite of inorganic and organic contaminants. Data from each site were interpreted relative to the site-specific conditions and relevant soil and water assessment and remediation criteria (primarily Canadian Council of Ministers of the Environment (CCME) criteria). A preliminary risk assessment was carried out for each site and a summary of environmental problems and recommended actions was presented. This summary is reproduced in Table 1.1.

Table 1.1 Project Summary - Preliminary Environmental Assessment Haines-Fairbanks Pipeline

Site	Problems Detected	Risk	Recommended Action
Blanchard River Pump Station	• Hydrocarbon and inorganic element contaminated leachate from unknown source. • Hydrocarbon contaminated groundwater plume	• Evidence for possible input into fish bearing waters. • Direct input into Blanchard River	• Full site assessment to delineate source(s), composition, extent and migration of contaminants
Million Dollar Falls	• Possible low level PCB contamination of campground water supply aquifer • Elevated levels of zinc and DDT at the toe of the dump	• Possible human and ecosystem health risk implications • Potential migration to Takhanne River	• Detailed confirmatory sampling and analysis. • Remediation of dump under the supervision of an experienced hazardous waste professional.
Border Pump Station	• Soil and groundwater contaminated with hydrocarbons	• Potential for migration to Klehini River via Rainy Hollow site.	• Collate all available contaminant and geotechnical information and provide recommendations • Resample monitoring wells MW-8a and 8b in TH-8.
Haines Junction Pump Station	• Buried drums containing hydrocarbon products	• Probable future release of liquid content	• Excavation and removal of non-empty drums under the supervision of an experienced hazardous waste professional
Mile 207.6 Spill Site	• Extensive hydrocarbon contamination of soil	• Past impact to vegetation has occurred; however, recovery is evident. Little if any, potential for future risk.	• None is required at this site. Caution is recommended in extrapolation to other spill sites.

Map 1.1: Locations of the Five Study Sites



1.2 Scope and Objectives

A Contribution Agreement was signed between Arctic Environmental Strategy - Action on Waste and Royal Roads University - Applied Research Division on the 2nd day of February, 1996 in order to address issues arising from the Preliminary Environmental Assessment of the Haines-Fairbanks Pipeline summarized in Table 1.1. The objectives of this agreement included:

1. Delineation of hydrocarbon and inorganic element contamination from leachate plume at Blanchard River
2. Detailed characterization of the chemical components of the Blanchard River leachate plume.
3. Confirmation of the absence of PCBs at Blanchard River.
4. Further investigation of hydrocarbons, mercury and pesticides in the vicinity of Test Hole 8 at Border Station
5. Additional investigation of zinc and DDT contamination at the base of the dump at Million Dollar Falls.
6. Investigation of the ecotoxicological significance of petroleum hydrocarbon contamination.
7. Set up of an analytical system for the field measurement of PCBs, BTEX, TPH, and Pesticides in soil and water samples.

There was no requirement at this stage for additional sampling; archived samples collected from Million Dollar Falls, Blanchard River and Border Pump Station in July 1995 were analyzed for one or more of the following substances: total extractable hydrocarbons (TEH), metals, PCBs, pesticides, unsubstituted and alkylated PAHs, chlorobenzenes, alkanes, hopanes and isoprenoids. This report contains the detailed data analysis and interpretation. The methodology and equipment required for field analyses (Objective 7) was provided to Action on Waste on March 4, 1996.

1.3 Organization of the Report

This report is presented in five chapters:

Chapter 1: Introduction - outlines the background and the scope and objectives of the study.

Chapter 2: Methodology - reviews the sample selection and the analytical program. Maps showing the sample locations are also presented.

Chapter 3: Results and Discussions - presents the overall results for PCB, pesticides and hydrocarbon contamination, as well as site specific summaries and recommendations for Million Dollar Falls, Blanchard River and Border Station.

Chapter 4: Appendices - describes the analytical methods employed in this study, the QA/QC protocols and data and the environmental implications and review of Alkylated PAHs.

2. METHODOLOGY

2.1 Sample Selection

2.1.1 Million Dollar Falls

Million Dollar Falls is located above the Takhanne River. This site was a communications relay station in the early 1940s. It was also used as a highway construction camp in 1943 for the Haines Road and later as a pipeline construction camp from 1954 to 1955. The site is presently used as a recreational area and campsite. All that remains from the original buildings are cement pads presently found among the sites at the Million Dollar Falls campground. A large day-use shelter and a groundwater supply pump situated near the centre of the site are also located at the campground. Two dump areas occur at the base of the ravine cliff on the west side of the site, along the edge of the surrounding forest. The largest of these, roughly 30 m by 20 m, consists of wood scraps (some burned), metal straps and cans, rubber, barrels and car parts. A second smaller dump is situated further to the south near the Takhanne River and contains mostly domestic refuse such as cans. Both areas drain into a small creek approximately 3 m away, which subsequently flows north for 50 m to intersect with the Takhanne River just below the falls.

Concentrations of most inorganic substances in samples collected at Million Dollar Falls (UMA/AMBIO 1995[1]) were comparable to or slightly higher than the CCME Assessment Criteria, and well below the CCME R/P Soil Remediation Criteria. The only exception were concentrations of zinc at MD1S004 (269 mg/g) and MD1S005 (497 mg/g) along the toe of the larger dump which exceeded the CCME Assessment Criteria; the larger value of these was also comparable to the R/P Soil Remediation Criterion. DDTs (50 and 62 ng/g) were also detected in samples collected along the toe of the dump. The total concentrations of pesticides however were

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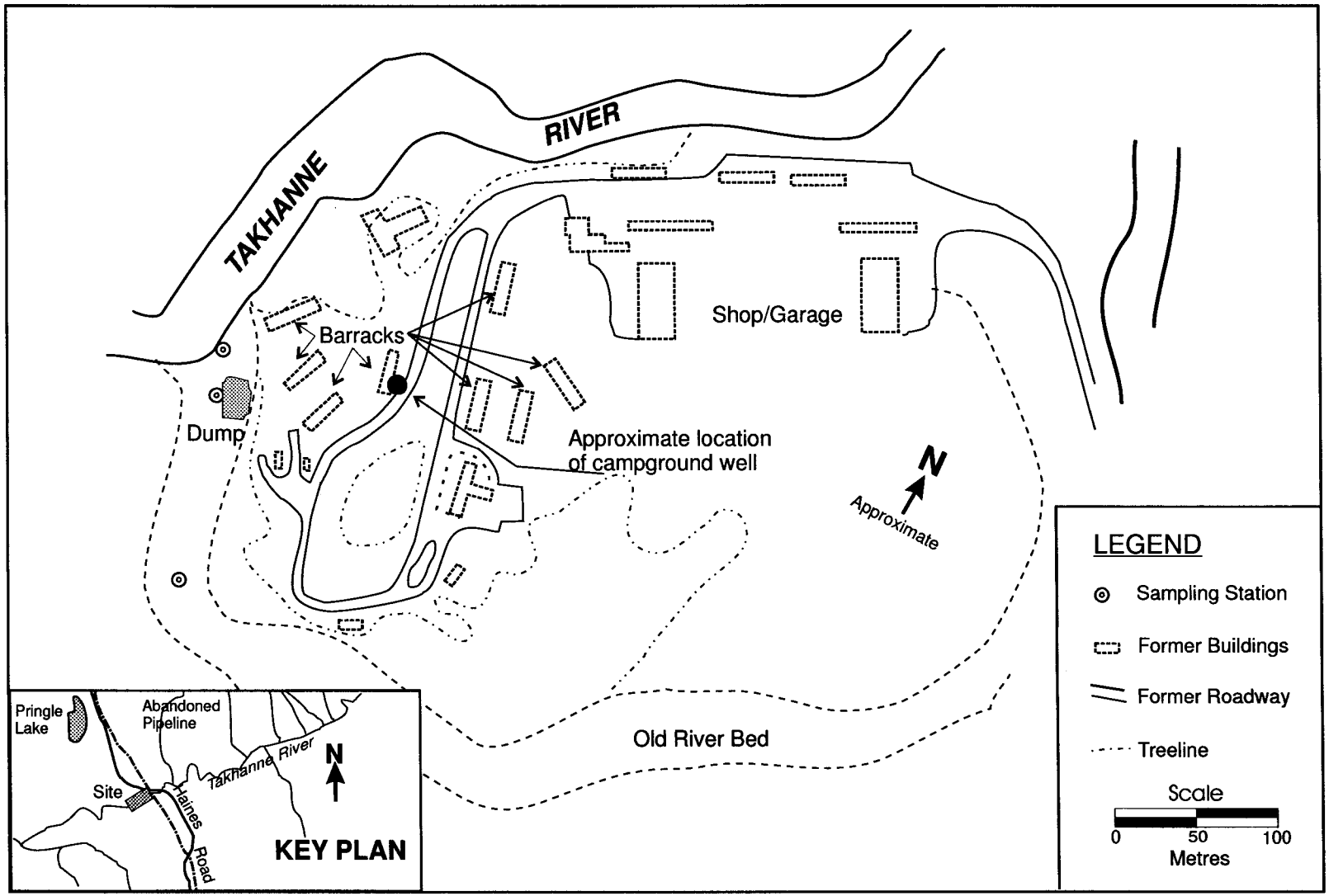
[1] UMA/AMBIO, 1995. Preliminary Environmental Assessment, Haines-Fairbanks Pipeline. Prepared for the Action on Waste Office, Department of Indian Affairs and Northern Development, Whitehorse, Yukon by UMA Engineering Ltd. and AMBIO Research Associates Inc. in August 1995.

below the BC MOE Level B Criterion. Low levels of PCB Aroclor 1254 were also detected in these samples (1.7 to 2.0 ng/g) which were well below the CCME Assessment Criterion.

In order to ascertain if zinc and DDTs detected in the dump, were migrating towards Takhanne River, an archived water sample (MD1W002) collected from a stream below the dump which flows into the river was analyzed for metals and chlorinated pesticides. The layout of the Million Dollar Falls site showing the original camp buildings and sampling locations is provided as Map 2.1.



Map 2.1: Layout of Million Dollar Falls showing the original station buildings and sampling stations

2.1.2 Blanchard River

This former pump station site is located at Mile 87 of the pipeline above its namesake. The original station was constructed in 1962 along with five other stations in the Yukon and Alaska in response to the need for increased pipeline throughput. Blanchard River Station originally consisted of one main multi-purpose building which housed the engine room, pumps, generators, maintenance shop and water supply; and six accommodation trailers used as family housing. Two POL storage tanks were also located at the south end of the site. Portions of the original pump station were either modified or removed when the site was taken over by Yukon Highways in the mid 1980's. An accommodation building was also constructed on the original site of the trailers to house the highway workers; these areas have been entirely fenced in. Demolition debris was buried to the north of the site and old transformers were apparently buried to the west of the existing buildings.

The main operations site was relatively clean with no evidence of spillage or debris. A rust-coloured leachate was observed in a spring emanating from the ground near the top of the slope at the north end of the site; an oily sheen was also noted on the water surface. This discolouration suggested the presence of buried materials somewhere in the north portion of the site. This stream is one of a few along this slope which follows a drainage pathway through a low wooded area dominated by willow (*Salix* sp.) and horsetail (*Equisetum* sp.) to a wet marshy area along the shore of the Blanchard River.

A water sample (BL1GW004) obtained from the top of the rust-coloured leachate plume and a second surface water sample (BL1W001) obtained from a small horsetail dominated marsh (by the Blanchard River) which received drainage from the leachate plume were analyzed for PAHs, OCs, PCBs, inorganic elements, herbicides and VOCs. The concentrations of substances detected were low and below the CCME Assessment Criteria for water (UMA/AMBIO 1995). One soil sample (BL1S012) from near the top of the plume contained a TEH concentration of 6800 μg/g, which was considerably higher than that found for a background sample BL1S014 (<20 μg/g) collected in the foothills east of the site. The leachate plume soil value also far exceeded the US Federal/State Guidelines adopted by Alaska (200 μg/g). Concentrations for

most VOCs (excluding BTEX) in this soil sample were below detection. In this present work, one archived soil sample obtained from a red rusty spring below the plume (BLS0112) was analyzed for PAHs, alkanes, hopanes PCBs, pesticides and chlorobenzenes in order to further characterize the chemical components of this leachate plume.

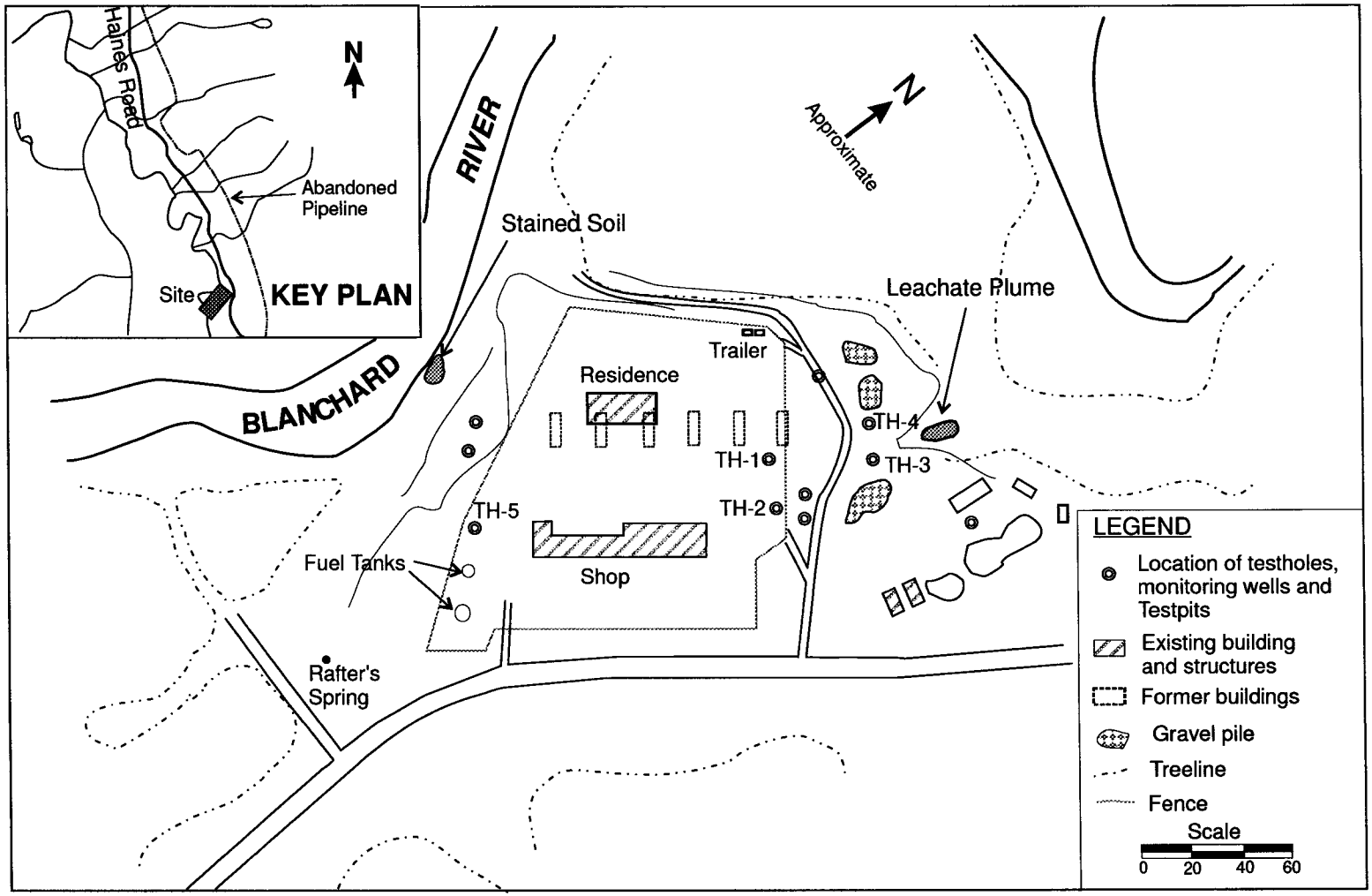
Two samples from the rusted leachate plume located at the top (BL1S013) and at mid-slope (BL1S010) were also analyzed for inorganic elements in the previous study (UMA/AMBIO 1995). A number of analytes exceeded the CCME R/P Remediation Criteria at these locations including arsenic (138 and 85 μg/g), barium (2360 and 4770), cobalt (55 and 90 μg/g), selenium (3.1 μg/g at the top of the plume), and zinc (1490 μg/g and 3570 μg/g); all other analytes were comparable to, or slightly lower than the CCME Assessment Criteria for soils. To investigate the ecotoxicological significance of metal contamination, six archived plant samples collected from drainage areas below the leachate plume were analyzed. One plant sample obtained from a background location along a stream in foothills approximately 200 m east of the station was also analyzed for comparison.

The TEH concentration in a groundwater sample (BL1GW003) taken by mini-peizometer from a stained soil area along the west side of the site in the previous study was 4700 μg/g. This exceeded the US Federal/State Guidelines adopted by Alaska. An archived soil sample collected from this stain (BL1S003) was therefore analyzed for PAHs, alkanes, hopanes PCBs and chlorobenzenes in order to delineate and further characterize the hydrocarbon contamination.

Other groundwater samples from a number of test holes and water supply locations at the station were also examined for various potential contaminants including TEHs, inorganic elements, OCs, VOCs, PCBs and pesticides in the previous study (locations of the wells are shown in Map 2.2). TEHs were found in samples collected from TH-5 (3700 μg/L) and TH-1 (690 μg/L). Concentrations for nearly all other analytes were well below the CCME Assessment Criterion for water, with the exception of mercury, ethylbenzene and benzene. Mercury levels in groundwater at TH-1 were comparable to the CCME Assessment Criterion for water while concentrations of ethylbenzene at TH-2 and TH-5 exceeded the CCME Criteria for Drinking

Water (< 2.4 μg/L based on aesthetic objectives). The level of benzene at TH-2 (11 μg/L) also exceeded the CCME Drinking Water Criterion (5 μg/L).

Soil samples from profiles in selected test pits and holes were also analyzed for TEHs, VOCs and/or inorganic elements in the previous study. Tests for TEHs in soils from TH-1, TH-2 and TH-5 indicated concentrations of up to 360-370 μg/g. Concentrations of all VOC analytes (excluding BTEX) were below detection in the soil profile sample obtained from TH-5. Inorganic element concentrations in profile samples at test pits were comparable to, or less than CCME Assessment Criteria for soils. Further characterization of TEH contamination in these test holes was achieved by analyzing one archived sample each from TH-1, TH-2 and TH-5 for PAHs, alkanes, hopanes PCBs, pesticides and chlorobenzenes in this study. Archived samples from TH-1 (two), TH-2 (two), TH-3 (one), TH-4 (one) and TH-5 (four) were also analyzed in order to investigate the vertical distribution of TEH in the test pits. Layout of the site and sampling locations are shown in Map 2.2.



Map 2.2: Layout of Blanchard River Pump Station showing the original pump station buildings, present highways maintenance camp and locations of testholes, monitoring wells and testpits

2.1.3 Border Pump Station

Border Station, which was one of the largest pump stations, was constructed in the mid 1950's near the Klehini River. The facilities were used as a base camp for the Haines Road re-alignment in 1978 and 1979, and for mineral exploration from 1983 to 1987. The station was finally closed in 1987 at which time a cleanup was conducted by BC Ministry of Forests. All of the buildings and facilities at the site were subsequently demolished by the Department of Public Works (now Government Services, Canada) under contract in 1992-3, and buried on site.

The station was relatively free of debris; a number of recently worked areas occur throughout the site. A few stains were also discovered toward the west end of the site, including a large hydrocarbon stain measuring approximately 20 m^2, just north of where the accommodation facilities were once located. DDT contaminated soils, removed during the excavation of buried canisters at Rainy Hollow in 1994, were encapsulated in a liner and placed in a fenced area at Border Station. This secure storage facility appeared to be in good condition.

Selected soil and water samples from four test holes (TH-6 to TH-9) and a stained location at the northwest end of the station were analyzed for various potential contaminants including total extractable hydrocarbons (TEHs), volatile organic compounds (VOCs, some including the BTEX suite), organochlorine pesticides (OCs), phenoxyacid herbicides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (UMA/AMBIO, 1995).

The concentration of TEH in soil samples from the large stain area near the northwest end of the site (BO1S001/002) was quite high (3200 μg/g) and far exceeded the US Federal/State Guidelines adopted by Alaska (200 μg/g). Levels of all inorganic elements and organochlorines in samples from the stain area and TH-6 were either below detection or much lower than CCME R/P Criteria. Archived samples collected from these two locations, therefore, were not analyzed.

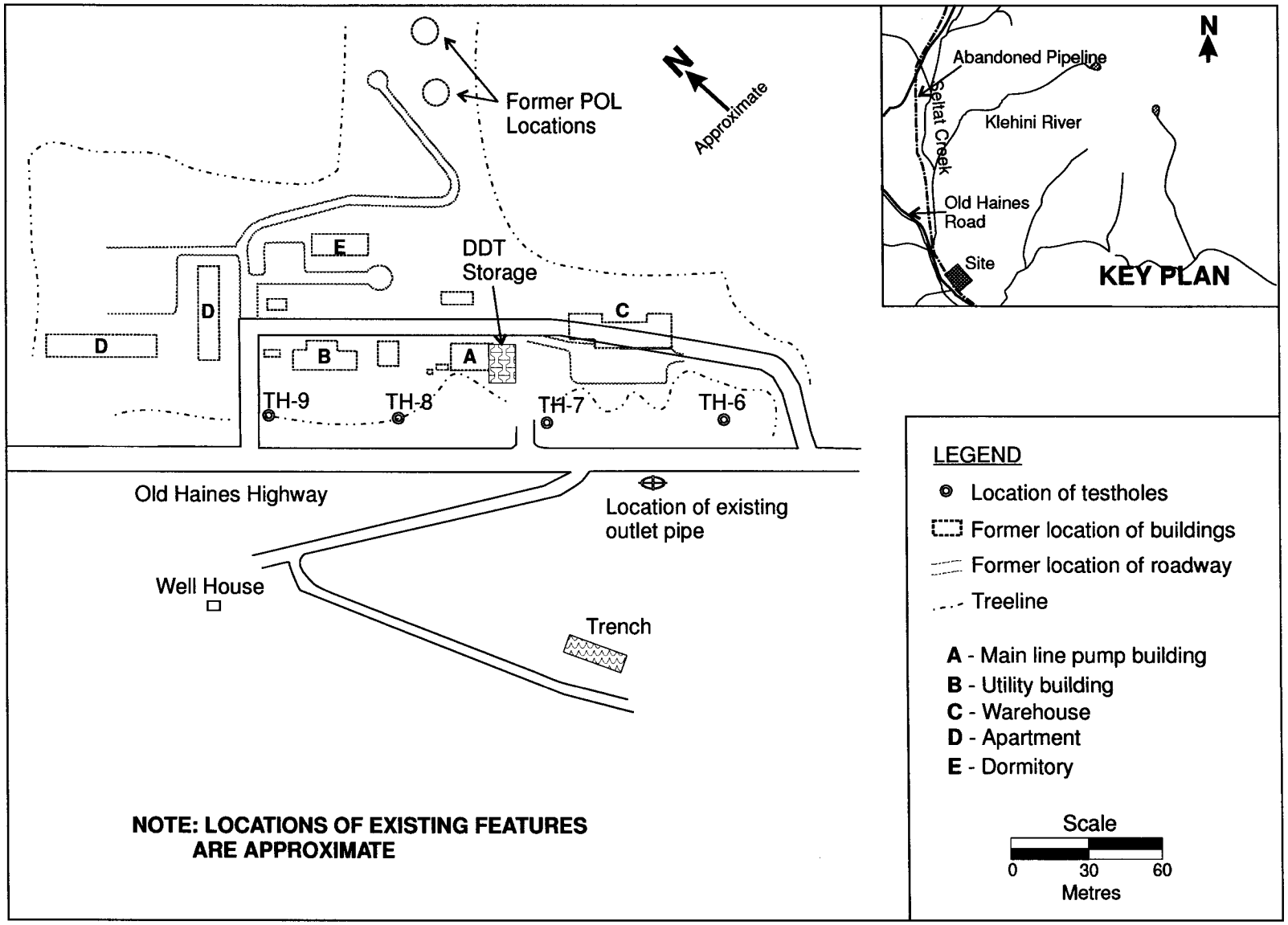
Concentrations of TEH in TH-7 decreased with depth from 1300 to <50 mg/g; concentrations at the two shallower depths (1300 and 260 mg/g, respectively) exceeded the US Federal/State Guidelines adopted by Alaska (200 $\mu g\ g^{-1}$). An archived soil sample collected from this test hole was therefore analyzed for PAHs, alkanes, hopanes, PCBs and chlorobenzenes in

order to characterize the hydrocarbon contamination. The vertical distribution of hydrocarbon contamination was also investigated by analyzing seven archived soil samples.

Groundwater samples from two nested wells at TH-8 (BO1GW001 at 17.5 m and BO1GW002 at 9.5 m depth), contained 1200 and 150,000 μg/L of TEH respectively (UMA/AMBIO, 1995). Inorganic element concentrations in both wells were well below CCME Assessment Criteria for water with slightly higher concentrations observed in the shallower well. The only exceptions were for mercury concentrations (0.12 and 0.33 μg/L) in the deeper and shallower wells, respectively) which were present at a level greater than CCME assessment criteria for water and aquatic life, but well were below the CCME Drinking Water Criteria (1 μg/L). Out of the suite of organochlorine compounds analyzed in the shallower well sample (BO1GW002 - 9.5 m well) only p,p'-DDD (8.9 ng/L) were detected. This concentration was below the range of the CCME Drinking Water Criteria (700 to 280,000 ng/g) but within range of CCME Freshwater Aquatic Life Criteria (1 to 4000 ng/g). Further investigation of hydrocarbons, mercury and pesticides in Test Hole 8 was carried out for this report. This was achieved by analyzing two archived soil samples for metals, seven for TEH and five for pesticides.

Concentrations of TEH in TH-9 decreased with increasing depth from 77 to < 20 μg/g and were considerably lower than the Alaska guidelines (UMA/AMBIO, 1995). Concentrations of all VOC analytes were below detection while inorganic elements were comparable to the CCME Assessment Criteria for soils. One archived soil sample from this test hole was therefore analyzed for inorganic elements.

The layout of Border Station is shown in Map 2.3.



Map 2.3: Layout of Border Pump Station showing the original pump station buildings, DDT storage area and locations of testholes

2.1.4 Summary of Analytical Program

A summary of the analytical program is given in Table 2.1 below.

Table 2.1 Analytical Program

Site	*Metals*			*Pesticides*		*PCBs*	*TEH*	*Choro-benzene*	*PAH*	*Hop-anes*	*Alk-anes*
	Soils	*Plants*	*Water*	*Soils*	*Water*	*Soils*					
Million Dollar Falls	-	-	1	-	1	-	-	-	-	-	-
Blanchard River	-	4		2	-	5	10	5	5	5	5
Border Station	3	-	-	7	-	7	14	1	1	1	1
Total	**3**	**4**	**1**	**9**	**1**	**12**	**24**	**6**	**6**	**6**	**6**

2.2 Environmental Criteria

A detailed review of environmental quality criteria has been presented in Chapter 1.2 of the 1995 report "Preliminary Environmental Assessment Haines-Fairbanks Pipeline" (UMA/AMBIO 1995). Briefly, the Canadian Council of Ministers of the Environment (CCME) Interim Environmental Quality Criteria for Contaminated Sites criteria were used to evaluate data from metals, and PAH analyses, while pesticides were considered in terms of the British Columbia soil guidelines. Data were also interpreted relative to site-specific conditions.

The "Canadian Council of Ministers of the Environment (CCME) Interim Environmental Quality Criteria for Contaminated Sites" which were published in 1991 are largely based on values that have been used in other jurisdictions. They are considered to be interim pending an increased amount of information about some contaminants, and future advances in the scientific understanding of contaminant dose - impact relationships. Two classes of criteria are described for both soil and water - Assessment Criteria and Remediation Criteria. The CCME Interim Assessment Criteria indicate the background concentrations or analytical detection limit for contaminants. The detection of substances at concentrations higher than the Assessment Criteria may or may not be indicative of contamination or pollution, but generally require further investigation. Results of such investigations are evaluated in terms of the CCME Interim Remediation Criteria.

2.2.1 Water

The Remediation Criteria for Water are divided into four usage categories - freshwater aquatic life, irrigation, livestock watering, and drinking water. For surface waters at the pumping stations, remediation criteria for freshwater aquatic life are relevant, as are drinking water standards where there is some reasonable expectation that the water might be used by humans. The archived water samples were analyzed for metals and pesticides. The pesticides included alpha HCH, beta HCH, gamma HCH, Heptachlor, Aldrin, Oxychlordane, trans-Chlordane, cis-Chlordane, o,p'-DDE, p,p'-DDE, trans-Nonachlor, cis-Nonachlor, o,p'-DDD, p,p'-DDD, o,p'-

DDT, p,p'-DDT, Mirex, Heptachlor, Epoxide, alpha-Endosulphan (I), Dieldrin, Endrin, and Methoxychlor. CCME Assessment and Remediation criteria for the metals analyzed are given in Table 2.2 below; pesticides are given in Table 2.3.

Table 2.2: CCME Assessment and Remediation Criteria for Metals Analyzed in the Archived Water Samples.

	Assessment Criteria	Remediation Criteria	
		Freshwater Aquatic Life	Drinking Water
Metals			
Aluminum	--	5-100	--
Antimony	--	--	--
Arsenic	5	50	25
Barium	50	--	1000
Beryllium	--	--	--
Boron	--	--	--
Cadmium	1	0.2 - 1.8	5
Calcium	--	--	--
Chromium	15	2 - 20	50
Cobalt	10	--	--
Copper	25	2 - 4	≤1000
Iron	--	300	≤300
Lead	10	1 - 7	10
Magnesium	--	--	--
Manganese	--	--	--
Mercury	0.1	0.1	1
Molybdenum	5	--	--
Nickel	10	25 - 150	--
Phosphorus	--	--	--
Potassium	--	--	--
Selenium	1	1	10
Silicon	--	--	--
Silver	5	0.1	--
Sodium	--	--	≤200 mg/L
Strontium	--	--	--
Tin	--	--	--
Titanium	--	--	--
Vanadium	--	--	--
Zinc	50	30	≤5000
Zirconium	--	--	--

Notes: All values are in μg/L unless otherwise stated.

Table 2.3: Available CCME Assessment and Remediation Criteria for Pesticides Analyzed in the Archived Water Samples.

	Assessment Criteria	Remediation Criteria	
		Freshwater Aquatic Life	Drinking Water
Aldrin and diedrin	--	4	9
DDT	--	1 ng/L	30
Endosulphan	--	0.02	--
Heptaclor and metabolites	--	0.01	3
Methoxychlor	--	--	900

Notes: All values are in µg/L unless otherwise stated.

2.2.2 Soils

The CCME Remediation Criteria for soils are divided into three categories - agricultural (AG), residential/parkland (R/P), and commercial/industrial (C/I). These, in turn, serve as benchmarks to evaluate the need for further investigation or remediation with respect to a specified land use. The residential/parkland criteria was deemed to be the most appropriate for soils at pumping stations along the Haines-Fairbanks pipeline many of which occur in parklands. The archived soil samples were analyzed for one or more of the following parameters metals, chlorobenzenes, pesticides, PCBs, PAHs, alkanes, isoprenoids and hopanes. Chemical or elemental components of these suite of substances and their relevant CCME criteria are given in Tables 2.4 to 2.7.

Table 2.4: CCME Criteria for Metals Analyzed in the Archived Soil Samples.

Metals	CCME Assessment Criteria	CCME Remediation Criteria Residential/Parkland (R/P)
Aluminum		
Antimony	20	20
Arsenic	5	30
Barium	200	500
Beryllium	4	4
Boron	1	--
Cadmium	0.5	5
Calcium	--	--
Chromium	20	8
Cobalt	10	50
Copper	30	100
Iron	--	--
Lead	25	500
Magnesium	--	--
Manganese	--	--
Mercury	0.1	2
Molybdenum	2	10
Nickel	20	100
Phosphorus	--	--
Potassium	--	--
Selenium	1	3
Silicon	--	--
Silver	2	20
Sodium	--	--
Strontium	--	--
Tin	5	50
Titanium	--	--
Vanadium	25	200
Zinc	60	500
Zirconium	--	--

Notes : all concentrations in μg/g dry weight basis, -- value not established.

Table 2.5: CCME Assessment and Residential/Parkland Remediation Criteria for Chlorobenzenes, Pesticides and Polychlorinated biphenyls Analyzed in the Archived Soil Samples.

Substances	CCME Assessment Criteria	CCME Remediation Criteria Residential/Parkland (R/P)
Chlorobenzenes		
Dichlorobenzenes	0.05	2
Trichlorobenzenes	0.05	2
Tetrachlorobenzenes	0.05	2
Pentachlorobenzene	0.05	2
Hexachlorobenzene	0.1	2
Pesticides		
alpha HCH	--	--
beta HCH	--	--
gamma HCH	--	--
Heptachlor	--	--
Aldrin	--	--
Oxychlordane	--	--
trans-Chlordane	--	--
cis-Chlordane	--	--
o,p'-DDE	--	--
p,p'-DDE	--	--
trans-Nonachlor	--	--
cis-Nonachlor	--	--
o,p'-DDD	--	--
p,p'-DDD	--	--
o,p'-DDT	--	--
p,p'-DDT	--	--
Mirex	--	--
Heptachlor Epoxide	--	--
alpha-Endosulphan (I)	--	--
Dieldrin	--	--
Endrin	--	--
Methoxychlor	--	--
PCBs		
Aroclor 1242	0.1	5
Aroclor 1254	0.1	5
Aroclor 1260	0.1	5

Notes : all concentrations in μg/g dry weight basis, -- value not estabilished.

Table 2.6: Polycylic Aromatic Hydrocarbons (PAHs) Analyzed in the Archived Soil Samples and their CCME Assessment and Residential/Parkland Remediation Criteria.

Substance	CCME Assessment Criteria	CCME Remediation Criteria Residential/Parkland (R/P)
Naphthalene	0.1	5
Acenaphthylene	--	--
Acenaphthene	--	--
Fluorene	--	--
Phenanthrene	0.1	5
Anthracene	--	--
Fluoranthene	--	--
Pyrene	0.1	10
Benz(a)anthracene	0.1	1
Chrysene	--	--
Benzofluoranthenes	--	--
Benzo(e)pyrene	--	--
Benzo(a)pyrene	0.1	1
Perylene	--	--
Dibenz(ah)anthracene	0.1	1
Indeno(1,2,3-cd)pyrene	0.1	1
Benzo(ghi)perylene	--	--
C1 naphthalenes	--	--
C2 naphthalenes	--	--
C3 naphthalenes	--	--
C4 naphthalenes	--	--
C1 phen,anth	--	--
C2 phen,anth	--	--
C3 phen,anth	--	--
C4 phen,anth	--	--
Dibenzothiophene	--	--
C1 dibenzothiophene	--	--
C2 dibenzothiophene	--	--

Notes : all concentrations in μg/g dry weight basis, -- value not estabilished.

Table 2.7: Alkanes, Isoprenoids and Hopanes Analyzed in the Archived Soil Samples and their CCME Assessment and Residential/Parkland Remediation Criteria.

Metals	CCME Assessment Criteria	CCME Remediation Criteria Residential/Parkland (R/P)
Alkanes and Isoprenoids		
Dodecane (nC12)	0.3	--
2,6-Dimethyl Undecane	--	--
Norfarnesane	--	--
Tridecane (nC13)	0.3	--
Farnesane	--	--
Tetradecane (nC14)	0.3	--
2,6,10-Trimethyl Tridecane	--	--
Pentadecane (nC15)	0.3	--
Hexadecane (nC16)	0.3	--
Norpristane	--	--
Heptadecane (nC17)	0.3	--
Pristane	--	--
Octadecane (nC18)	0.3	
Phytane	--	--
Nonadecane (nC19)	0.3	--
Eicosane (nC20)	0.3	--
Heneicosane (nC21)	0.3	--
Docosane (nC22)	0.3	--
Tricosane (nC23)	0.3	--
Tetracosane (nC24)	0.3	--
Pentacosane (nC25)	0.3	--
Hexacosane (nC26)	0.3	--
Heptacosane (nC27)	0.3	--
Octacosane (nC28)	0.3	--
Nonacosane (nC29)	0.3	--
Triacontane (nC30)	0.3	--
Untriacontane (nC31)	0.3	--
Dotriacontane (nC32)	0.3	--
Tritriacontane (nC33)	0.3	--
Tetratriacontane (nC34)	0.3	--
Pentatriacontane (nC35)	0.3	--
Hexatriacontane (nC36)	0.3	--
Hopanes		
18Ê(H)trisnorhopane(C27Ê)	--	--
17ß(H)trisnorhopane(C27ß)	--	--
17Ê(H),21ß(H)norhopane(C29ÊÊß)	--	--
17Ê(H),21ß(H)hopane(C30ÊÊß)	--	--
S-17Ê(H),21ß(H)homohopane(C31ÊÊß)	--	--
R-17Ê(H),21ß(H)homohopane(C31ÊÊß)	--	--

Notes : all concentrations in µg/g dry weight basis, -- value not estabilished.

3. RESULTS AND DISCUSSION

3.1 Overall Results

3.1.1 Chlorobenzenes, PCBs and Pesticides

Six soil samples were analyzed for chlorobenzenes; nine were analyzed for pesticides. These substances were either below detection or occurred at concentrations well below the CCME R/P criteria. The concentrations of PCBs detected in the archived soil samples analyzed (7 samples at Border Station; 5 samples at Blanchard River) were all very low and well below the CCME R/P criteria. PCBs can be discounted as a contaminant of concern, since Aroclor levels in all samples, except two, were below the analytical detection limits (<0.18 ppb to < 27 ppb). The maximum PCB concentration found was 15 ppb as Aroclor 1242 (compared with a CCME R/P criterion of 1000 ppb). If hot spots were present near these areas, the levels in the areas sampled would be elevated due to short-range atmospheric redistribution from the source. **The extremely low PCB levels strongly suggests that no major local sources are present.**

3.1.2 Metals

Metal levels detected in three soil samples were all below the CCME R/P criteria. One water sample was also analyzed and found to contain metals at concentrations well below the CCME Drinking Water criteria. Cadmium, copper and lead concentrations were elevated relative to background in only one out of the seven plant samples collected from Blanchard River.

3.1.3 Total Extractable Hydrocarbons and Contributing Constituents

Total extractable hydrocarbons (TEHs - sometimes referred to as total petroleum hydrocarbons, TPHs) were detected at elevated levels in several surface and subsurface water and soil samples at Border Station and Blanchard River (UMA/AMBIO, 1995[1]). Additional analyses

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[1] UMA/AMBIO, 1995. Preliminary Environmental Assessment, Haines-Fairbanks Pipeline. Prepared for the Action on Waste Office, Department of Indian Affairs and Northern Development, Whitehorse, Yukon by UMA Engineering Ltd. and AMBIO Research Associates Inc. in August 1995.

of archived samples in this study confirm the elevated 'hydrocarbon' levels, which may in part indicate a ground water contamination issue.

Some regulatory jurisdictions have developed clean-up or response criteria for TEHs; e.g. British Columbia [Volatile Extractable Hydrocarbons -excluding BTEX (VEH): Urban Park/Residential = 200 ppm (μg/g); Light Extractable Petroleum Hydrocarbons (LEPH): Urban Park/Residential = 1000 ppm; Heavy Extractable Petroleum Hydrocarbons (HEPH): Urban Park/Residential = 1000 ppm] (BCMOE, 1995). Because TEH analyses, however, provide only a surrogate measure of hydrocarbon contamination by any of a broad range of contaminants, no conclusion can be drawn about the potential for environmental toxicity. The criteria therefore must be regarded as somewhat arbitrary. Analytes for which toxicity is better understood include the unsubstituted PAHs and BTEX (benzene, toluene, ethylenes, xylenes), but these were found only at low levels (below any relevant remediation criterion) even in samples with high TEH levels.

Further characterization of hydrocarbons was achieved by analyzing six samples for parent and alkyl-substituted polycyclic aromatic hydrocarbons (PAHs), alkanes, hopanes and isoprenoids (aliphatic and non-aromatic cyclic hydrocarbons). The distribution of PAHs, n-alkanes, and isoprenoids have been used to monitor the degree of weathering and processes involved during the chemical composition changes and biodegradation of petroleum hydrocarbons[2,3,4]. A lightly degraded oil is usually indicated by partial depletion of *n*-alkanes; a moderately degraded one is often indicated by heavy loss of *n*-alkanes and partial loss of lighter PAH compounds. For highly degraded oil, the *n*-alkanes could be mostly lost along with PAHs and their alkyl homologues. Several indices have been proposed to provide a better understanding of the weathering mechanism[2]. One index is the ratio of nC-17/pristane and nC-

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[2] D. E. Rogues, E. B. Overton and C. B. Henry, Using GC/MS fingerprint analyses to document progress and progess of oil degradation, J. Environ. Qual, 1994, 23: 851-855.

[3] Z Wang., M. Fingas and G. Sergy Chemical characterization of crude oil residues from an Arctic beach by GC/MS and GC/FID, Environ. Sci. Tech., 1995, 29: 2622-2631.

[4] B. M. Didyk and B. R. T. Simoneit, Hydrothermal oil of Guaymas Basin and implications for petroluem formation mechinisms, Nature, 1989, 342:65-69.

18/phytane. As the more easily degraded normal hydrocarbons (nC-17 and nC-18) are lost, the more resistant isoprenoids (pristane and phytane) are conserved (i.e., more weathered samples would have nC-17/pristane and nC-18/phytane ratios of less 1). In highly weathered samples appreciable levels of isoprenoids are also lost. For such samples other substances such as hopanes are used[1]. Hopanes are conserved until the last stages of degradation and are especially produced if weathering occurs by biodegradation. Thus, they have been proposed as internal standards (biomarkers) for monitoring oil biodegradation in the environment. As the oil becomes more degraded, the relative concentration of the biomarker should increase. Low concentrations of hopanes suggest loss of oil by a route or mechanism other than biodegradation.

Data for the alkanes indicate that nC-12 to nC-20 compounds account for a substantial portion of the TEHs; hopanes were generally very low or below detection.

The results for PAHs show that alkylated PAHs are present at levels far in excess of the unsubstituted PAHs as would be expected for any petroleum-based contamination. There is no formal regulatory guidance anywhere in the world for dealing with contamination by substituted PAHs, including alkylated forms, but the open scientific literature does suggest that alkylated forms can sometimes be at least as toxic as their unsubstituted PAH counterparts, depending on specifics of molecular structure. A review of the current state of knowledge of alkylated PAHs with respect to environmental implications is presented in Chapter 5: Appendices.

3.2 Results for Million Dollar Falls

3.2.1 Metals and Pesticides

In order to ascertain if zinc and DDTs detected in the dump, were migrating towards Takhanne River, an archived water sample (MD1W002) collected from a stream which flows into the river was analyzed for metals and chlorinated pesticides. Concentrations of pesticides were all below detection; metal levels were either less than the limit of detection or well below the CCME assessment criteria (Table 3.1). **There is no evidence, therefore, for extensive down-gradient migration of DDT or its breakdown products from the dump.** Metals and

metalloids are also not considered to be contaminants of concern on the basis of the low levels detected.

Table 3.1: Metals and Pesticides Results for Million Dollar Falls Water Samples

Report Sample No.: MD1W002 Lab Sample No.: 9514-114 Field Sample No.: WS-7				
Metals	**Concentration (µg/L)**		**Pesticides**	**Concentration (ng/L)**
Aluminum	0.094		**Hexachlorobenzene**	<0.14
Antimony	< 0.15		**alpha HCH**	<0.95
Arsenic	< 0.001		**beta HCH**	<1.8
Barium	0.091		**gamma HCH**	<1.6
Beryllium	< 0.003		**Heptachlor**	<1.0
Boron	0.08		**Aldrin**	<0.33
Cadmium	< 0.0002		**Oxychlordane**	<1.8
Calcium	46.3		**trans-Chlordane**	<0.25
Chromium	<0.001		**cis-Chlordane**	<0.26
Cobalt	< 0.02		**o,p'-DDE**	<0.15
Copper	0.002		**p,p'-DDE**	<0.56
Iron	0.24		**trans-Nonachlor**	<0.23
Lead	<0.001		**cis-Nonachlor**	<0.21
Magnesium	8.1		**o,p'-DDD**	<0.14
Manganese	0.016		**p,p'-DDD**	<0.16
Mercury	< 0.05		**o,p'-DDT**	<0.29
Molybdenum	< 0.04		**p,p'-DDT**	<0.27
Nickel	< 0.025		**Mirex**	<3.2
Phosphorus	< 0.4		**Heptachlor Epoxide**	<0.07
Potassium	2.02		**alpha-Endosulphan (I)**	<0.07
Selenium	< 0.001		**Dieldrin**	<0.08
Silicon	9.2		**Endrin**	<0.15
Silver	< 0.0001		**Methoxychlor**	<0.39
Sodium	3.9			
Strontium	0.12			
Tin	< 0.03			
Titanium	< 0.006			
Vanadium	< 0.01			
Zinc	<0.015			
Zirconium	< 0.015			

3.3 Results for Blanchard River

3.3.1 Chlorobenzenes, Pesticides and PCBs

The concentration of Aroclor PCBs, pesticides and chlorobenzenes in the archived soil samples collected from the drainage area below the leachate plume and drill holes TH-1, TH-2 and TH-5 are given in Table 3.2. Almost all of these substances were less than the limit of detection and those detected were well below the CCME Assessment criteria. **Thus the occurrence of these substances in the test holes and leachate plume is of minor concern.**

Table 3.2: Chlorobenzenes, Pesticides and PCB Results for Blanchard River Station Soil Samples

Report Sample No. Lab Sample No. Field Sample No.	BL1S003 9514-80 SS-69	BL1S012 9514-137 SS-90	BL1SS020 9514-144 SS-97	BL1SS028 9514-152 SS-105	BL1SS043 9514-170 SS-123
Dichlorobenzenes	<4.7	<6.8	<1.55	0.52	<3.30
Trichlorobenzenes	NDR 18.6	NDR 69	NDR 2.08	<0.08	<0.5
Tetrachlorobenzenes	NDR 0.21	NDR 4.6	<0.17	<0.04	NDR 0.4
Pentachlorobenzene	<0.09	<0.35	<0.06	<0.02	0.22
Hexachlorobenzene	<0.14	<0.55	<0.1	<0.02	<0.14
alpha HCH		NDR 68			NDR 3.2
beta HCH		<2.8			<1.3
gamma HCH		NDR 42			NDR 9.4
Heptachlor		<5.5			<1.3
Aldrin		<2.0			<0.49
Oxychlordane		<9.0			<2.2
trans-Chlordane		<1.1			<0.29
cis-Chlordane		<1.2			<0.3
o,p'-DDE		NDR 2.7			NDR 1.9
p,p'-DDE		NDR 7.9			NDR 5.0
trans-Nonachlor		<0.98			<0.23
cis-Nonachlor		<0.83			<0.19
o,p'-DDD		<0.88			<0.22
p,p'-DDD		<0.88			<0.22
o,p'-DDT		NDR 8.2			NDR 5.2
p,p'-DDT		<1.2			<0.41
Mirex		<1.9			<0.42
Heptachlor Epoxide		<0.11			<0.004
alpha-Endosulphan (I)		<0.14			<0.005
Dieldrin		<0.14			<0.005
Endrin		<0.23			<0.008
Methoxychlor		<1.2			<0.02
Aroclor 1242	15	<27	<2.5	<0.44	<4.2
Aroclor 1254	<4	<18	<3.6	<0.8	<4.6
Aroclor 1260	<4.5	<19	<3.9	<0.6	<5.7
Locations	Below terrace , 2m from river, at SW side of site	Red rusty spring on north slope of site; near top where effluent appears	Drill Hole 1: 8 m S of N border fence of site near station entry road	Drill Hole 2: 20 m E of Drill Hole 1 along fence; 2' increments to 18'	Drill Hole 5: S side of station; 3m N of border fence; top of slope above terrace along river

Notes: Concentrations are in µg/g or ppb. NDR = Peak detected but did not meet quantification criteria

3.3.2 Total Extractable Hydrocarbons

The concentrations of TEHs in additional soil samples analyzed from Drill Holes 1 to 5 are given in Table 3.3. Levels detected in Drill Hole 1 (130 and 430 μg/g) confirmed hydrocarbon contamination observed by the soil vapour survey. The highest subsurface contamination in Drill Hole 1 therefore occurs at a depth of about 3 m. One sample from Drill Hole 2 contained 48 μg/g of TEHs while the concentration in the second sample was below detection. TEH concentrations in the samples from Drill Holes 3 and 4 were below detection. Concentrations in Drill Hole 5 showed a declining gradient from 2500 μg/g to 120 μg/g at 8 to 10 m depth. These results confirmed the soil vapor survey data (UMA/AMBIO, 1995).

Table 3.3: Total Extractable Hydrocarbons (TEHs) Results for Blanchard River Soil Samples

Report Sample No.	Lab Sample No.	Field Sample No.	TEH (μg/g)	Description
Drill Hole 1				
BL1SS019	9514-143	SS-96	130	8-10' profile in moist sand with gravel
BL1SS020	9514-144	SS-97	430	10-12' profile in silty sand till; HC odour
Drill Hole 2				
BL1SS028	9514-152	SS-105	48	10-12' profile in sand-gravel substrate
BL1SS032	9514-156	SS-109	<20	12-14' profile in damp sand with gravel; slight HC odour
Drill Hole 3				
BL1SS033	9514-157	SS-110	<20	8-10' profile in silt-sand substrate with stones; slight HC odour
Drill Hole 4				
BL1SS036	9514-163	SS-116	<20	8-10' profile in coarse damp sand and gravel
Drill Hole 5				
BL1SS038	9514-165	SS-118	2500	26-28' profile in dry clay; strong HC odour
BL1SS039	9514-166	SS-119	1900	28-30' profile in dry clay soil; strong HC odour
BL1SS041	9514-168	SS-121	510	32-34' profile in sandy gravel with clay; HC odour
BL1SS044	9514-171	SS-124	120	24-26' profile medium dry sand; HC odour

3.3.3 PAHs, n-Alkanes, Isoprenoids and Hopanes

Samples from the leachate plume and drill holes were also analyzed for parent and alkyl-substituted PAHs, *n*-alkanes, hopanes and isoprenoids in order to characterize the TEH contamination. The results are given in Tables 3.4 and 3.5.

Data for the alkanes show nC-12 to nC-20 compounds account for a substantial portion of the TEHs in samples from the leachate plume and Drill Hole 5. The ratios of nC-17/pristane and nC-18/phytane indicate samples from the leachate plume are more weathered than that from Drill Hole 5. The relatively low concentrations of hopanes detected, relative to the hydrocarbon components, suggest biodegradation is not very significant. Concentrations of the parent PAHs were all below the CCME R/P criteria. The alkylated PAHs were consistently higher in concentrations than the unsubstituted ones. A discussion of alkylated is presented in Chapter 4: Appendices.

Table 3.4: *n*-Alkanes, Isoprenoids and Hopanes Results for Blanchard River Soil Samples

Report Sample No. Lab Sample No. Field Sample No.	BL1S003 9514-80A SS-69	BL1S003 B 9514-80B SS-69	BL1S012 9514-137 SS-90	BL1SS020 9514-144 SS-97	BL1SS028 9514-152 SS-105	BL1SS043 9514-170 SS-123
n-Alkanes and Isoprenoids						
Dodecane (nC12)	75000	110000	180000	4500	540	6800
2,6-Dimethyl Undecane	40000	69000	120000	3600	470	2900
Norfarnesane	38000	81000	110000	3000	590	2400
Tridecane (nC13)	89000	190000	230000	4200	870	9500
Farnesane	37000	86000	98000	2300	710	3300
Tetradecane (nC14)	80000	190000	220000	3500	810	11000
2,6,10-Trimethyl Tridecane	40000	86000	120000	1800	570	4800
Pentadecane (nC15)	72000	170000	230000	2600	780	13000
Hexadecane (nC16)	53000	130000	150000	2000	440	10000
Norpristane	33000	78000	NDR 58000	1500	290	5200
Heptadecane (nC17)	41000	100000	52000	1400	200	8700
Pristane	56000	130000	43000	2100	270	6400
Octadecane (nC18)	44000	110000	26000	1400	110	9400
Phytane	43000	99000	16000	1300	94	5000
Nonadecane (nC19)	37000	89000	15000	1200	61	7900
Eicosane (nC20)	30000	78000	8300	790	42	6500
Heneicosane (nC21)	18000	48000	4500	580	27	4600
Docosane (nC22)	9900	31000	2600	400	17	3100
Tricosane (nC23)	5400	16000	1400	220	11	1700
Tetracosane (nC24)	2200	5700	<430	<83	7.0	800
Pentacosane (nC25)	710	2300	<480	<91	10	280
Hexacosane (nC26)	<310	380	<540	<100	4.0	63
Heptacosane (nC27)	<340	<280	<590	<110	5.0	13
Octacosane (nC28)	<380	<310	<640	<120	4.0	<4
Nonacosane (nC29)	<380	<300	<810	<140	4.0	<3
Triacontane (nC30)	<440	<340	<930	<160	3.0	<4
Untriacontane (nC31)	<490	<390	<1000	<180	3.0	<4
Dotriacontane (nC32)	<560	<440	<1200	<200	2.0	<5
Tritriacontane (nC33)	<640	<390	<1200	<230	NDR 4	<9
Tetratriacontane (nC34)	<620	<450	<1400	<310	4.0	<10
Pentatriacontane (nC35)	<680	<500	<1500	<340	2.0	<11
Hexatriacontane (nC36)	<760	<550	<1700	<380	<2.0	<12
Hopanes						
18Ê(H)trisnorhopane(C27Ê)	3.0	2.6	<340	3.8	1.6	<2.0
17ß(H)trisnorhopane(C27ß)	3.2	2.7	<340	3.4	1.8	<2.0
17Ê(H),21ß(H)norhopane(C29Êß)	5.6	4.8	<340	12	4.8	2.0
17Ê(H),21ß(H)hopane(C30Êß)	8.3	7.1	<340	22	9.7	3.1
S-17Ê(H),21ß(H)homohopane(C31Êß)	4.0	3.5	<340	6.9	2.7	<2.0
R-17Ê(H),21ß(H)homohopane(C31Êß)	3.6	2.8	<340	5.2	2.0	<2.0

Notes: Concentrations are in ng/g. NDR = peak detected but did not meet quantification criteria.

Table 3.5: Polycyclic Aromatic Hydrocarbon Results for Blanchard River Soil Samples

Report Sample No. Lab Sample No. Field Sample No.	BL1S003 9514-80 SS-69	BL1S003 D 9514-80 SS-69 Dup	BL1S012 9514-137 SS-90	BL1SS020 9514-144 SS-97	BL1SS028 9514-152 SS-105	BL1SS043 9514-170 SS-123
Naphthalene	75	NDR 82	NDR 76	110	51	150
Acenaphthylene	NDR 22	NDR 17	<0.84	NDR 2.9	<0.05	<0.33
Acenaphthene	NDR 170	NDR 200	NDR 480	13	2.2	68
Fluorene	NDR 50	66	NDR 140	13	2.5	200
Phenanthrene	160	NDR 140	200	5.1	1.7	450
Anthracene	NDR 17	NDR 15	NDR 16	NDR 0.47	<0.07	<0.49
Fluoranthene	NDR 38	NDR 43	<1.4	2	NDR 0.26	7
Pyrene	470	450	54	2.8	0.53	55
Benz(a)anthracene	<2.2	NDR 5.1	<3.1	NDR 0.23	<0.11	<1.1
Chrysene	130	100	28	1.2	NDR 0.29	6.9
Benzofluoranthenes	NDR 1.8	NDR 1.6	<0.51	NDR 0.49	<0.16	0.52
Benzo(e)pyrene	2.3	2.3	NDR 1.6	NDR 0.26	<0.13	NDR 0.32
Benzo(a)pyrene	NDR 0.3	NDR 0.4	<0.6	<0.18	<0.15	<0.2
Perylene	NDR 0.98	NDR 1.4	<0.62	<0.18	<0.15	<0.2
Dibenz(ah)anthracene	<15	<0.11	<0.61	<0.19	<0.17	<0.22
Indeno(1,2,3-cd)pyrene	NDR 0.51	NDR 0.52	<0.61	<0.17	<0.16	<0.21
Benzo(ghi)perylene	NDR 0.7	NDR 0.6	NDR 1	NDR 0.28	<0.13	NDR 0.38
C1 naphthalenes	310	290	110	210	160	3300
C2 naphthalenes	2400	2200	14000	660	200	10000
C3 naphthalenes	5900	5700	59000	1700	310	8200
C4 naphthalenes	9300	9700	32000	1200	300	3100
C1 phen,anth	1700	1600	3100	16	4.5	2000
C2 phen,anth	8400	8800	360	34	9.9	3000
C3 phen,anth	16000	15000	5400	22	4.4	1700
C4 phen,anth	7200	6400	1500	4	<0.1	350
Dibenzothiophene	170	140	NDR190	NDR 3.5	NDR 1	240
C1 dibenzothiophene	690	790	1100	8.2	2.2	600
C2 dibenzothiophene	2300	2300	2000	2.9	0.67	710
Location	Below terrace, 2m from river, at SW side of site		Red rusty spring on north slope of site; near top where effluent appears	Drill Hole 1: 8 m S of N border fence of site near station entry road	Drill Hole 2: 20 m E of Drill Hole 1 along fence; 2' increments to 18'	Drill Hole 5: S side of station; 3m N of border fence; top of slope above terrace along river
Description	Dead moss over coarse sand-gravel soil		Surface sample of silty organic sediment over dark organic layer	10-12' profile in silty sand till; HC odour	10-12' profile in sand-gravel substrate	30-32' profile in dry clay; moderate HC odour

Notes: Concentrations are in ng/g. NDR = peak detected but did not meet quantification criteria.

3.3.4 Plants

The concentrations of arsenic, barium, cobalt, selenium, and zinc in soil samples collected from the leachate plume exceeded the CCME R/P Remediation Criteria in the previous study (UMA/AMBIO, 1995). In order to investigate the ecotoxicological significance of this metal contamination, six archived plant samples comprising *Equisetum* sp. and *Salix* sp. collected from drainage areas below the leachate plume were analyzed; one *Equisetum* sp. sample obtained from a background location along a stream in the foothills approximately 200 m east of the station was also analyzed for comparison. The results are presented in Table 3.6.

Apart from the concentrations of cadmium, copper and lead in sample (BL1P001), metal levels in the plant samples from the leachate plume were comparable to background. Arsenic (0.15 ppm) was detected in BL1P001 while the concentration in the background sample (BL1P007) was below detection. The elevated arsenic concentration in the plant corresponded to the elevated levels in soil. Copper concentration in BL1P001 was four times the background level and lead exceeded the background sample by over ten fold; copper and lead were not particularly elevated in the soil samples. Even though barium, cobalt and zinc concentrations in the soil samples exceeded the CCME R/P criteria, levels in the plants were comparable to background.

Table 3.6: Metal Results for Blanchard River Plant Samples

Report Sample No. Lab Sample No. Field Sample No.	BL1P001 9514-125 SS-75 P1	BL1P002 9514-127 SS-75 P2S	BL1P003 9514-129 SS-75 P2R	BL1P004 9514-131 SS-76 P1	BL1P005 9514-133 SS-76 P2S	BL1P006 9514-134 SS-76 P2R	BL1P007 9514-250 SS-165 P
Aluminum	358	152	282	181	124	134	1710
Antimony	<5	<5	<5	<5	<5	<5	<5
Arsenic	0.15	<0.05	0.05	<0.05	<0.05	<0.05	<0.05
Barium	40	28	76	85	33	83	82
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	26	21	16	24	23	17	24
Cadmium	2.98	0.57	0.67	0.63	1.55	1.9	0.38
Calcium	17200	10400	10900	19300	11400	10200	15800
Chromium	4.3	2.1	3.2	<1.5	<1.5	2.3	7
Cobalt	<0.5	<0.5	<0.5	0.6	<0.5	<0.5	<0.5
Copper	53	12	12	15	10	7.5	13
Iron	793	220	500	2910	655	244	1530
Lead	4.58	0.8	1.95	0.4	0.3	0.53	0.3
Magnesium	3760	1710	550	3670	2500	718	3890
Manganese	120	42	189	1620	170	56	110
Mercury	0.075	0.025	0.025	0.03	0.015	0.01	0.02
Molybdenum	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Nickel	17	7.5	9.5	6.3	10	8.5	15
Phosphorus	8150	6650	1870	8850	7950	1700	7200
Potassium	47500	13700	3775	37625	15650	2345	36850
Silver	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Sodium	297	29	80	150	67	29	75
Strontium	59	34	43	62	38	45	63
Tin	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Titanium	21	4.8	16	5.5	5	5.1	76
Vanadium	1.2	<0.5	3.7	0.9	<0.5	<0.5	3.4
Zinc	52	62	46	78	110	72	42
Locations	Drainage at bottom of N slope of site	Drainage at bottom of N slope of site	Drainage at bottom of N slope of site	Rust coloured drainage half way down N slope of site	Rust coloured drainage half way down N slope of site	Rust coloured drainage half way down N slope of site	Background location along stream in foothills, roughly 200m E of station
Description	Equisetum sp.; whole; separate organic and inorganic subsamples	Salix sp.:shoots; separate organic and inorganic subsamples	Salix sp.:roots; separate organic and inorganic subsamples	Equisetum sp.; whole; separate organic and inorganic subsamples	Salix sp.:shoots; separate organic and inorganic subsamples	Salix sp.:roots; separate organic and inorganic subsamples	Equisetum sp.; whole; separate organic and inorganic subsamples

Notes: Concentrations are in μg/g or ppm

3.4 Results for Border Station

3.4.1 Metals, Chlorobenzenes, Chlorinated Pesticides and PCBs

The concentrations of metals in the three soil samples analyzed are given in Table 3.7. Metals were well below the CCME R/P criteria. In particular, the maximum concentration of mercury detected was 0.009 ppm and that for zinc was 59 ppm. Pesticides and chlorobenzenes were also present at very low levels (Table 3.8). PCBs were found in only one sample (0.47 ppb). This concentration is well below the CCME Assessment criteria and comparable to background levels (see section 2.1).

Table 3.7: Metal Results for Border Station Soil Samples

Report Sample No.	BO1SS032	BO1SS033	BO1SS047
Lab Sample No.	9514-233	9514-234	9514-260
Field Sample No.	SS-157	SS-158	SS-177
Antimony	<10	<10	<10
Aluminum	17100	9060	11400
Arsenic	3.5	0.69	3
Barium	86	57	90
Beryllium	<1	<1	<1
Boron	24	17	18
Cadmium	<0.25	<0.25	0.34
Calcium	14200	4960	25700
Chromium	83	20	21
Cobalt	13	8	9
Copper	39	26	34
Iron	27700	17600	22200
Lead	2	3	5
Magnesium	13300	5510	7700
Manganese	404	238	363
Mercury	0.005	0.005	0.009
Molybdenum	< 4	<4	<4
Nickel	34	14	9
Phosphorus	1580	1400	1520
Selenium	<0.5	<0.5	<0.5
Silver	<2	<2	<2
Sodium	63	316	429
Strontium	67	19	53
Tin	<5	<5	<5
Titanium	531	316	571
Vanadium	63	38	47
Zinc	47	48	59

Notes: Concentrations are in µg/g or ppm.

Table 3.8: Chlorobenzenes, Pesticides and PCB Results for Border Station Soil Samples

Report Sample No. Lab Sample No. Field Sample No.	BO1SS009 9514-209 SS-133	BO1SS018 9514-219 SS-143	BO1SS027 9514-228 SS-152	BO1SS029 9514-230 SS-154	BO1SS030 9514-231 SS-155	BO1SS031 9514-232 SS-156	BO1SS034 9514-235 SS-159
Sample Size (g dry):	9.94	8.86	9.79	11.5	9.44	9.96	11.5
Moisture (%)	17	18	5.6	4.3	11	4.8	5.4
Dichlorobenzenes		<2.93					
Trichlorobenzenes		NDR 15.44					
Tetrachlorobenzenes		NDR 1.52					
Pentachlorobenzene		<0.08					
Hexachlorobenzene	<0.07	<0.11	<0.02	<0.07	<0.08	<0.08	<0.02
alpha HCH	NDR 0.82	NDR 3.0	<0.08	<0.74	<0.6	<0.51	<0.07
beta HCH	<1.2	NDR 1.6	<0.16	<1.2	<0.94	<0.8	<0.13
gamma HCH	NDR 2.3	NDR 2.1	<0.14	<1.1	<0.87	<0.73	<0.11
Heptachlor	<0.55	<1.2	<0.13	<0.46	<0.69	<0.72	<0.08
Aldrin	<0.28	<0.57	<0.04	<0.25	<0.29	<0.3	<0.04
Oxychlordane	<2.1	<3	<0.24	<2.2	<2.6	<1.3	<0.14
trans-Chlordane	<0.15	<0.22	<0.04	<0.13	<0.16	<0.16	<0.02
cis-Chlordane	<0.16	<0.23	<0.04	<0.14	<0.17	<0.16	<0.02
o,p'-DDE	NDR 0.8	0.82	<0.02	NDR 1.2	NDR 0.63	NDR 0.12	<0.01
p,p'-DDE	NDR 0.89	NDR 0.91	<0.07	NDR 0.91	<0.24	<0.13	<0.06
trans-Nonachlor	<0.13	<0.2	<0.03	<0.12	<0.13	<0.13	<0.02
cis-Nonachlor	<0.11	<0.17	<0.03	<0.1	<0.11	<0.11	<0.02
o,p'-DDD	<0.19	<0.42	<0.03	<0.17	<0.19	<0.17	<0.02
p,p'-DDD	<0.19	<0.42	<0.03	<0.17	<0.19	<0.18	<0.02
o,p'-DDT	NDR 0.45	<0.75	<0.06	NDR 0.56	NDR 1.1	<0.36	<0.05
p,p'-DDT	<0.31	<0.68	<0.06	<0.32	2.4	<0.33	<0.05
Mirex	<0.26	<0.36	<0.33	<0.27	<0.31	<0.32	<0.28
Heptachlor Epoxide	<0.01	<0.03	0.04	<0.02	<0.02	<0.02	<0.007
alpha-Endosulphan (I)	<0.02	<0.03	<0.06	<0.02	<0.01	<0.02	<0.008
Dieldrin	<0.02	<0.03	<0.07	<0.03	<0.01	<0.02	<0.008
Endrin	<0.03	<0.06	<0.12	<0.05	<0.02	<0.03	<0.01
Methoxychlor	<0.05	<0.08	<0.12	<0.04	<0.05	<0.05	<0.04
Aroclor 1242	<1.2	<2.6	0.47	<1.2	<1.2	<1.6	<0.18
Aroclor 1254	<2.2	<4.3	<0.47	<2.4	<2.8	<2.5	<0.27
Aroclor 1260	<2.3	<4.2	<0.62	<2.5	<2.9	<2.5	<0.34
Locations	Drill Hole 7: 84m W of Hole 6, 8m N of old Haines Rd., 10m S of DDT facility	Drill Hole 7: 84m W of Hole 6, 8m N of old Haines Rd., 10m S of DDT facility	Drill Hole 8: 69m E of Hole 7, 15m N of old Haines Rd near site entry point	Drill Hole 8: 69m E of Hole 7, 15m N of old Haines Rd near site entry point	Drill Hole 8: 69m E of Hole 7, 15m N of old Haines Rd near site entry point	Drill Hole 8: 69m E of Hole 7, 15m N of old Haines Rd near site entry point	Drill Hole 8: 69m E of Hole 7, 15m N of old Haines Rd near site entry point
Descriptions	14-16' profile in coarse sand; HC odour	10-12' profile in wet silt; faint HC odour	10-12' profile in medium-fine sand; no odour	30-32' profile in dampd coarse sand with gravel; HC odour	40-42' profile in silt with fine sand; strong HC odour	52-54' profile in medium-coarse sand; strong HC odour	72-74' profile in damp fine sand with silt; trace HC odour

Notes: Concentrations ae ng/g or ppb. NDR = Peak detected but did not meet quantification criteria

3.4.2 Total Extractable Hydrocarbons

High levels of TEHs were detected in samples from Drill Holes 7 and Drill Hole 8 (Table 3.9). The highest contamination in Drill Hole 7 occurred at a depth of 3 m. A second sub-surface maximum was also found at the 15 m depth. These results confirmed hydrocarbon contamination observed by soil vapour survey (UMA/AMBIO, 1995). Concentrations in Drill Hole 8 showed a maximum at a depth of 9 m and also collaborated the previous soil vapor survey data.

Table 3.9: Total Extractable Hydrocarbons (TEHs) Results for Blanchard River Soil Samples

Report Sample No	Lab Sample No.	Field Sample No.	TEH (µg/g)	Description
Drill Hole 7				
BO1SS009	9514-209	SS-133	2800	10-12' profile in wet silt; faint HC odour
BO1SS010	9514-211	SS-135	85	18-20' profile in fine-medium sand
BO1SS011	9514-212	SS-136	53	22-24' profile in fine-medium sand; trace HC odour
BO1SS013	9514-214	SS-138	26	32-34' profile in medium sand; HC odour
BO1SS016	9514-217	SS-141	150	44-46' profile in moist sandy till; HC odour
BO1SS017	9514-218	SS-142	120	50-52' profile in fine sand with stones; HC odour
BO1SS022	9514-223	SS-147	<20	66-68' profile in silty sand; slight HC odour
Drill Hole 8				
BO1SS027	9514-228	SS-152	<20	10-12' profile in medium-fine sand; no odour
BO1SS028	9514-229	SS-153	220	26-28' profile in coarse granular mix of silt, sand and gravel
BO1SS029	9514-230	SS-154	1500	30-32' profile in dampd coarse sand with gravel; HC odour
BO1SS030	9514-231	SS-155	650	40-42' profile in silt with fine sand; strong HC odour
BO1SS031	9514-232	SS-156	200	52-54' profile in medium-coarse sand; strong HC odour
BO1SS032	9514-233	SS-157	340	40-42' profile in silt with fine sand; strong HC odour
BO1SS034	9514-235	SS-159	<20	72-74' profile in damp fine sand with silt; trace HC odour

3.4.3 PAHs, n-Alkanes, Isoprenoids and Hopanes

Concentrations of the parent PAHs were all below the CCME R/P criteria and the alkylated homologues were present at higher levels (Table 3.10). The alkane results indicated nC-12 to nC-20 compounds account for a substantial portion of TEHs in the sample and the ratios of nC-17/pristane and nC-18/phytane suggested some weathering has occurred.

Table 3.10: Polycyclic Aromatic Hydrocarbon, Alkanes, Isoprenoids and Hopanes Results for Border Station Soil Sample

Alkanes and Isoprenoids	
Report Sample No.	**BO1SS018**
Lab Sample No.	**9514-219**
Field Sample No.	**SS-143**
Dodecane (nC12)	17000
2,6-Dimethyl Undecane	16000
Norfarnesane	23000
Tridecane (nC13)	20000
Farnesane	20000
Tetradecane (nC14)	18000
2,6,10-Trimethyl Tridecane	16000
Pentadecane (nC15)	13000
Hexadecane (nC16)	6400
Norpristane	5100
Heptadecane (nC17)	3300
Pristane	6100
Octadecane (nC18)	3000
Phytane	3100
Nonadecane (nC19)	2200
Eicosane (nC20)	1400
Heneicosane (nC21)	930
Docosane (nC22)	520
Tricosane (nC23)	310
Tetracosane (nC24)	<140
Pentacosane (nC25)	<160
Hexacosane (nC26)	<170
Heptacosane (nC27)	<190
Octacosane (nC28)	<210
Nonacosane (nC29)	<200
Triacontane (nC30)	<230
Untriacontane (nC31)	<260
Dotriacontane (nC32)	<300
Tritriacontane (nC33)	<340
Tetratriacontane (nC34)	<390
Pentatriacontane (nC35)	<430
Hexatriacontane (nC36)	<480
Hopanes	
18Ê(H)trisnorhopane(C27Ê)	1.3
17ß(H)trisnorhopane(C27ß)	1.9
17Ê(H),21ß(H)norhopane(C29Êß)	6.0
17Ê(H),21ß(H)hopane(C30Êß)	13
S-17Ê(H),21ß(H)homohopane(C31Êß)	4.8
R-17Ê(H),21ß(H)homohopane(C31Êß)	2.5

Polycyclic Aromatic Hydrocarbons	
Report Sample No.	**BO1SS018**
Lab Sample No.	**9514-219**
Field Sample No.	**SS-143**
Naphthalene	890
Acenaphthylene	<0.37
Acenaphthene	120
Fluorene	190
Phenanthrene	110
Anthracene	NDR 5.2
Fluoranthene	1.4
Pyrene	NDR 2.3
Benz(a)anthracene	<1.5
Chrysene	<1.6
Benzofluoranthenes	<0.18
Benzo(e)pyrene	<0.19
Benzo(a)pyrene	<0.21
Perylene	<0.22
Dibenz(ah)anthracene	<0.2
Indeno(1,2,3-cd)pyrene	<0.19
Benzo(ghi)perylene	NDR 0.26
C1 naphthalenes	8800
C2 naphthalenes	22000
C3 naphthalenes	12000
C4 naphthalenes	3600
C1 phen,anth	290
C2 phen,anth	260
C3 phen,anth	78
C4 phen,anth	4.4
Dibenzothiophene	NDR 35
C1 dibenzothiophene	68
C2 dibenzothiophene	28

3.5 Site-Specific Recommendations

Recommendations for follow-up actions based on preliminary site investigations were provided previously (UMA/AMBIO, 1995; Section 6). Additional recommendations or amendments arising from the second round of sample analysis (this report) for Million Dollar Falls, Blanchard River Pump Station and Border Pump Station are provided below. In general, the original recommendations are still relevant in light of the new information. The additional contaminant analyses, however, allows for a more directed approach to detailed investigations carried out for the purpose of developing clean up plans. PCBs, for example, do not require additional investigation at any of the three sites. Other chlorinated pesticides were not found to be a problem either, except for the presence of a possible source of DDT in one of two dumps at Million Dollar Falls, based on the presently available data. Some generic recommendations have been made in Appendix C on assessing the environmental implications of alkylated PAH components common in hydrocarbon-contaminated soils or other matrices. Surface contamination, such as localized stains, was not identified as a problem at any of these three sites based on the presently available data.

3.5.1 Million Dollar Falls

Possible contaminant problems arising from the preliminary site investigation at Million Dollar Falls (UMA/AMBIO, 1995) included the possibility of PCBs in the groundwater supply and a dump in the gully that contained soil contaminated with zinc and DDT. Subsequent re-sampling and re-analysis of the groundwater by AES confirmed that the low levels of PCBs detected as part of the initial investigation were a laboratory artifact: The PCB concentration in the original water sample was within the range of the laboratory analytical blank, and subsequent analyses using more sensitive methods failed to detect any PCBs in the water (B. Hartshorne, *personal communication*).

A water sample was collected in the stream leading to the Takhanne River, down gradient from the dump which was identified initially as having DDT and zinc contamination. This sample, however, did not contain elevated contaminant levels (section 3.2). The low aqueous

solubility of DDT or its break-down products, or the tendency of zinc to adhere to humic substances in sediments, would limit the water-born as opposed to sediment-bound concentrations. The water concentrations, nonetheless, do suggest that substantial leachate migration from the dump has not occurred. The available data indicate that contaminated leachate from the dump was not entering the Takhanne River during the sampling period (July, 1995; summer-time runoff and stream flows).

We re-iterate our recommendations that the dump be considered as a possible future source of DDT and other contaminants, and that action be taken to eliminate any possibility of future contaminant releases. Since the dump in the gully comprises mostly surface debris, one possible course of action would be to have trained and experienced personnel sort the materials into hazardous versus non-hazardous waste and remove the hazardous debris. Soils within the dump affected by any sorting activity should be subjected to confirmatory testing using immunoassay-based field test kits and other field techniques. Present-day environmental risks down slope from the dump appear to be minimal and no further action is, therefore recommended.

3.5.2 Blanchard River Pump Station

Possible contaminant problems arising from the preliminary site investigation at the Blanchard River Pumping Station (UMA/AMBIO, 1995) included a rust-coloured leachate emanating from the slope on the north side of the site, and hydrocarbon contamination in the groundwater.

Soil and plant samples collected near the Blanchard River and down-gradient from the rust-coloured stain where groundwater emerges from the slope did not contain any substances at elevated concentrations. For the most part, metal concentrations in plant samples collected from the base of the slope were similar to those found in the plant sample from a more remote, background location. The spatial extent of contaminant migration from the leachate source appears to be limited, with no evidence based on the presently available data for any ecological risk or any substantial inputs of contaminants into the Blanchard River.

Additional chemical analyses of subsurface samples confirms the presence of substantial hydrocarbon contamination in the groundwater. The additional data for alkylated PAHs, other heterocyclic hydrocarbon compounds and aliphatic fractions indicate a largely unweathered, non-degraded petroleum-based source. Data on unsubstituted PAHs or BTEX do not adequately define the extent of contamination, nor the associated environmental risks. TPH (or TEH) appears to be a good, relatively inexpensive surrogate measure for delineating the hydrocarbon contaminant plume. It is important to note, however, that the actual environmental risks are expected to change where the hydrocarbon mixture emerges at the soil surface, at the base of the slope, or in the river - with a concomitant change in potential toxicity. There are no ecological risks associated with the hydrocarbons while the aquifer remains below the surface and isolated from the adjacent river, since there are no immediate ecological receptors.

It is recommended that a full sub-surface site assessment be conducted, using a network of monitoring wells and test pits, in order to delineate the extent of subsurface contamination (including the source of the rust-coloured leachate on the north slope) and to provide accurate predictions of environmental fate and ecological risk. The next phase should include an examination of the available remedial options, if remediation is deemed to be necessary (i.e., if contaminated groundwater is emerging or will emerge in an area that could lead to impact). The discussion of remedial options and risk should take into account the specific composition of the hydrocarbon contaminants, not just surrogate measures such as TPH.

3.5.3 Border Pump Station

Subsurface hydrocarbon contamination was identified as the major concern arising from the previous preliminary investigation of Border station (UMA/AMBIO, 1995). The original recommendations also acknowledged that the subsurface contaminant issues at Border Pumping Station and the Rainy Hollow site are closely interrelated. A review of the data and documentation from both sites is in progress, and will be presented as a separate report[5]. As for

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[5] Haines-Fairbanks Pipepline: Environmental Issues at Border Pump Station and Rainy Hollow Sites. Prepared for the Action on Waste Office, Department of Indian Affairs and Northern Development, Whitehorse, Yukon by Royal Roads University, Applied Research Division, 1996.

Blanchard River, it is recommended that a full sub-surface site assessment be conducted using existing bore holes and establishing new ones (up and down gradient) in the vicinity of Test Holes 8 and 9 as appropriate for the confident delineation of the contaminant plume, both vertically and horizontally. Again, the primary objectives should include the delineation of contamination, accurate assessment of likely fate over the short-term or long-term and detailed examination/prediction of environmental risks.

Recommendations regarding the composition of hydrocarbons in subsurface soils and water as aliphatics, hetrocyclic hydrocarbons and unsubstituted or alkyl-substituted PAHs as stated above for the Blanchard River site also apply to the Border/Rainy Hollow site. TPH levels may be used as an inexpensive tool to delineate the extent of contamination, but adequate prediction of fate in the environment and possible effects will require a through understanding of the actual composition of the hydrocarbon mixture. Given the history of the Rainy Hollow site, subsequent analyses of subsurface soils and water should include DDT and its breakdown products, in order to ensure that these contaminants are not being entrained in hydrocarbon ground water enroute to the Klehini River.

APPENDIX A: ANALYTICAL METHODS

1. ANALYSIS OF POLYCHLORINATED BIPHENYLS (PCBS), CHLOROBENZENES, AND CHLORINATED PESTICIDES IN SOILS, SEDIMENTS AND WATER SAMPLES

1.1 Summary

The above analyses were conducted by Axys Analytical Services Ltd. of Sidney, BC Each sample was clearly labeled and locked in a secure frozen storage area until retrieved by the analyst.

All samples were spiked with an aliquot of surrogate standard (2,4,5,6-tetrachloro-m-xylene, PCB 209 and d_4-alpha endosulphan) prior to analysis by gas chromatography with electron capture detection (GC/ECD); for gas chromatography with mass spectrometry (GC/MS), the samples were spiked with aliquots of ^{13}C labeled surrogate standard (PCB 101, PCB 180, PCB 209, gamma-BHC, Mirex, p,p'-DDE, p,p'-DDT and d_4-alpha endosulphan). Sediments were extracted with a solvent on a shaker table. Tissues were ground with sodium sulphate, packed in a glass chromatographic column and eluted with solvent. Water was liquid/liquid extracted with dichloromethane. Sample extracts were separated into three fractions on a Florisil column. The first fraction was also analyzed for PCBs as Aroclors, chlorobenzenes and chlorinated pesticides by GC/ECD or GC/MS. The second and third fractions were analyzed for chlorinated pesticides by GC/ECD.

1.2 Extraction

1.2.1 Soils/Sediments

The sediment sample was thoroughly homogenized and a subsample taken for the determination of wet weight/dry weight ratio.

Wet sediment sample, to which an aliquot of surrogate standard had been added, was extracted once with 80 mL of 1:1 dichloromethane/methanol by shaking on a shaker table for 30 minutes. The extraction procedure was repeated using 80 mL of dichloromethane. The extracts were combined, washed with solvent-extracted water, dried over anhydrous sodium sulphate and concentrated by Kuderna Danish techniques. After the addition of activated copper to remove sulphur, the extract was separated on a Florisil column.

1.2.2 Water

A 1 L sample was placed in a separatory funnel and spiked with aliquots of surrogate standard solution and methanol. The sample was extracted with three 100 mL portions of dichloromethane. The solvent was collected, dried over anhydrous sodium sulphate, spiked with hexane and reduced in volume by rotary evaporation, prior to cleanup and fractionation on a Florisil column.

1.3 Sample Cleanup and Separation

1.3.1 Cleanup for GC/ECD

The extract was quantitatively transferred to a Florisil column and eluted with three solvent systems consisting of hexane (Fraction-1), 85:15 dichloromethane/hexane (Fraction-2) and 50:50 dichloromethane/hexane (Fraction-3).

An aliquot of surrogate standard was added to each of Fraction-2 to allow quantification since the surrogate standard added at the beginning of the procedure eluted into Fraction-1 and Fraction-3. Each fraction was concentrated, transferred to a microvial, and an aliquot of recovery standard (4,4'-dibromooctafluorobiphenyl and PCB 204 to Fraction-1 and Fraction-2 and ^{13}C-PCB 153 to Fraction-3) added prior to analysis by GC/ECD.

Fraction-1 was analyzed by GC/ECD for PCBs as Aroclors, chlorobenzenes, and mildly polar chlorinated pesticides.

Fraction-2 was analyzed by GC/ECD for moderately polar chlorinated pesticides.

Fraction-3 was analyzed by GC/ECD for the most polar chlorinated pesticides.

1.3.2 Cleanup for GC/MS

The extract was quantitatively transferred to a Florisil column. The column was eluted with hexane followed by 85:15 dichloromethane/hexane. The eluates were combined (Fraction-1). The column was eluted with 50/50 dichloromethane/hexane (Fraction-2)

Each fraction was concentrated, transferred to a microvial and spiked with an aliquot of recovery standard (^{13}C-PCB 153) prior to instrumental analysis.

Fraction-1 was analyzed by GC/MS for PCBs as Aroclors, PCB congeners, and non-polar and moderately polar chlorinated pesticides.

Fraction-2 was analyzed by GC/ECD for the most polar chlorinated pesticides.

1.4 Instrumental Analysis

1.4.1 GC/ECD Analysis

Each fraction was analyzed for chlorinated organic compounds using an HP 5830A gas chromatogram equipped with a ^{63}Ni electron capture detector (GC/ECD), a 60 m DB-5 column (0.25 mm i.d x 0.1 μm film thickness) and HP 3392 integrator. Fraction-1 was simultaneously analyzed for PCBs as Aroclors and PCB congeners. Chromatographic conditions were as follows - Initial Temp: 100 °C; Injection: splitless, 1 min; Initial time: 2 min; Ramp: 10 °C/min to 150 °C, 3 °C/min to 300 °C; Final time: 5 min. Column conditions were: Carrier gas, helium; Pressure, 21 psi; Flow rate, 60 mL/min; and Split ratio, 15:1.

The instrument was calibrated daily using a solvent blank and standards of Aroclor 1242, Aroclor 1254 and Aroclor 1260. For each Aroclor, the sum of the areas of three characteristic peaks was used to calculate its response factor against the internal standard. The area of the same three peaks was used to determine the concentration of each Aroclor in the sample.

All values reported in the tables are in ppb (ng/g) on a dry weight basis for soil samples. Procedural blank information is given in Appendix B; the levels obtained demonstrated no blank interferences with the sample results.

1.4.2 Low Resolution GC/MS

Fraction-1 was analyzed for PCB congeners, Aroclors and non-polar and moderately polar chlorinated pesticides using a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 GC, a CTC autosampler and a DG 10 data system running INCOS 50 (Rev 9) software. Chromatographic separation of pesticides was achieved with a 60 m DB-5 column (0.25 mm i.d. and 0.10 μm film thickness). The mass spectrometer was operated in the electron impact (EI) mode at unit mass resolution in the multiple ion detection (MID) mode acquiring two characteristic ions for each target analyte and surrogate standard.

2. DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH), ALKANES AND HOPANES IN SEDIMENT/SOIL SAMPLES

2.1 Summary

All samples were spiked with an aliquot of surrogate standard solution containing perdeuterated analogues of acenaphthene, chrysene, naphthalene, perylene, phenanthrene, pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene and 2 methylnaphthalene for analysis of PAHs. An additional surrogate standard containing perdeuterated dodecane (nC12), hexadecane (nC16), tetracosane (nC24), hexatriacontane (nC36) was added for analysis of alkanes. Sediment samples were base digested, and extracted with pentane. Each extract was fractionated on silica gel into polar and non polar fractions. The non polar fraction was analyzed for alkanes and hopanes, and the polar fraction analyzed for parent and alkylated PAHs by high resolution gas chromatography with low resolution (quadrupole) mass spectrometric detection (HRGC/LRMS).

2.2 Digestion and Extraction

A subsample of homogenized sediment was dried overnight at 105°C for moisture determination.

A wet sediment sample was accurately weighed into a 500 mL round bottom flask and spiked with an aliquot of each surrogate standard solution. Methanol and a potassium hydroxide solution were then added and the mixture was heated under reflux for 1 hour, cooled, and extracted water was then added through the condenser. Refluxing was resumed for an additional hour.

The digest was transferred to a separatory funnel with methanol rinses and extracted with pentane (3 x 100 mL). The pentane layers were combined, washed with extracted water 3 times, and dried

over anhydrous sodium sulphate. The pentane extract was then concentrated in a Kuderna Danish flask prior to column cleanup.

2.3 Column Chromatography

The extract was loaded onto a silica gel column and eluted with pentane (F1) followed by dichloromethane (F2). F1 contains the alkanes and hopanes, and F2 contains parent and alkylated PAHs.

Each fraction was concentrated to a small volume, transferred to an autosampler vial and an aliquot of recovery standard containing deuterated benzo(b)fluoranthene, fluoranthene, and acenaphthylene was added prior to GC/MS analysis.

2.4 Instrumental Analysis

Analysis of the extract was carried out using a Varian 3400 gas chromatograph with a Finnigan Incos 50 mass spectrometer, a CTC autosampler and a DG 10 Data system. A 30 metre DB 5 (0.25 mm i.d. x 0.25 mm film thickness) chromatography column, used for GC separation, was coupled to the MS source.

The mass spectrometer was operated in the EI mode (70 Ev) selected ions acquired using Multiple Ion Detection (MID) to enhance sensitivity, acquiring at least two characteristic ions for each target analyte and surrogate standard. A split/splitless injection sequence was used.

3. TOTAL EXTRACTABLE HYDROCARBONS (TEH) IN SOIL SAMPLES

Total extractable hydrocarbons in soils were determined with methodology based upon US EPA Method 8015 and BC MOELP Environmental Laboratory Manual (1994) Method X366, involving dichloromethane extraction and analysis using GC/FID. Components in the C10 to C30 range are included, using an alkane standard for quantification.

4. ANALYSIS OF INORGANIC ELEMENTS IN SOIL AND WATER SAMPLES

Metal and inorganic analysis was carried out using inductively coupled argon plasma - atomic emission spectrometry (ICP-AES), based on US EPA Method 6010 and BC MOELP Environmental Laboratory Manual (1994) Method Section 2.5.3.

4.1 Digestion

Soil samples were thoroughly homogenized and approximately 5 to 15 grams of sample were accurately subsampled and subjected to a strong acid (aqua regia: nitric/hydrochloric acid) digestion. The soil sample was placed in a clean, acid washed 250 mL beaker along with 10 mL nitric acid and 20 mL hydrochloric acid. The mixture was placed on a hot plate and reduced to a volume of 10 mL. The extract was diluted with ultra pure water to a volume of 100 mL. A soil sub-sample was weighed, dried and re-weighed in order to determine wet:dry conversion factors.

4.2 ICP Analyses

Analysis was performed on the digest for all elements reported. The instrument used was a Jarrel ash Model # 975 Inductively Coupled Plasma Spectrograph (ICP), equipped with a Minipuls 2 peristaltic pump and an all glass MAK pressure nebulizer.

The instrument was calibrated using solutions prepared from pure metals or pure metal salts obtained from Johnson Matthey or from Spex Industries. Calibration was checked after every ten solutions (blanks, certified standards, or sample solutions) were analyzed; the instrument was recalibrated if the deviation from the standard curve was over 2%.

For this study, the ICP analysis was undertaken using a general purpose ICP program which consists of thirty elements and their associated calibration standard solutions. This was done to ensure that computer corrections for spectral interferences caused by elements such as aluminum, magnesium and titanium could be carried out. This elemental array with calibration standards are used on a daily basis for analysis of water, biological tissues, geological materials and alloys.

4.3 Arsenic, and Cadmium in Soil

Arsenic and cadmium levels in soils were analyzed by graphite furnace atomic absorption spectrometry (GFAAS) of the aqua regia acid digest. GFAAS was performed using Zeeman background correction and with palladium and nickel as matrix modifiers in the graphite tube.

4.4 Zinc in Water

Zinc in water was analyzed by atomic absorption spectrometry

4.5 Mercury in Soil and Water.

Mercury was analyzed in soil samples using Cold Vapour Atomic Absorption Spectrometry (CVAAS). Mercury in water samples was also analyzed by CVAAS following prior digestion with acid permanganate.

5. ANALYSIS OF INORGANIC ELEMENTS IN PLANT SAMPLES

5.1 Digestion

Prior to digestion, each sample was air dried then ground to provide a homogenous sample.

Sample dissolution of the air dried sample was achieved after accurately weighing out representative samples into acid washed Pyrex beakers with watch glasses. To each sample, 7 mL of Fisher Chemical trace metal grade nitric acid was added and digested over low heat for a period of 4 hours. After the initial nitric acid digestion, the samples were allowed to cool and 5 mL of a Merck analytical grade hydrogen peroxide was added. Samples were again allowed to cool and then diluted to 50 mL with ultra pure water. A minimum of two reagent blanks and the National Institute of Standards and Technology (NIST) Citrus Leaves (1579) and Orchard Leaves (1571) certified reference materials were digested and analyzed concurrently.

5.2 ICP Analyses

Instrumental analysis was similar to the method for soils (see Section A.4.2 above)

5.3 Mercury

Mercury was determined using a Pharmacia Model 100 M Mercury Monitor equipped with a Servo Graphic Recorder Model 410. No pretreatment of the solutions was needed prior to the mercury determination.

5.4 Arsenic, Cadmium and Lead

These elements were determined using a Varian Model 400 Zeeman Background Correction Graphite Furnace.

APPENDIX B: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

1. INTRODUCTION

The analyses of the archived samples were carried out at either Axys Analytical Services Ltd., Sidney, BC, or under subcontract by Cantest Ltd., Vancouver, BC. A quality assurance/quality control program was set up by the laboratories to monitor data quality and reliability. All samples were run in batches of varying sizes with QA/QC samples which accompanied the set through the entire analytical procedure. These samples included the following:

- internal spikes (using a known concentration of an analyte), surrogate standards and/or reference material (depending on the type of analysis) to monitor analytical accuracy;
- internal blanks to monitor interferences from potential lab contamination and other analytes; and
- analytical or procedural duplicates of samples to monitor internally the precision or repeatability of the results.

2. INORGANIC ELEMENT (METAL) ANALYSIS

2.1 Soil

Analytical precision for inorganic elements analysis was performed internally by Cantest using NRC (National Research Council) Standard Reference Material PACS-1 for soils. Generally, determined values which fall within the range indicated by the certified value are considered to indicate reasonable to good analytical accuracy. Good agreement was found for a majority of the inorganic analytes in the reference material suggesting good analytical precision for the soil analysis (Table B.1). A few elements, however, exhibited determined values outside of the certified range such as selenium (which was overestimated) and molybdenum, antimony, strontium and titanium (which were underestimated) suggesting fair to poor precision for these particular analytes. This discrepancy may have been due to differences in the analytical methods employed.

One pair of soil sample was analyzed to monitor analytical precision. Agreement between the duplicates can be measured either by direct comparison or by calculating the relative standard deviation (RSD), which is simply the standard deviation of the duplicates divided by the mean (expressed as a percentage). Values of RSD less than 30 % indicate reasonable to good precision, while those exceeding this value are fair to poor. Good precision was indicated for all analytes based on the RSD. The only exception was the RSD for arsenic (33 %) which suggested poor precision for this particular analyte.

2.2 Plants

Analytical precision for inorganic elements in plants was performed internally by CANTEST using National Bureau of Standards (NBS) certified reference material citrus leaves NBS 1572 and orchard leaves NBS 1571. Good agreement was found for all inorganic analytes in the reference material suggesting good analytical precision for the analysis (Table B.3).

Three pairs of plant samples were analyzed to monitor analytical precision. Good precision was indicated for all analytes based on the RSD (Table B-4).

Table B.1: Inorganic Element Results for National Research Council Standard Reference Material PACS-1 for Soils

Element	Determined µg/g	Certified µg/g	Recovery %
Arsenic	196	171 ±14	60
Barium	387	-	-
Cadmium	2.1	2.38 ±0.20	88
Chromium	67.5	113 ±8	60
Cobalt	20.5	17.5 ±1.1	117
Copper	460	452 ±16	102
Lead	424	404 ±20	105
Mercury	0.80	4.57 ±0.16	18
Molybdenum	8.5	12.9 ±0.9	66
Nickel	41.5	44.1 ±2.0	94
Selenium	0.90	1.09 ±0.11	83
Silver	<15	-	-
Tin	36.5	41.1 ±3.1	89
Zinc	910	824 ±22	110
Antimony	103	171 ±14	60
Beryllium	<3.0	-	-
Boron	93	-	-
Strontium	96.5	277 ±11	35
Titanium	1405	4210 ±66	33
Vanadium	91	127 ±5	71

Table B.2: Inorganic Element Results for Duplicate Soil Analyses

Sample:	SS157	SS157	Average	RSD (%)
	Concentration (µg/g)			
Antimony	<	<	nc	nc
Arsenic	2.9	4.0	3.5	33
Barium	90	81	86	10
Cadmium	<	<	nc	nc
Chromium	78	87	83	12
Cobalt	14	13	13	2.5
Copper	40	39	39	0.9
Lead	2	2	2	nc
Mercury	0.004	0.005	0.005	nc
Molybdenum	<	<	nc	nc
Nickel	33	35	34	4.9
Selenium	<	<	nc	nc
Silver	<	<	nc	nc
Tin	<	<	nc	nc
Zinc	47	48	47	1.7
Aluminum	17300	16900	17100	2.3
Beryllium	<	<	nc	nc
Boron	25	24	24	5.0
Calcium	14390	13970	14180	5.0
Iron	28800	26700	27700	7.6
Magnesium	12390	14170	13280	13
Manganese	400	408	404	2.0
Phosphorus	1500	1670	1580	11
Sodium	65	61	63	6.6
Strontium	70	64	67	10
Titanium	571	490	531	15

RSD = Relative Standard Deviation
nc = not calculated

Table B.3: Inorganic Element Results for National Bureau of Standards Certified Materials Citrus Leaves (NBS 1572) and Orchard Leaves (NBS 1571)

	Citrus Leaves (NBS 1572)			Orchard Leaves (NBS 1571)		
	Determined	Certified	Recovery	Determined	Certified	Recovery
	µg/g	µg/g	(%)	µg/g	µg/g	(%)
Aluminum	70	92	76	NC	-	-
Antimony	<0.5	0.04 (NC)	-	<5	2.9	-
Arsenic	3.2	3.1	103	9.5	10	95
Barium	19	21	90	41	44	93
Beryllium	NC	-	-	<0.1	0.027	-
Boron	NC	-	-	29	33	88
Cadmium	<0.05	-	-	0.10	0.11	91
Calcium	31300	31500	99	20200	20900	97
Chromium	<1.5	0.08	-	2.6	2.6	100
Cobalt	NC		-	<0.5	0.2	
Copper	17	16.5	103	11	12	-
Iron	96	90	106	245	300	82
Lead	12	13.3	75	46	45	102
Magnesium	5250	5800	90	5600	6200	90
Manganese	22	23	96	86	91	95
Mercury	0.08	0.08	100	0.14	0.155	90
Molybdenum	<1	0.17	-	<1	0.3	-
Nickel	<1.5	0.06	-	<1.5	1.3	-
Potassium	19900	18200	109	14000	14700	95
Silver	NC		-	NC		-
Sodium	155	160	96	60	82	73
Strontium	97	100	97	35	37	94
Tin	NC		-	NC		-
Titanium	NC		-	NC		-
Vanadium	NC		-	NC		-
Zinc	31	29	106	22	25	88

Notes NC = Not certified, Results expressed as µg/g or ppm

Table B.4: Inorganic Element Results for Duplicate Analysis of Plant Samples

	SS-75 P1			SS-76 P1			SS-76 P2R		
	Results 1	Results 2	RSD	Results 1	Results 2	RSD	Results 1	Results 2	RSD
	µg/g	µg/g	%	µg/g	µg/g	%	µg/g	µg/g	%
Aluminum	358	358	0	191	170	12	141	127	10
Antimony	<	<	-	<	<	-	<	<	-
Arsenic	0.14	0.15	14	<	<	-	<	<	-
Barium	40	40	0	86	85	1.8	84	82	3.0
Beryllium	<	<	-	<	<	-	<	<	-
Boron	27	25	5.8	24	24	0.0	17	17	0.0
Cadmium	3.05	2.9	5.0	0.65	0.63	8.0	1.95	1.85	5.3
Calcium	17300	17100	1.2	19300	19400	0.5	10400	9950	4.4
Chromium	4.3	4.4	2.3	<	<	-	2.3	2.3	0.0
Cobalt	<	<	-	<	1.2	-	<	<	-
Copper	46	60	26	16	14	15	7.0	8.0	13
Iron	845	740	13	2950	2870	2.7	253	235	7.4
Lead	5.00	4.15	19	0.35	0.45	25	.60	.45	28
Magnesium	3780	3750	0.8	3650	3690	1.1	740	695	6.3
Manganese	120	120	0	1620	1620	0.0	57	54	6.3
Mercury	0.080	0.075	13	0.030	0.030	0.0	0.1	0.1	0.0
Molybdenum	<	<	-	<	<	-	<	<	-
Nickel	17	16	6.1	6.5	6.0	8.0	9.0	8.0	12
Potassium	47750	47150		37800	37450	0.9	2405	2285	5.1
Silver	<	<	-	<	<	-	<	<	-
Sodium	298	297	0.3	140	150	6.9	31	28	8.5
Strontium	59	59	0	62	62	0.0	46	45	3.3
Tin	<	<	-	<	<	-	<	<	-
Titanium	20	21	4.9	5.5	5.5	0.0	5.5	4.7	5.1
Vanadium	1.2	1.3	4.1	0.8	1.0	29	<	<	-
Zinc	53	52	2.9	76	81	5.8	75	68	9.8

Notes: Results expressed as µg/g or ppm; < : Less than the detection limit; RSD: Relative Standard Deviation

3. TOTAL EXTRACTABLE HYDROCARBONS (TEH) IN SOILS

Three spiked samples were used internally by CANTEST to monitor analytical precision for soils (Table B.5). Reasonable accuracy for soil analysis was indicated by the % recovery results for these spiked samples. The values for the soil spikes were slightly high indicating that the soil results for TEH may be slightly over-estimated.

Table B.5: TEH Spike Data

Cantest ID	Component	% Recovery
Spike Jan 25/95	Kerosene	118
Spike Jan 29/95	Kerosene	112
Spike Jan 30/95	Kerosene	112

Three blank samples were used to monitor interferences internally (Table B.6). The TEH values for all of these samples were below detection.

Table B.6: TEH Blank Data

Cantest ID	Concentration (µg/g)
Blank Jan 25/95	<20
Blank Jan 29/95	<20
Blank Jan 30/95	<20

Three pairs of analytical duplicates for were also analyzed to monitor precision internally by CANTEST. Good analytical precision was found (Table B.7).

Table B.6: TEH Duplicate Data

Cantest ID	Results 1	Results 2	RSD (%)
	concentration (µg/g)		
60124066 Duplicate	61	66	7.8
60126034 Duplicate	<20	<20	-
60129033 Duplicate	<20	<20	-

4. POLYCHLORINATED BIPHENYLS (PCBS), CHLOROBENZENES, AND CHLORINATED PESTICIDES IN SOILS

Analytical accuracy was monitored internally by Axys using two spiked matrix for soils (Table B.7). Recovery values for various analytes ranged from 80 to 124 % suggesting reasonable to good accuracy for the analysis. A combination of 13 surrogate standards were also analyzed with soil and water samples to monitor analytical accuracy. Average recovery values of standards in the samples were quite variable ranging from 28 to 86 %. These results suggest a fair to reasonable degree of accuracy.

Two analytical blanks were analyzed to monitor internally for interferences. Concentrations of analytes in nearly all samples were below detection with the exception of trace levels of dichlorobenzene and in the soil and water blanks, and p,p'-DDE (Table B.8).

Two pairs of soil samples were analyzed to monitor of analytical precision. Good agreement was found between both detectable and non-detectable analytes (based on similar detection limit values) indicating an acceptable degree of precision (Table B.9).

Table B-7: Spiked Matrix and Surrogate Recoveries for Chlorobenzenes, PCBs and Pesticides in Soils

Compounds	Determined ng/g	Expected ng/g	Recovery %	Determined ng/g	Expected ng/g	Recovery %
Dichlorobenzenes	13.1	11.4	115			
Trichlorobenzenes	12.8	12.4	103			
Tetrachlorobenzenes	12.1	11.4	106			
Pentachlorobenzene	4.0	3.9	102			
Hexachlorobenzene	6.1	5.6	109	5.9	5.6	105
alpha HCH	5.5	5.6	98	5.2	5.6	93
beta HCH	8.6	8.2	105	8.2	8.2	100
gamma HCH	6.1	5.4	113	6.0	5.4	111
Heptachlor	4.9	5.8	84	6.2	5.8	107
Aldrin	4.4	3.6	122	4.2	3.6	117
Oxychlordane	8.4	6.4	131	7.8	6.4	122
trans-Chlordane	3.6	3.2	112	3.6	3.2	113
cis-Chlordane	5.1	4.8	106	5.0	4.8	104
o,p'-DDE	7.0	5.7	123	6.6	5.7	116
p,p'-DDE	6.2	5.2	119	6.1	5.4	113
trans-Nonachlor	4.5	4.1	110	4.4	4.1	107
cis-Nonachlor	2.9	3.0	97	3.0	3.0	100
o,p'-DDD	5.3	5.6	95	5.2	5.6	93
p,p'-DDD	5.4	6.2	87	5.4	6.2	87
o,p'-DDT	8.0	7.6	105	7.8	7.6	103
p,p'-DDT	6.4	6.2	103	6.5	6.2	105
Mirex	5.6	5.4	104	5.6	5.4	104
Heptachlor Epoxide	3.5	4.0	88	4.0	4.0	100
alpha-Endosulphan (I)	3.7	4.0	93	3.7	4.0	93
Dieldrin	4.8	5.2	92	5.4	5.2	104
Endrin	8.2	11	75	9.2	11	84
Methoxychlor	24	25	96	20	25	80
Aroclor 1242	55	45	122	55	45	122
Aroclor 1254	57	46	124	55	46	120
Aroclor 1260	48	46	104	47	46	102
Surrogate Standards	**Recovery %**			**Recovery %**		
13C-1,4-Dichlorobenzene	28					
13C-1,2,4-Trichlorobenzene	36					
13C-1,2,4,5-Tetrachlorobenzene	44					
13C-Pentachlorobenzene	53					
13C-Hexachlorobenzene	64			74		
13C-gamma HCH	77			79		
13C-p,p'-DDE	84			78		
13C-p,p'-DDT	73			74		
13C-Mirex	67			72		
13C-PCB 101	76			75		
13C-PCB 180	78			84		
13C-PCB 209	72			83		
d4-alpha-Endosulphan	76			86		

Table B-8: Procedural Blanks and Surrogate Standard Recoveries for Chlorobenzenes, PCBs and Pesticides in Soils

Compounds	Concentration ng/g	(SDL)	Concentration ng/g	(SDL)
Dichlorobenzenes	0.48	0.39		
Trichlorobenzenes	ND	0.1		
Tetrachlorobenzenes	ND	0.04		
Pentachlorobenzene	ND	0.03		
Hexachlorobenzene	ND	0.04	NDR (0.01)	0.008
alpha HCH	ND	0.18	ND	0.05
beta HCH	ND	0.28	ND	0.1
gamma HCH	ND	0.25	ND	0.09
Heptachlor	ND	0.22	ND	0.08
Aldrin	ND	0.1	ND	0.03
Oxychlordane	ND	0.46	ND	0.15
trans-Chlordane	ND	0.05	ND	0.02
cis-Chlordane	ND	0.06	ND	0.02
o,p'-DDE	ND	0.03	NDR 0.05	0.01
p,p'-DDE	0.04	0.03	ND	0.01
trans-Nonachlor	ND	0.05	ND	0.02
cis-Nonachlor	ND	0.04	ND	0.02
o,p'-DDD	ND	0.04	ND	0.02
p,p'-DDD	ND	0.04	ND	0.02
o,p'-DDT	ND	0.06	ND	0.03
p,p'-DDT	ND	0.06	ND	0.03
Mirex	ND	0.42	ND	0.32
Heptachlor Epoxide	ND	0.005	ND	0.01
alpha-Endosulphan (I)	ND	0.006	ND	0.01
Dieldrin	ND	0.007	ND	0.01
Endrin	ND	0.01	ND	0.02
Methoxychlor	ND	0.03	ND	0.06
Aroclor 1242	ND	0.37	ND	0.11
Aroclor 1254	ND	1.0	ND	0.3
Aroclor 1260	ND	0.73	ND	0.34
Surrogate Standards	**% Recovery**		**% Recovery**	
13C-1,4-Dichlorobenzene	28			
13C-1,2,4-Trichlorobenzene	35			
13C-1,2,4,5-Tetrachlorobenzene	41			
13C-Pentachlorobenzene	52			
13C-Hexachlorobenzene	60		55	
13C-gamma HCH	73		68	
13C-p,p'-DDE	75		66	
13C-p,p'-DDT	96		84	
13C-Mirex	81		65	
13C-PCB 101	78		67	
13C-PCB 180	83		71	
13C-PCB 209	95		74	
d4-alpha-Endosulphan	81		79	

1. SDL = Sample Detection Limit
2. ND = Not Detected
3. NDR = Peak detected but did not meet quantification criteria.
4. Concentrations are recovery corrected

Table B-9: Analytical Duplicates for Chlorobenzenes, PCBs and Pesticides in Soils

Report Sample No. Lab Sample No. Field Sample No.	BL1SS043 9514-170 SS-123	Duplicate	BO1SS029 9514-230 SS-154	Duplicate
Compounds				
Dichlorobenzenes	<3.30	<4.2		
Trichlorobenzenes	<0.5	<0.81		
Tetrachlorobenzenes	NDR 0.4	NDR 0.37		
Pentachlorobenzene	0.22	<0.08		
Hexachlorobenzene	<0.14	<0.12	<0.07	<0.07
alpha HCH	NDR 3.2	NDR 1.6	<0.74	<0.88
beta HCH	<1.3	<1.1	<1.2	<1.4
gamma HCH	NDR 9.4	NDR 3.8	<1.1	<1.3
Heptachlor	<1.3	<1.2	<0.46	<0.77
Aldrin	<0.49	<0.47	<0.25	<0.26
Oxychlordane	<2.2	<2.3	<2.2	<2.6
trans-Chlordane	<0.29	<0.26	<0.13	<0.17
cis-Chlordane	<0.3	<0.27	<0.14	<0.18
o,p'-DDE	NDR 1.9	NDR 2.5	NDR 1.2	NDR 1.1
p,p'-DDE	NDR 5.0	NDR 4.4	NDR 0.91	NDR 0.77
trans-Nonachlor	<0.23	<0.24	<0.12	<0.14
cis-Nonachlor	<0.19	<0.2	<0.1	<0.12
o,p'-DDD	<0.22	<0.21	<0.17	<0.2
p,p'-DDD	<0.22	<0.21	<0.17	<0.2
o,p'-DDT	NDR 5.2	NDR 4.1	NDR 0.56	NDR 0.59
p,p'-DDT	<0.41	<0.36	<0.32	<0.38
Mirex	<0.42	<0.41	<0.27	<0.25
Heptachlor Epoxide	<0.004	<0.006	<0.02	<0.03
alpha-Endosulphan (I)	<0.005	<0.008	<0.02	<0.03
Dieldrin	<0.005	<0.008	<0.03	<0.03
Endrin	<0.008	<0.01	<0.05	<0.06
Methoxychlor	<0.02	<0.03	<0.04	<0.04
Aroclor 1242	<4.2	<3.3	<1.2	<1.4
Aroclor 1254	<4.6	<5.1	<2.4	<2.4
Aroclor 1260	<5.7	<5.6	<2.5	<2.8

NDR = Peak detected but did not meet quantification criteria
< = Concentrations are less than the detection limit indicated.

5. POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS

Analytical accuracy was monitored internally by Axys using one spiked matrix for soils (Table B.10). Recovery values for various analytes ranged from 81 to 125 % suggesting reasonable to good accuracy for the analysis. A combination of 10 surrogate standards were also analyzed to monitor analytical accuracy. Average recovery values of standards in the samples were good ranging from 79 to 92 %.

One analytical blank was analyzed to monitor internally for interferences Naphthalene (0.92 μg/g), Acenaphthylene (0.14 μg/g), Fluorene (0.11 μg/g), Phenanthrene (0.44 μg/g), Anthracene (0.18μg/g) Fluoranthene (0.12μg/g) and Pyrene (0.13 μg/g) were detected (Table B.11).

One soil sample was analyzed in duplicate to monitor of analytical precision (Table B.12). Good agreement was found between both detectable (based on relative standard deviations which ranged between 0.0 and 18%) and non-detectable analytes (based on similar detection limit values).

Table B-10: Spiked Matrix and Surrogate Recovery for PAHs in Soils

Compounds	Determined ng/g	Expected ng/g	Recovery %
Naphthalene	220	240	92
Acenaphthylene	250	200	125
Acenaphthene	220	230	96
Fluorene	240	250	96
Phenanthrene	230	240	96
Anthracene	230	250	92
Fluoranthene	240	250	96
Pyrene	200	210	95
Benz(a)anthracene	200	210	95
Chrysene	200	210	95
Benzofluoranthenes	220	270	81
Benzo(e)pyrene	200	220	91
Benzo(a)pyrene	160	190	84
Perylene	200	210	95
Dibenz(ah)anthracene	220	240	92
Indeno(1,2,3-cd)pyrene	190	180	106
Benzo(ghi)perylene	200	210	95

Surrogate Standards	Recovery %
Naphthalene d-8	87
Acenaphthene d-10	83
Phenanthrene d-10	82
Pyrene d-10	88
Chrysene d-12	86
Benzo(a)pyrene d-12	92
Perylene d-12	81
Dibenz(ah)anthracene d-14	88
Benzo(ghi)perylene d-12	88
2-Methylnaphthalene d-10	79

1. Concentrations are recovery corrected

Table B-11: Procedural Blanks and Surrogate Standard Recoveries for PAHs in Soils

Compounds	Concentration ng/g	SDL ng/g
Naphthalene	0.92	0.04
Acenaphthylene	0.14	0.06
Acenaphthene	ND	0.05
Fluorene	0.11	0.02
Phenanthrene	0.44	0.07
Anthracene	0.18	0.08
Fluoranthene	0.12	0.06
Pyrene	0.13	0.06
Benz(a)anthracene	ND	0.11
Chrysene	ND	0.12
Benzofluoranthenes	ND	0.12
Benzo(e)pyrene	ND	0.12
Benzo(a)pyrene	ND	0.14
Perylene	ND	0.15
Dibenz(ah)anthracene	ND	0.14
Indeno(1,2,3-cd)pyrene	ND	0.15
Benzo(ghi)perylene	ND	0.13
C1 naphthalenes	ND	0.08
C2 naphthalenes	ND	0.06
C3 naphthalenes	ND	0.04
C4 naphthalenes	ND	0.04
C1 phen,anth	ND	0.04
C2 phen,anth	ND	0.07
C3 phen,anth	ND	0.12
C4 phen,anth	ND	0.10
Dibenzothiophene	ND	0.04
C1 dibenzothiophene	ND	0.06
C2 dibenzothiophene	ND	0.03
Surrogate Standards	**Recovery %**	
Naphthalene d-8	82	
Acenaphthene d-10	81	
Phenanthrene d-10	81	
Pyrene d-10	90	
Chrysene d-12	90	
Benzo(a)pyrene d-12	100	
Perylene d-12	90	
Dibenz(ah)anthracene d-14	69	
Benzo(ghi)perylene d-12	73	
2-Methylnaphthalene d-10	74	

1. SDL = Sample Detection Limit
2. ND = Less than the detection limit indicated
3. NDR = Peak detected but did not meet quantification criteria
4. Concentrations are recovery corrected

Table B-12: Analytical Duplicates for PAH in Soils

Compound	SS-69	SS-69 Duplicate	Mean	RSD
	ng/g	ng/g	ng/g	%
Naphthalene	75	NDR 82		
Acenaphthylene	NDR 22	NDR 17		
Acenaphthene	NDR 170	NDR 200		
Fluorene	NDR 50	66		
Phenanthrene	160	NDR 140		
Anthracene	NDR 17	NDR 15		
Fluoranthene	NDR 38	NDR 43		
Pyrene	470	450	460	3.1
Benz(a)anthracene	<2.2	NDR 5.1		
Chrysene	130	100	115	18
Benzofluoranthenes	NDR 1.8	NDR 1.6		
Benzo(e)pyrene	2.3	2.3	2.3	0.0
Benzo(a)pyrene	NDR 0.3	NDR 0.4		
Perylene	NDR 0.98	NDR 1.4		
Dibenz(ah)anthracene	<15	<0.11		
Indeno(1,2,3-cd)pyrene	NDR 0.51	NDR 0.52		
Benzo(ghi)perylene	NDR 0.7	NDR 0.6		
C1 naphthalenes	310	290	300	4.7
C2 naphthalenes	2400	2200	2300	6.1
C3 naphthalenes	5900	5700	5800	2.4
C4 naphthalenes	9300	9700	9500	3.0
C1 phen,anth	1700	1600	1650	4.3
C2 phen,anth	8400	8800	8600	3.3
C3 phen,anth	16000	15000	15500	4.6
C4 phen,anth	7200	6400	6800	8.3
Dibenzothiophene	170	140	155	13
C1 dibenzothiophene	690	790	740	9.6
C2 dibenzothiophene	2300	2300	2300	0.0

1. NDR = Peak detected but did not meet quantification criteria
2. < = Concentrations are less than the detection limit indicated.

6. ALKANES AND HOPANES ANALYSIS

One spiked soil and one spike water sample were used to monitor accuracy internally by Axys (Table B-13). Recovery values for various analytes ranged from 27 - 150 %. Recoveries for the high boiling compounds were significantly lower and therefore concentrations were corrected.

One blank each for soil and water were used to monitor internally for interferences (Table B-14). Low levels of some of the alkanes (up to 17 ng/g) were detected.

Precision was monitored using one pair of soil samples (Table B-15). Reproducibility was poor due to the heterogeneous nature of the matrix and high concentrations of the analyte. The samples consisted of dark brown grainy soils with small roots and hydrocarbon odour. The duplication was, therefore, considered acceptable.

Table B-13: Spiked Matrix and Surrogate Recovery for Alkane and Hopane Analysis

Compounds	Determined µg/g	Expected µg/g	Recovery %
Dodecane (nC12)	59	95	62
Tetradecane (nC14)	65	100	65
Hexadecane (nC16)	76	110	69
Pristane	74	100	74
Octadecane (nC18)	87	100	87
Eicosane (nC20)	120	100	120
Docosane (nC22)	150	100	150
Tetracosane (nC24)	150	110	140
Hexacosane (nC26)	140	100	136
Octacosane (nC28)	110	100	110
Triacontane (nC30)	72	110	65
Dotriacontane (nC32)	41	100	41
Tetratriacontane (nC34)	41	110	37
Hexatriacontane (nC36)	30	110	27
Surrogate Standards	**Recovery %**		
Dodecane (nC12)-d26	23		
Hexadecane (nC16)-d34	29		
Tetracosane (nC24)-d50	63		
Hexatriacontane (nC36)-d74	12		

1. Concentrations are recovery corrected
2. To satisfy requirements of the scientific authority, all analytes have been quantitated with respect to d50-nC24; other surrogates serve only to monitor recovery of compounds boiling lower or higher than nC24. Concentrations of low or high boiling compounds may be significantly under-reported due to low recoveries and the data should be interpreted accordingly

Table B-14: Procedural Blanks and Surrogate Standard Recoveries for Alkane and Hopanes Analysis

Compounds	Concentration (ng/g)	(SDL)	Compounds	Concentration (ng/g)	(SDL)
Dodecane (nC12)	17	3.0	Tricosane (nC23)	1.0	0.4
2,6-Dimethyl Undecane	5.0	3.0	Tetracosane (nC24)	1.0	0.5
Norfarnesane	ND	3.0	Pentacosane (nC25)	ND	0.6
Tridecane (nC13)	3.0	2.0	Hexacosane (nC26)	ND	0.6
Farnesane	ND	1.0	Heptacosane (nC27)	ND	0.7
Tetradecane (nC14)	4.0	1.0	Octacosane (nC28)	ND	0.8
2,6,10-Trimethyl Tridecane	ND	1.0	Nonacosane (nC29)	ND	0.8
Pentadecane (nC15)	3.0	1.0	Triacontane (nC30)	ND	0.9
Hexadecane (nC16)	6.0	1.0	Untriacontane (nC31)	ND	1.0
Norpristane	2.0	0.7	Dotriacontane (nC32)	ND	1.0
Heptadecane (nC17)	4.0	0.7	Tritriacontane (nC33)	ND	1.0
Pristane	5.0	0.9	Tetratriacontane (nC34)	ND	1.0
Octadecane (nC18)	5.0	0.9	Pentatriacontane (nC35)	ND	1.0
Phytane	4.0	0.9	Hexatriacontane (nC36)	ND	2.0
Nonadecane (nC19)	4.0	0.6			
Eicosane (nC20)	3.0	0.7			
Heneicosane (nC21)	2.0	0.6			
Docosane (nC22)	2.0	0.7			

Surrogate Standards	% Recovery
Dodecane (nC12)-d26	31
Hexadecane (nC16)-d34	48
Tetracosane (nC24)-d50	48
Hexatriacontane (nC36)-d74	28

1. SDL = Sample Detection Limit
2. ND = Less than the detection limit indicated
3. NDR = Peak detected but did not meet quantification criteria
4. Concentrations are recovery corrected
5. To satisfy requirements of the scientific authority, all analytes have been quantitated with respect to d50-nC24; other surrogates serve only to monitor recovery of compounds boiling lower or higher than nC24. Concentrations of low or high boiling compounds may be significantly under-reported due to low recoveries and the data should be interpreted accordingly

Table B-15: Analytical Duplicates for Alkane and Hopane Analysis

Compound	SS-69 ng/g	SS-69 Duplicate ng/g	Mean ng/g	RSD %
Alkanes				
Dodecane (nC12)	75000	110000	92500	27
2,6-Dimethyl Undecane	40000	69000	54500	38
Norfarnesane	38000	81000	59500	51
Tridecane (nC13)	89000	190000	139500	51
Farnesane	37000	86000	61500	56
Tetradecane (nC14)	80000	190000	135000	58
2,6,10-Trimethyl Tridecane	40000	86000	63000	52
Pentadecane (nC15)	72000	170000	121000	57
Hexadecane (nC16)	53000	130000	91500	60
Norpristane	33000	78000	55500	57
Heptadecane (nC17)	41000	100000	70500	59
Pristane	56000	130000	93000	56
Octadecane (nC18)	44000	110000	77000	61
Phytane	43000	99000	71000	56
Nonadecane (nC19)	37000	89000	63000	58
Eicosane (nC20)	30000	78000	54000	63
Heneicosane (nC21)	18000	48000	33000	64
Docosane (nC22)	9900	31000	20450	73
Tricosane (nC23)	5400	16000	10700	70
Tetracosane (nC24)	2200	5700	3950	63
Pentacosane (nC25)	710	2300	1505	75
Hexacosane (nC26)	<310	380	-	-
Heptacosane (nC27)	<340	<280	-	-
Octacosane (nC28)	<380	<310	-	-
Nonacosane (nC29)	<380	<300	-	-
Triacontane (nC30)	<440	<340	-	-
Untriacontane (nC31)	<490	<390	-	-
Dotriacontane (nC32)	<560	<440	-	-
Tritriacontane (nC33)	<640	<390	-	-
Tetratriacontane (nC34)	<620	<450	-	-
Pentatriacontane (nC35)	<680	<500	-	-
Hexatriacontane (nC36)	<760	<550	-	-
Hopanes				
18Ê(H)trisnorhopane(C27Ê)	3.0	2.6	2.8	10
17ß(H)trisnorhopane(C27ß)	3.2	2.7	3.0	12
17Ê(H),21ß(H)norhopane(C29Êß)	5.6	4.8	5.2	11
17Ê(H),21ß(H)hopane(C30Êß)	8.3	7.1	7.7	11
S-17Ê(H),21ß(H)homohopane(C31Êß)	4.0	3.5	3.8	9.4
R-17Ê(H),21ß(H)homohopane(C31Êß)	3.6	2.8	3.2	18

< = Concentrations are less than the detection limit indicated.
RSD = Relative Standard Deviation

Appendix C: Review of the Environmental, Toxicological and Regulatory Significance of Alkyl-substituted PAHs

CONTENTS:

SUMMARY

Alkylated polycyclic aromatic hydrocarbons (PAHs), like their unsubstituted counterparts may be routinely found in hydrocarbon-contaminated soils and sediments. In fact, PAH contamination from a petroleum-based (or petrogenic) source is generally characterized by higher concentrations of alkylated PAHs than unsubstituted, or parent PAHs. Unlike unsubstituted PAHs, however, the environmental fate (including persistence) and toxicological significance of alkylated PAHs is virtually unknown. Limited data suggest that alkylated PAHs, in general, may be more or less toxic, or of comparable toxicity to their unsubstituted PAH counterparts, depending on the positions and numbers of alkyl- groups around the ring structure; however, a poor understanding of structure-activity relationships precludes any meaningful prediction of potential for adverse environmental effects. This severely restricts the ability to manage and regulate PAHs. Many environmental regulations specify acceptable concentrations of contaminants in soil, sediment, water, or wastes. The environmental consequences of contaminant inputs, however, are more directly related to the bioavailability and chemical form of the contaminant in target organism(s). Very little is known about effects of alkyl-substitution on bioavailability, metabolic modification and elimination rates, or toxicity (e.g. acute lethality, carcinogenicity, steroidal effects).

The lack of scientific and regulatory guidance on the issue of alkyl-PAH contamination means that any practical response to hydrocarbons as part of contaminated site investigations will include a great deal of uncertainty. Some interim guidance can nonetheless be provided, taking into account likely routes of exposure and ecological receptors *on a site-specific basis.* There is no *a priori* reason, for example to believe that alkyl-substituted naphthalenes or other PAHs are any less deleterious to fish than unsubstituted forms where exposure concentrations are of similar magnitude. Under Canadian law, therefore, evidence of substantial inputs of alkylated PAHs to fish-bearing waters would have roughly the same implications under the Federal Fisheries Act as for unsubstituted PAHs. Conversely, where isolated hydrocarbon spills on surface and sub-surface soils are not accompanied by any plausible exposure pathway to major biological receptors, or where the spill is historical - provided no new impacts are expected and a reasonable rate of environmental recovery is occurring - the associated lack of evidence for human health or ecological risk would dictate only a limited requirement for remedial action.

The chemical composition of hydrocarbon mixtures, including data on the relative concentrations of various alkyl-PAH groups is useful for a variety of reasons. First, the alkyl-PAH along with unsubstituted PAH data can provide information on the major contaminant sources, and can be used to apportion the relative contribution where more than one source is suspected (e.g., long-range atmospheric transport source versus local source; different local sources). Second, the relative concentration of different alkyl- homologue groups potentially provides meaningful information on the extent of weathering of a hydrocarbon mixture in the environment. The change in unsubstituted and alkyl-PAH composition in an environmental compartment over time is influenced by several factors, including *in situ* degradation. The open scientific literature provides some hints about how alkyl-PAHs might be used to assess the extent and site-specific rates of contaminant degradation and other loss processes; however, more scientific studies will be needed before this is of practical value.

GLOSSARY OF TECHNICAL TERMS USED

This section is written for both a technical and non-technical audience. The following technical terms, however, are unavoidably used variously throughout this review document; therefore, a glossary has been included up front. Where appropriate, the structure of specific PAHs and related compounds has been illustrated.

Alkyl-substituted PAHs (= alkyl-PAH): PAHs with alkyl-groups (straight and branched groups of carbon and hydrogen atoms) variously attached around the ring structure.

Bioaccumulation: the assimilation of a substance by an organism from its surroundings.

Biomagnification: increase in concentration of a contaminant from lower levels in the food web to higher trophic levels; e.g. elevated contaminant levels in predatory animals relative to the tissues of their prey.

Carcinogen: a substance capable of inducing cancer, usually in a vertebrate animal.

HPAHs: high molecular weight PAHs.

Halogenated: contained atom(s) of fluorine, bromine, and/or chlorine.

Homologues: two or more compounds with the same general structure and molecular weight, but differing slightly in the arrangement of specific substituents.

Hydrocarbons: organic molecules composed primarily of carbon and hydrogen atoms, usually biologically produced, and common in oil and coal deposits, which are derived from plant and animal remains.

LPAHs: low molecular weight PAHs.

Kinetically-favoured: compounds exhibiting a rapid rate of formation from a group of reactants, and, therefore, tending to dominate during and immediately following the initial stages of chemical reaction.

Metabolites: products of the enzymatic modification of substances in living organisms.

Mutagen: a substance capable of inducing a mutation in the genome of an organism.

Polycyclic Aromatic Hydrocarbons (PAHs): group of organic chemicals made of principally of carbon and hydrogen atoms arranged in a series of rings with resonant double bonds.

Petrogenic: derived from petroleum-based sources; e.g., crude oils and their distillates.

Pyrogenic: produced as a result of pyrolysis, or combustion-based processes, such as forest fires or municipal waste incineration.

Substituted PAHs: PAHs with one or more added substituents around the arene ring structure, such as methyl groups ($-CH_3$), isopropyl groups ($CH_3CH_2CH_3$), hydroxy groups (-OH), or chlorines (-Cl).

Triterpenoids (and diterpenoids): organic compounds, produced primarily by plants such as conifers, that exhibit three (or two for diterpenoids) five- to six-sided carbon rings and a wide variety of side chains.

Thermodynamically-favoured: compounds with an energy state sufficiently low that they are resistant to further chemical reaction in the absence of additional large amounts of added energy.

Unsubstituted PAHs: PAHs without additional side groups (often referred to as **parent PAHs)**.

1. BACKGROUND AND SCOPE OF THIS DOCUMENT

1.1 Background

The Arctic Environmental Strategy (AES), Action on Waste office, Whitehorse, is tasked with the investigation and cleanup of contaminated sites in the Yukon Territories, Canada. One major group of contaminants commonly encountered in areas where hydrocarbons were spilled include polycyclic aromatic hydrocarbons (PAHs). While there have been many major scientific studies of the environmental fate and effects of some other persistent organic contaminants in Arctic and sub-arctic environments (e.g., chlorinated pesticides, toxaphene, PCBs), the environmental risks attributable to PAHs, either on a local or broad regional scale remain largely unknown (Yunker and Macdonald, 1995). Although PAHs may be accumulated by living organisms through ingestion or a limited number of other routes, they are not biomagnified (Law and Biscaya, 1994). PAHs tend to be readily metabolized by most organisms; i.e., converted enzymatically to polar metabolites that are readily excreted.

Polycyclic Aromatic Hydrocarbons (PAHs) are found extensively in the environment. PAHs are a group of complex hydrocarbons comprised of two or more arene rings. PAHs can be produced during combustion, released from fossil fuels and other petroleum products, and formed from natural plant and bacterial products. **PAHs are common constituents of fuels and lubricating oils. Obvious possible sources of PAHs inputs to a site include fuel spills, and leaks from above-ground and underground storage tanks.** The combustion of fuels and coal has caused widespread environmental PAH contamination on a global scale in association with atmospheric transport pathways (Laflamme and Hites, 1978). The combustion of organic material, especially of coal and wood, can also produce PAHs. Many PAHs also have natural sources - in combustion of organics during forest fires or as primary or secondary products of natural plant and microbial metabolism.

Several PAHs are suspected or known mutagens and carcinogens, and - hence - have been the subject of government regulations and intensive scientific study. Several of the PAHs are known or suspected carcinogens (Alexander *et al.*, 1992): a list is provided in Table C-1.

Table C-1: List of PAHs with known mutagenic or carcinogenic activity.

benz(a)anthracene	dibenzo(a,l)pyrene,
dibenzo(a,h)anthracene	benzo(b)fluoranthene
benzo(a)pyrene	benzo(j)fluoranthene
dibenzo(a,h)pyrene	benzo(k)fluoranthene
dibenzo(a,e)pyrene	5-methylchrysene
dibenzo(a,i)pyrene	indeno(1,2,3-cd)pyrene

Benzo(a)pyrene, or BaP, is one of the most mutagenic of the PAHs.

"Substituted" PAHs exhibit other substituents at one or more positions around the arene ring structure; these substituents include alkyl-groups, chlorines and/or bromines, hydroxy-, dihydroxy-, or dihydrodiol- groups, arene oxides, methylsulfones, or other groups. There is a large body of scientific literature on unsubstituted PAHs, including studies of physicochemical properties, environmental fate, ecotoxicology and particulars of environmental degradation [Varanasi (1989) and Wilson and Jones (1993) provide good reviews]. **The environmental and toxicological significance of substituted PAHs, however, is largely unknown; yet alkyl-substituted PAHs, in particular, comprise a much greater portion of most petroleum deposits and products than unsubstituted PAHs.**

1.2 Scope

The lack of regulatory and outside scientific guidance for dealing with alkyl-PAH contaminants at AES sites in the Yukon and Northwest Territories prompted a review of the overall environmental and toxicological significance of this group of compounds. The following brief review specifically addresses what is known and what remains to be answered with regard to alkyl-substituted, or alkylated PAHs. The obvious intent of the review is to provide a basis for addressing a practical and immediate problem; that of alkyl-PAH

contamination of subsurface soils and water at some of the now-abandoned pumping stations along the Haines-Fairbanks pipeline.

The issues are also common to a large variety of other hydrocarbon-contaminated sites throughout the world, and at all latitudes, although the emphasis here is on alkyl-PAH fate and effects in arctic and sub-arctic environments. This review generally does not cover the unsubstituted PAHs (sometimes called parent PAHs) or PAHs with side-group attachments other than alkyl-groups. A review of unsubstituted PAHs was carried out very recently by the Canadian government (CEPA, 1994) (see Section 7).

From a practical view, outstanding questions about alkyl-PAHs as environmental contaminants include the following:

- Can the concentrations of alkyl-PAH in environmental samples be effectively ignored? (e.g., are alkyl-PAHs of limited environmental concern?)
- If not, can alkyl-PAH data be used effectively in a human health or ecological risk assessment?
- Can appropriate dose-response models be applied for the effective management of specific sites?
- Can appropriate cleanup strategies and triggers be devised for specific sites? Can generic guidelines be developed?
- What, if any additional knowledge is required to appropriately regulate alkyl-PAHs in the future?

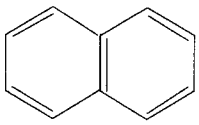
2. SOURCES, STRUCTURE AND OTHER PROPERTIES OF ALKYLATED PAHS

2.1 General Structure of PAHs

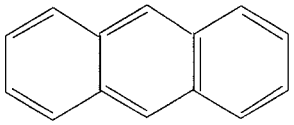
PAHs are often divided into two classes: low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAHs) (Figure C-1). LPAHs (e.g., naphthalene, acenaphthalene, fluorene, phenanthrene) tend to have a core structure of two to three arene rings (six-sided aromatic rings of carbon). HPAHs tend to have molecular structures of four or more arene rings, and include fluoranthene, pyrene, benzo(a)pyrene, and benzofluoranthenes. The discrimination between different PAHs based on molecular weight is a useful one, since the bioaccumulation, carcinogenicity, resistance to biodegradation, and overall environmental persistence generally increase with increasing molecular weight. LPAHs such as naphthalene tend to be more acutely toxic to aquatic organisms than HPAH since they are more water soluble.

The toxicity and environmental cycling of PAHs may be further modified by the presence of various molecular side groups around the central ring structure. Alkylated PAHs, having attached carbon-hydrogen chains (especially methyl groups, but also isopropyl or other alkyl groups), have been frequently identified in environmental samples. In addition, the environmental chemistry of halogenated PAHs, especially those containing chlorine or bromine atoms, is of strong current interest to several environmental chemists. These aromatic chloro- and bromohydrocarbons may be produced by the combustion of PCB oils, municipal waste incineration, fuel consumption, wood fires, or other methods. Processes such as pulp krafting or bleaching, waste water disinfection and wood preservative/pesticide manufacture could also produce halogenated PAHs (e.g., polychloroanthracenes, polychloropyrenes). Basic research on alkylated and halogenated PAHs in the environment has been very limited up to the last five to ten years; therefore, knowledge of environmental cycling or toxicity is very limited.

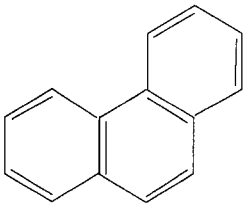
Figure C-1: Structure of some Common Unsubstituted, or Parent PAHs.



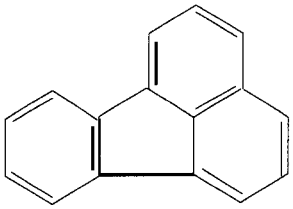
Napthalene



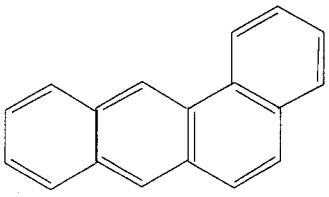
Anthracene



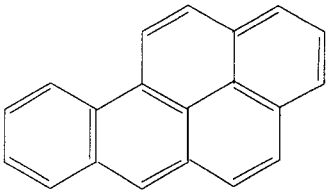
Phenanthrene



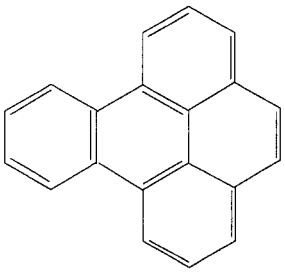
Fluoranthene



Benzo(a)anthracene



Benzo(a)pyrene



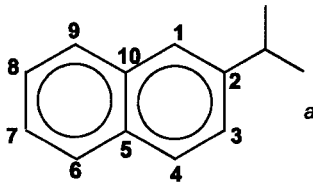
Benzo(e)pyrene

LPAHs

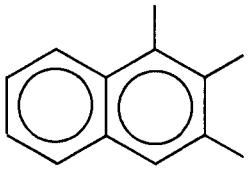
HPAHs

2.2 Alkyl-PAH Nomenclature and Analytical Considerations

Alkyl-PAHs can be analyzed as individual isomers (e.g., as 2,6-dimethylnaphthalene) as well as the sums of homologue groups (C0-, C1-, C2-, C3-, C4-, C5-,...) derived from total ion chromatograms using gas chromatographic/mass spectrometric analysis. For example -



and



2-isopropylnaphthalene **1,2,3-trimethylnaphthalene**

the two alkyl-PAHs shown above would have the same molecular weight, and would jointly be reported as C3-naphthalenes; i.e., naphthalene compounds with three carbons attached as part of side groups. Homologue group totals are derived assuming that all compounds with identical mass are structural isomers, and the chromatographic peaks do not represent other, unrelated compounds.

There are presently at least 18 commercially available authentic individual alkylated PAH standards (Table C-2).

Table C-2: Commercially available Alkyl-PAH Standards

1- methylnaphthalene	3,6-dimethylphenanthrene
2-methylnaphthalene	1-methyl-7-isopropylphenanthrene (retene)
2,6-dimethylnaphthalene	2-methylanthracene
2,3,5-trimethylnaphthalene	9,10-dimethylanthracene
2,3,6- trimethylnaphthalene	2-methylfluoranthene;
1-methylphenanthrene	1-methylpyrene
2-methylphenanthrene	2-methylpyrene
3-methylphenanthrene	3-methylbenz(j)aceanthrylene (3-methyl cholanthrene)
4-methylphenanthrene	7,12-dimethylbenz(a)anthracene

Dominant PAH homologues in petrogenic sources include naphthalenes and phenanthrenes/anthracenes with two to four alkyl- carbons, fluoranthenes/ pyrenes with one to three alkyl- carbons, and dibenzothiophenes with two alkyl- carbons (see Section 3). Analytical standards do not presently exist for many of these alkylated PAHs.

Individual scientists have synthesized alkylated PAHs in support of their basic research, including 11 isomers of x-fluoro-7-methyl-benz(a)anthracene (Newman, 1977), trimethylbenz(a)anthracenes (Newman and Huang, 1977), methylchrysenes (Hecht *et al*, 1978), or 33 trimethylphenanthrenes (Budzinski *et al*, 1993). Trimethyl- and dimethylphenanthrenes have been synthesized through the oxidative photocyclization of alkylstilbenes (Radke *et al*, 1990).

Another source of substituted PAHs for research is the National Cancer Institute (U.S.) repository, where compounds with possible carcinogenic activity are stored.

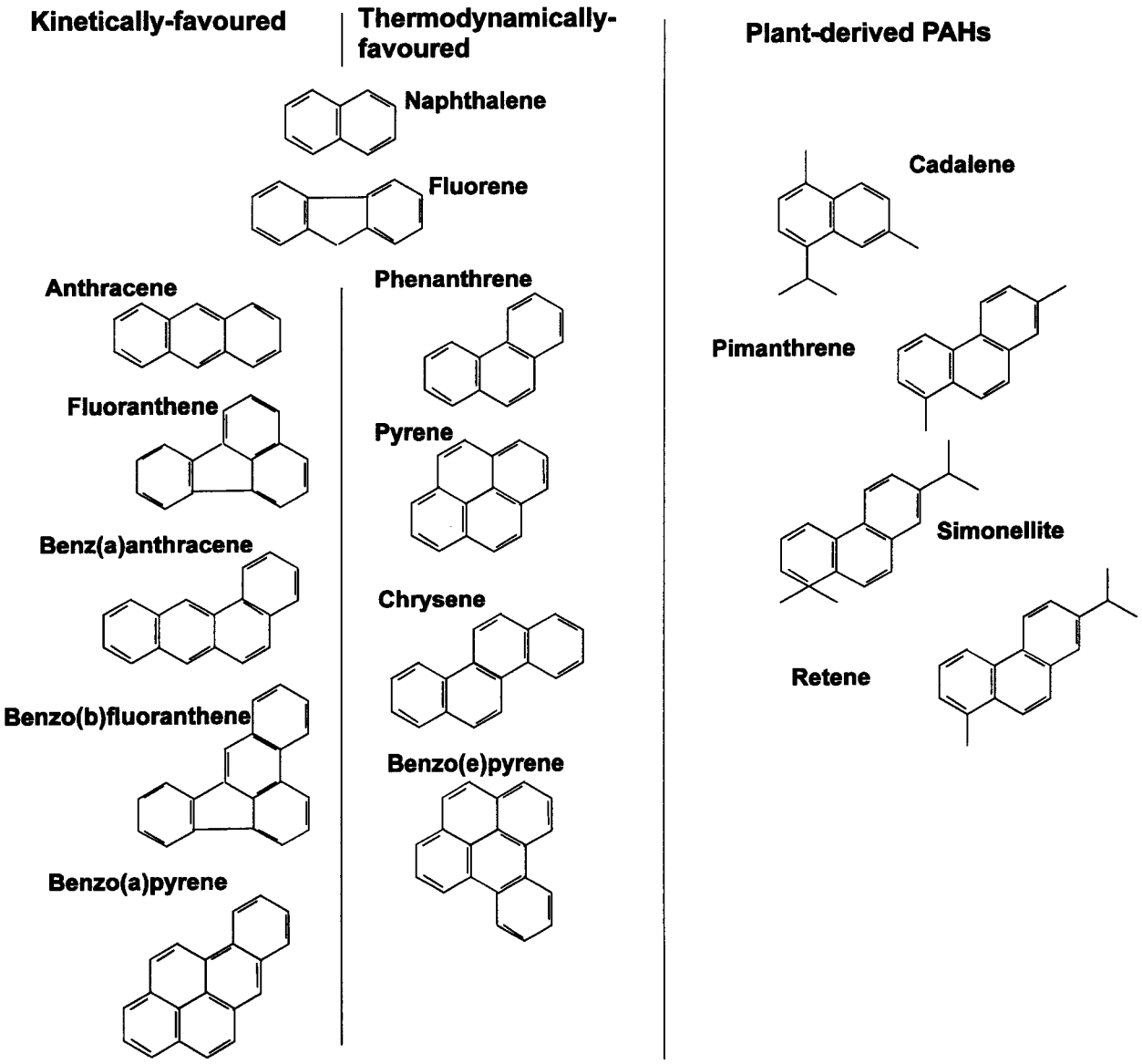
2.3 Sources

There is a complex mixture of unsubstituted and substituted PAHs in most environmental samples, the composition of which may depend on the source(s) of input, and possible environmental transformations (Figure C-2). The expected impact on the ecosystem may also be inferred from this composition. The signature, or compositional pattern of PAHs, for example, can be used to distinguish between combustion-based (pyrogenic) versus petrogenic inputs, or more recent, plant-derived PAHs. The PAH composition in contaminated environmental samples is also useful in delineating between different anthropogenic sources, especially in urbanized, industrialized areas.

Alkyl-PAHs and unsubstituted PAHs can be categorized as (i) kinetically-favoured: those preferentially produced through combustion processes; (ii) thermodynamically-favoured: PAHs which are energetically stable over long periods of time and tending to be progressively enhanced in more mature environmental/geological compartments such as crude oil or coal deposits; and (iii) PAH derived directly from plant products, and synthesized, at least in part, through biologically-mediated processes (Figure C-2).

A small number of both unsubstituted and alkylated PAHs are known natural products of plant and microbial compounds. The C4-phenanthrene *retene* (1-methyl-7-isopropal phenanthrene) may be derived from di- and triterpenoid precursors produced by plants (Bouloubassi and Saliot, 1993). Similarly, *pimanthrene* (1,7-dimethyl phenanthrene), *cadalene* (4-isopropyl-1,6-dimethylnaphthalene) and *simonellite* (1,1-dimethyl-1,2,3,4-tetrahydro-7-isopropylphenanthrene) may be produced from naturally-produced plant terpenoids (Yunker and Macdonald, 1995).

Figure C-2: Structure of Several Petrogenic, Pyrogenic, and Plant-Derived PAHs.



There is also limited evidence that the unsubstituted PAH perylene may be formed through natural, biologically-mediated, petrogenic, or combustion-type processes.

Some individual alkyl-PAH isomers have been identified as markers for specific anthropogenic sources (Figure C-2); for example, acenaphthene, acenaphythlene, 4,5-methylene phenanthrene and others.

2.4 Alkyl-PAH Source Signatures

Figures C-3 to C5 provide histograms of the relative distributions of alkylated and unsubstituted PAHs in various source materials and in some environmental samples. **The presence of alkylated PAH, especially those with two to four rings (e.g., alkyl-naphthalenes, alkyl-phenanthrenes) is highly indicative of a petroleum-based source (Law and Biscaya, 1994). In contrast, production or release of PAHs through combustion processes usually favours the release of unsubstituted or lesser-alkylated forms of PAH over more highly alkylated forms, and the proportion of alkylated to unsubstituted PAHs varies as a function of combustion temperature** (Aboul-Kassim and Simoneit, 1995). Coal and wood smoke, for example, contain a phenanthrene mixture with unsubstituted phenanthrene constituting the highest concentration, followed by an exponential decline in C1-homologues (phenanthrenes with one methyl group attached), then C2-homologues (two attached methyl group or two alkyl carbons), C3- and finally C4-homologues (Aboul-Kassim and Simoneit, 1995). Vehicular emissions peak at the C1-phenanthrene.

Diesel, in particular, contains high concentrations of 1- and 2-methylnaphthalene relative to unsubstituted naphthalene (Lee *et al.*, 1992: Table C-3).

Figure C-3: Some Representative Alkyl-PAH Source Signatures

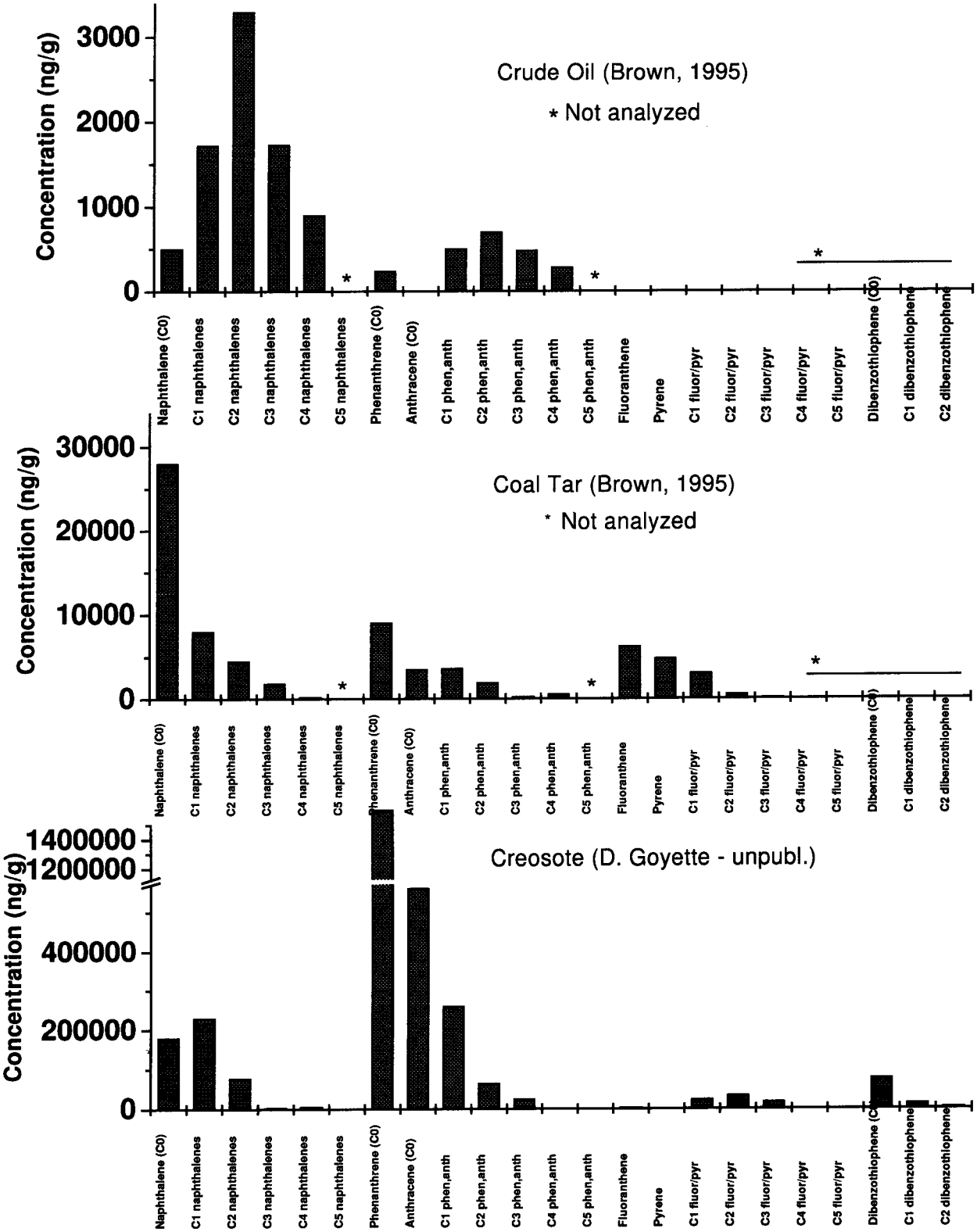


Figure C-4: Some Representative Alkyl-PAH Source Signatures

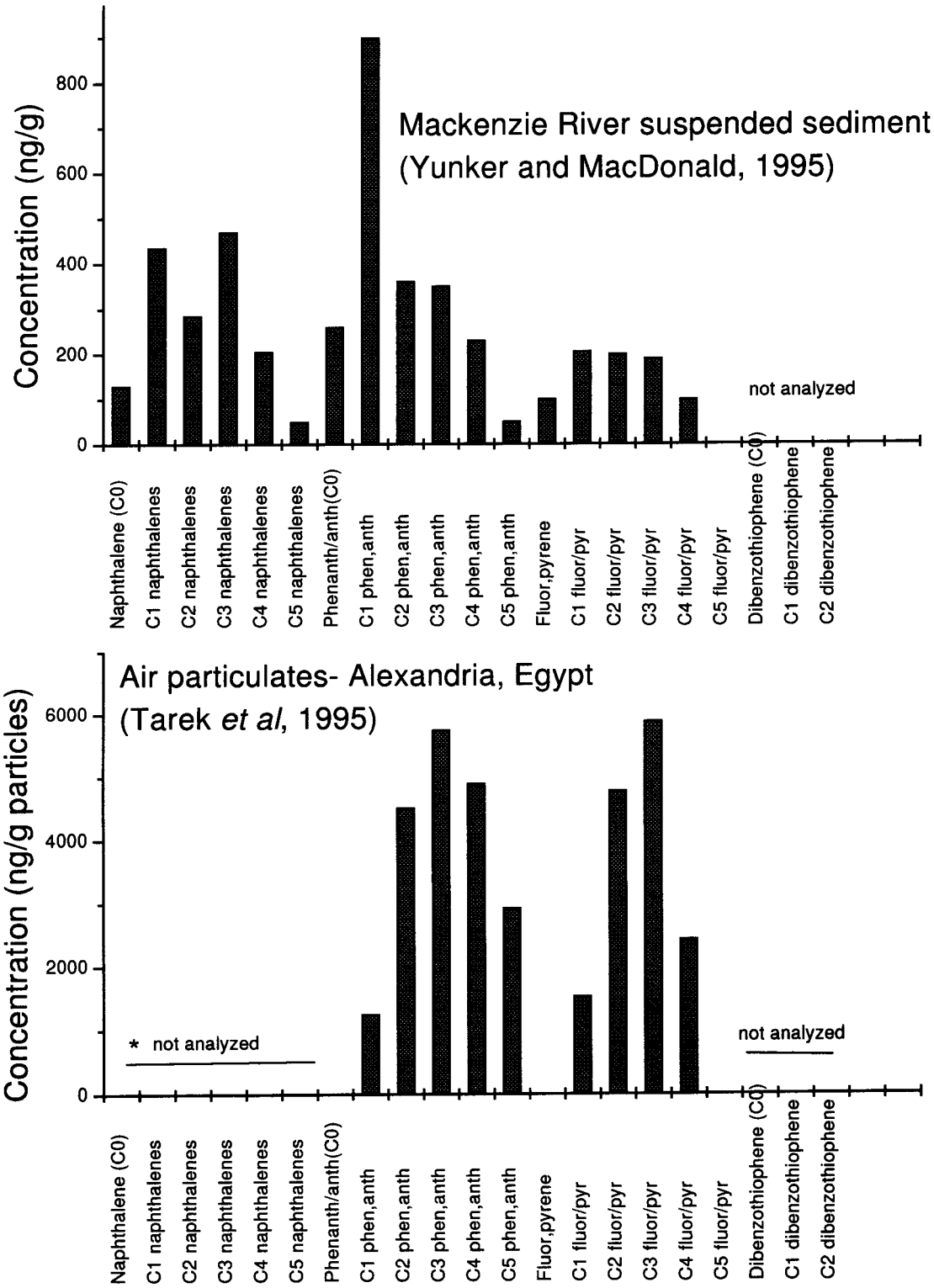


Figure C-5: Published Information on Environmental PAH Signatures

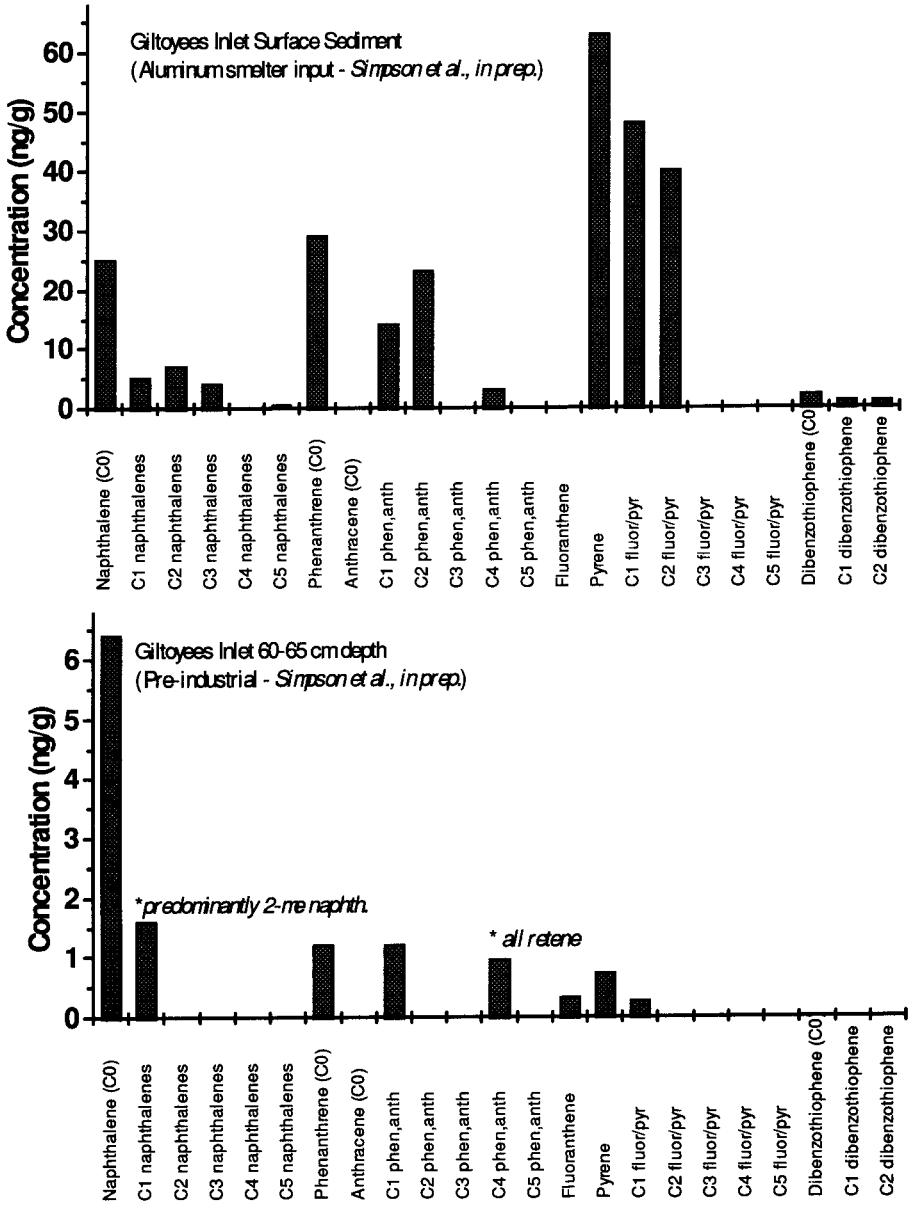


Table C-3: Concentration of Some Naphthalenes in Diesel, and Chemical Properties

Compound	Aqueous Solubility (25°C)	Log K_{ow} (±uncertainty)	Log K_{dw} (diesel-water partition coefficient -avg.)	conc. range (mg/L) in neat diesel
naphthalene	32	3.35 (0.1)	3.68	350-1,500
1-methylnaphthalene	27	3.87 (0.2)	4.30	2,000-4,000
2-methylnaphthalene	26	4.00 (0.2)	4.42	3,500-9,000

Coal tar tends to exhibit a strong dominance of unsubstituted PAH over alkylated forms, for both the naphthalene and anthracene + phenanthrene series, with a progressive decline in concentration associated with an increase in the extent of alkylation. Crude oil, on the other hand contains markedly more of the C2-homologue than either more- or less-highly alkylated forms (Brown *et al.,* 1995).

Yunker and Macdonald (1995) examined alkyl-PAH homologue distributions in suspended and deposited sediments from the Mackenzie River shelf, Beaufort Sea (Figure C-5). The relative contributions in the samples of C0 to C5 homologues for different PAH were as follows: The phenanthrene+anthracene series (3-ringed PAHs), and fluoranthene+pyrene series (4-ringed PAHs) exhibited a maximum average concentration for the C1-homologues. The naphthalenes exhibiting the highest concentrations were the C1 to C-3 homologues. The concentrations and pattern of PAHs and other hydrocarbons in the Mackenzie River samples was attributed to petrogenic sources; i.e., primarily natural relaeases from hydrocarbon deposits farther up the river; e.g., the Normal Wells oil field..

3. UNSUBSTITUTED AND ALKYL-PAH COMPOSITION OF HYDROCARBON-CONTAMINATED SOILS AND SEDIMENTS: EXAMPLES

Figure C-6 illustrates the relative concentrations of various PAHs in some samples collected from Arctic abandoned military sites by National Defence's Environmental Sciences Group in 1993 and analyzed for both unsubstituted and alkylated forms (Bright *et al.,* 1995).

The small subset of data shown are typical of alkyl-substitued and unsubstituted PAH data for hydrocarbon-contaminated soil samples from operational and abandoned military radar installations (including Distant Early Warning, or DEW Line sites) across the Canadian Arctic and the Canol Trail (Reimer *et al.*, unpublished data).

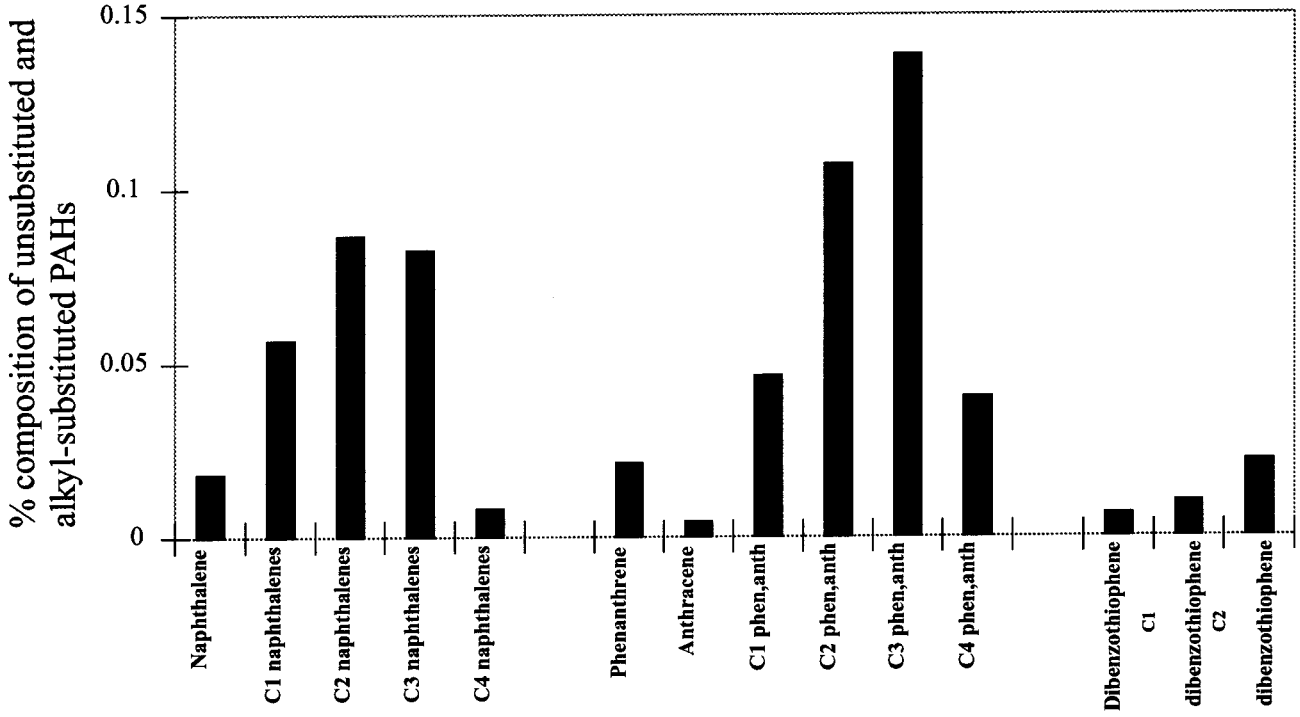
In sediments experimentally dosed with Hibernia crude oil (Hellou *et al.*, 1994) alkylated naphthalenes were the dominant PAHs present (30 to 60% of total concentration measures as the sum of 27 unsubstituted and alkylated PAHs). Flatfish, *Pseudopleuronectes americanus*, exposed to these sediments for four months accumulated a higher proportion of the alkylated naphthalenes relative to other PAH (alkylated naphthalenes accounted for 90-100% of the muscle PAH concentration).

4. SUBSTITUTED PAHS AS GEOCHEMICAL MARKERS

By far the greatest amount of research on alkyl-PAH has been carried out by organic geochemists interested in the origin, maturation and environmental redistribution of petroleum and coal constituents, as well as the large-scale redistribution of PAHs produced via combustion or from naturally-produced plant metabolites. Table C-4 lists some of the recent key references. The alkyl- and unsubstituted PAH composition, along with the composition of aliphatic hydrocarbons and other heterocyclic hydrocarbons, is useful in interpreting movements of natural and anthropogenically-produced materials in the environment. The studies also tend to include information on n-alkanes, alkenes, branched alkanes, cyclic alkanes (including terpenoid compounds such as hopanes and other plant steroidal residues), fatty acids, sterols (e.g. cholesterols); these tend to be biomarker compounds produced by terrestrial and aquatic organisms, and widely redistributed.

Figure C-6: Alkyl-PAH Signatures of Soil Samples from the Canadian Arctic.

a) Averaged Signature for Canol Trail Soils.



b) Averaged Signature for some Abandoned DEW Line Sites.

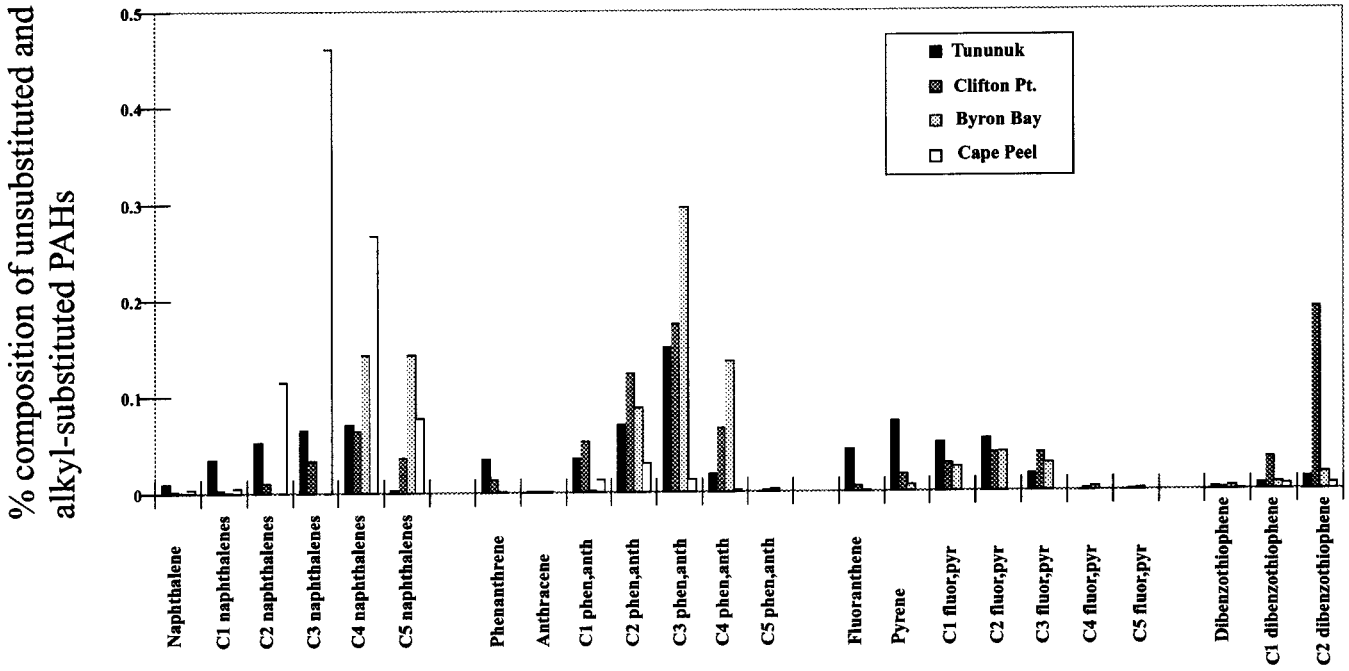


Table C-4: Examples of Organic Geochemistry Studies which Include Alkyl-PAH Data

Title	Reference
Dissolved, particulate and sedimentalry natrually derived polycyclic aromatic hydrocarbons in a coastal environment: geochemical significance.	Bouloubassi, I. and A. Saliot, 1993. Mar. Chem. 42: 127-143
Fluxes and transport of anthropogenic and natural poycyclic aromatic hydrocarbons in the western Mediterranean Sea.	Lipiatou, E. and A. Saliot, 1991. Mar. Chem., 32: 51-71.
Organic geochemistry of sediments from the continental margin off southern New England, U.S.A. - Part II. Lipids.	Venkatesan, M.I., E. Ruth, S. Steinberg and I.R. Kaplan, 1987. Mar. Chem., 21: 267-299.
Geochemistry and fluxes of hydrocarbons to the Beaufort Sea shelf: a multivariate comparison of fluvial inputs and coastal erosion of peat using PCA.	Yunker, M.B., R.W. Macdonald, B.R. Fowler, W.J.Cretney, S.R. Dallimore and F.A. McLaughlin, 1991. Geochim. Cosmochim. Acta, 55: 255-273.
Alkane, terpene and polycylclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie shelf: Riverine contributions to the Beaufort Sea coastal sediment.	Yunker, M.B., R.W. MacDonald, W.J. Cretney, B.R. Fowler and F. A. McLaughlin, 1993. Geochim. Cosmochim. Acta, 57: 3041-3061.
Maturity determination of organic matter in coals using the methylphenanthrene index.	Kvalheim, O.M., A.A. Christy, N. Telnaes and A Bjorseth, 1987. Geochim. Cosmochim. Acta, 51: 1883-1888.
Thermodynamic calculations on alkylated phenanthrenes: geochemical applications to maturity and origin of hydrocarbons.	Budzinski, H., Ph. Garrigues, M. Radke, J. Connan and J.-L. Oudin, 1993. Org. Geochem., 20: 917-926.
Distribution of naphthalenes in crude oils from the Java Sea: source and maturation effects.	Radke, M., J. Rullkotter and S.P. Vriend, 1994. Geochem. Cosmochim. Acta, 58: 3675-3689.

The relative concentrations of specific alkyl-PAH compounds have been used as tools by petroleum geochemists to reconstruct the origin and history of crude oil and coal deposits (Radke *et al.*, 1994; Budzinski *et al.*, 1993). As for different PAHs, different positional isomers of specific alkylated PAHs (e.g., 2-methyl- *versus* 4-methylphenanthrene) exhibit different thermodynamic stabilities, and more less stable isomers will tend to be preferentially converted to more stable isomers over time. Radke *et al.* (1982) demonstrated an increase in the abundance of 2- and 3-methylphenanthrene relative to 1- and 9-methylphenanthrene with an increase in the maturity of natural hydrocarbon deposits.

5. ENVIRONMENTAL FATE OF ALKYL-PAHS, INCLUDING ENVIRONMENTAL DEGRADATION

There are several reviews pertaining to the natural or enhanced degradation of unsubstituted PAHs or total extractable hydrocarbons in environmental samples (e.g.; Wilson and Jones, 1993; Aprill *et al.*, 1990; Bertrand *et al.,* 1989; Bossert and Bartha, 1986; Cerniglia, 1984; DeKreuk and Annokkee, 1988; Steiber *et al.*, 1990). The ability of bacteria and fungi to readily degrade PAHs containing three or fewer arene rings (e.g., naphthalenes and phenanthrenes) is well documented, and the scientific knowledge has been transferred into technologies appropriate for the bioremediation of sites contaminated with low molecular weight PAHs (LPAHs). Research is required, however, to extend our understanding of microbial biodegradation to examine influences of alkylation, using existing and freshly isolated microbial cultures, as well as field data. Specific questions of concern include whether the number and/or positions of alkyl- groups affect the rates of degradation of PAHs, and whether bacteria are important agents in the alkylation or dealkylation of PAHs.

Experimentally-derived and field data suggest that under aerobic conditions in soil and water, petrogenic unsubstituted LPAH may be rapidly degraded, and -hence- detoxified. **An increase in the degree of alkylation of the naphthalene and anthracene+phenanthrene series, however, appears to increase resistance to *in situ* break down**, as illustrated in Figure C-7. This is commonly indicated in field samples with historical rather than recent hydrocarbon inputs by the dominance of higher-alkylated (C4-, C5-substituted PAHs) over unsubstituted or lesser substituted forms (C0- to C3-). **Thus, alkylated naphthalenes and phenanthrenes occur in**

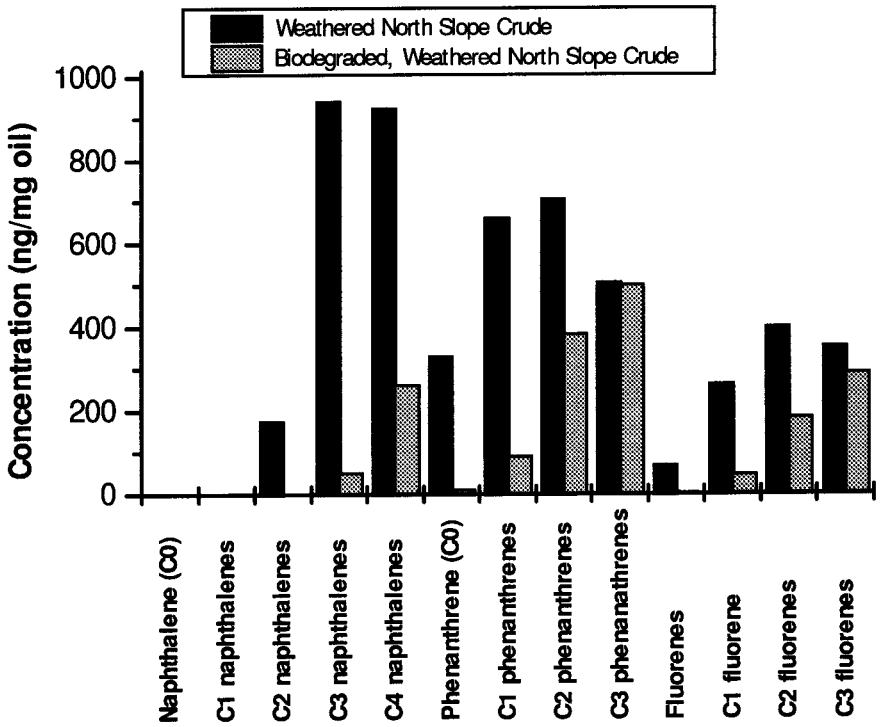
higher concentrations than unsubstituted naphthalenes and phenanthrenes, respectively, in petroleum based sources, and the degree of dominance further increases according to the extent of weathering in the environment. This tends to be the case for oil spills such as the Exxon Valdez spill (J.S. Brown, Arthur D. Little, Inc., *pers. com.*) and for hydrocarbon spills to terrestrial soils (*personal observations*). There is undoubtedly more information on alkyl-PAH degradation, and on the weathering of crude oils in the environment, in the grey literature (unpublished); we will continue to compile the information.

The apparent bias in degradation rates of PAHs with varying degrees of alkylation lead to two outstanding questions:

- **could the change in alkyl-homologue composition be used retrospectively to estimate *in situ* hydrocarbon degradation rates?**
- **does the change in composition due to differential degradation parallel a change in the risk to key receptors such as human beings, fish, wildlife, or other organisms?**

Neither of these two questions can be answered with any confidence based on the present state of knowledge.

Figure C-7: Possible Changes in PAH Composition Associated with Environmental Degradation



6. TOXICOLOGY AND RISKS OF ALKYL-PAHS

Possible concern over alkylated PAHs derives from both the routine occurrence of relatively high concentrations in hydrocarbon-contaminated environmental samples and the potential for adverse effects on living organisms. Lee *et al.* (1981) reviewed studies of the toxicity of alkylated PAHs relative to their unsubstituted (parent) analogues: Some alkylated PAHs are less toxic than the unsubstituted compound, whereas other alkylated forms are considerably more toxic. Chrysene, for example, is only slightly carcinogenic (cancer-causing), while 5-methylchrysene is a strong carcinogen. The location of alkyl groups around the ring structure may strongly influence carcinogenicity and other toxic effects; however, the existing theories on structure-activity relationships are not adequate to provide confident predictions of environmental risk.

Anthracene is generally considered to be non-carcinogenic, whereas 9,10-dimethylanthracene may be strongly carcinogenic (Searly, 1984). Similarly, unsubstituted benz[a]anthracene is classified as a weak carcinogen only, while 7- and 12-methylbenz[a]anthracene are more potent carcinogens, and 1- or 2-methylbenz[a]anthracene are aso only weakly carcinogenic. The C2-benz[a]anthracene 1,12-dimethylbenz[a]anthracene does not induce carcinogenesis in laboratory models, whereas 7,12-dimethylbenz[a]anthracene is strongly carcinogenic (Searly, 1984) and has been used extensively as a model carcinogen for cancer research. The effect of degree and position of methylation on carcinogenicity of benz(a)anthracene is apparent in Table C-3.

The relative carcinogenicity of different positional isomers (PAHs differing only in the position of the alkyl group) is probably related in part to the fact that PAHs must undergo metabolic activation in receptor organism to act as a carcinogen. It is the production of electrophilic, metabolic intermediates of PAHs that facilitates covalent bonding to the host cell DNA, leading possibly to neoplastic (cancerous) cell transformation. The position and number of alkyl groups will directly influence the stereochemistry (three dimensional molecular shape) of the 'activated' metabolic intermediates. Whereas 7,12-dimethylbenz[a]anthracene is strongly carcinogenic, 5,7,12-trimethylbenz[a]anthracene is not (Pullman, 1955).

Table C-5: Carcinogenic Activity of Unsubstituted and Alkyl-substitued Anthracenes (after Searly, 1984) ('-' inactive, '+' weak, '++' moderate, '+++' strong)

Compound	Experimentally Determined Activity
benz[a]anthracene	+
1-methylbenz[a]anthracene	±
2-methylbenz[a]anthracene	±
3- methylbenz[a]anthracene	±
4-methylbenz[a]anthracene	+
5-methylbenz[a]anthracene	+
6-methylbenz[a]anthracene	++
7-methylbenz[a]anthracene	+++
8-methylbenz[a]anthracene	++
9-methylbenz[a]anthracene	+
10-methylbenz[a]anthracene	+
11-methylbenz[a]anthracene	+
12-methylbenz[a]anthracene	++
1,12-dimethylbenz[a]anthracene	-
7,12-dimethylbenz[a]anthracene	++++

One metabolic pathway leading to formation of carcinogenic DNA adducts from unsubstituted benzo[a]pyrene involves enzyme-mediated biomethylation (enzyme-catalyzed attachment of a methyl- side group) in the receptor organism, to form 6-methylbenzo[a]pyrene. This is followed by oxidation of the methyl group to form a hydroxymethyl metabolite capable of reacting with DNA (Flesher, 1990; Stansbury *et al.*, 1994). Some methylated PAHs, therefore, appear to be more carcinogenic by virtue of the elimination of a requirement for an initial *in vivo* biomethylation step.

Carcinogenicity is only one of a large number of toxicological mechanisms whereby persistent organic contaminants can exert deleterious effects. The present scientific knowledge on mechanisms of toxicity other than mutagenicity or carcinogenicity is extremely limited. Knutzen (1995) summarized the ranges of acute toxicity of unsubstituted and alkyls-substituted PAHs to marine algae and animals (Table C-4). Ott *et al.* (1978) provide information on the relative toxicities of unsubstituted naphthalene or its methylated homologues to an estuarine copepod, *Eurytemora affinis*.

Table C-6: Acutely Toxic* PAH Levels (μg/L) to Aquatic Organism: Unsubstituted and Alkyl-PAH [after Knutzen (1995) - compiled from Neff (1979, 1985), NRC/Canada (1983) and Eisler (1987)].

Compound	Animals	Algae
Naphthalene	110-7,900 μg/L	2,800-96,000 μg/L
Monomethylnaphthalenes	1,000-3,400 "	1,700-4,500 "
Dimethylnaphthalenes	80-5,100 "	-
Trimethylnaphthalenes	320-2,000 "	-
Phenanthrene	30-1,100 "	200-1,000 "
Methylphenanthrenes	300-5,500 "	-
Anthracene	-	200 "
Fluoranthene	24-500 "	20 "
Benz(a)anthracene	10-1,000 "	5 (?) "
7,12-dimethylbenz(a)anthracene	<500 "	-
Benzo(a)pyrene	5->1,000 "	-

* Mostly LC_{50} concentrations: Concentration leading to mortality of 50% of organisms present, usually over a short exposure period (e.g., 24 to 96 h)

Overall, there appears to be little major difference in the acute toxicity of C1- or C2- versus unsubstituted PAHs, based on the very limited data available. The data, however, do not lead to rigorous interpretation, nor can they be used for generalized risk assessment predictions, since the ranges reported include a wide variety of different aquatic organisms, with different exposure regimes and metholodologies.

Näf *et al.* (1994) provide data on the concentrations of pyrene, 1-methylpyrene, and 2-methylpyrene in both marine sediments and Balthic clams, *Macoma balthica*, near a Swedish aluminu smelter. The relative tendency of the unsubstituted versus methylate pyrene to accumulate is indicated by the Biota-Sediment Accumulation Factor, "BSAF", which may be defined as -

$$(1) \qquad BSAF = \frac{\text{concentration of compound in organism } (\mu g/g \text{ dry wt.})}{\text{concentration of compound in sediment } (\mu g/g \text{ dry wt.})}$$

The BSAF for pyrene, 1-methylpyrene and 2-methylpyrene based on the data of Näf *et al.* was 1.25, 1.61 and 1.68 respectively, suggesting limited differences, if any, in the bioavailability of the monomethyl- versus unsubstituted pyrene.

We are not aware of any other information in the open literature on the effects of PAH alkylation on lipophilicity, bioavailability, resistance to metabolic breakdown and elimination in metazoa, hormone-like effects, effects on reproduction or development, or other factors associated with the health of individual organisms and ecosystems as a whole. **Overall, it is important to note that the scientific literature does NOT provide any compelling reason to dismiss alkylated PAHs as any less toxic than unsubstituted forms, either in association with their acute toxicity or carcinogenicity to mammals or other vertebrates.**

7. THE REGULATORY FRAMEWORK

The vast majority of government regulations or criteria in Canada make reference to only 16 of the parent or unsubstituted PAH compounds, namely those recommended as priority pollutants by the U.S. Environmental Protection Agency, World Health Organization, and European Economic Community. Regulations are essentially silent on the control or clean-up of alkylated forms, with minor exceptions: The "Criteria for Managing Contaminated Sites in British Columbia" include numerical guidelines for soils contaminated with 7,12-dimethyl benz(a)anthracene and 7-methyl cholanthrene, since these alkylated PAHs have been used extensively as model compounds in the study of carcinogenesis: both are widely recognized as extremely potent carcinogens.

At the federal level in Canada, PAHs were among a list of substances which were recently reviewed under provisions of the Canadian Environmental Protection Act (CEPA). The outcome of the review was that PAHs have been placed on the Toxic Substances List, which will require the adoption of amendments under CEPA within a limited time frame for the controlled production, release, and/or placement of limits on levels in the receiving environment.

Of particular note is that the CEPA review only addressed unsubstituted PAHs; substituted PAHs such as alkylated PAHs were excluded from the review, and there is little published scientific knowledge of environmental inputs, fates, or effects of alkylated PAHs.

> "Polycyclic aromatic hydrocarbons... ...are called "PAH derivatives" when an alkyl or other radical is introduced to the ring, and "heterocyclic aromatic compounds" (HACs) when any one carbon atom in a ring is replaced by a nitrogen, oxygen or sulphur atom. Heterocyclic aromatic hydrocarbons and PAH derivatives were not considered in this report since little is known about their presence in the Canadian environmnet." (Government of Canada, CEPA, 1994).

It is perhaps not surprising that various Canadian federal and provincial cleanup, remediation, or contaminated site criteria do not include numerical values for alkyl-substituted PAHs. Canadian Council of Ministers of the Environment (CCME) Soil Remediation Criteria or CCME "Draft Interim Sediment Quality Criteria" (CCME, 1995) provide no guidance on risks posed by alkyl-substituted PAHs at contaminated sites.

The United States Environmental Protection Agency (USEPA) has not promulgated any federal regulations or guidelines that deal specifically with alkylated PAHs either. Some jurisdictions have adopted as guidelines, criteria, standards, or regulations contaminated soil and sediment values; for example, Washington State Department of Ecology Sediment Quality Standards, or National Oceanographic Atmospheric Administration sediment "Effects Ranges"; however, alkyl-substituted PAHs have been overlooked.

Under the United States Compehensive Environmental Response, Compensation and Liability Act (CERCLA), commonly referred to as the "Superfund" program, specific remedial triggers at "National Priority List" sites are determined on a site-specific basis, usually after a complex risk assessment has been carried out. Many individual states, including Alaska (see UMA and Ambio, 1995) have developed guidance legislation for dealing with hydrocarbon contamination from above-ground and undeground storage tanks, but specifications are usually provided only for benzenes, toluene, ethylbenzenes and xylenes (BTEX) and for total petroleum hydrocarbons (TPH).

No guidance on dealing with alkyl-PAH contamination is available from European Community countries. According to Wilson and Jones (1993) -

> "Soil contamination has not been a priority of EC environmental policy until very recently, ... To date, no directive specifically defines guidelines or standards for clean up of contaminated soils with organic substances."

In essence, neither the European Community nor any of its member countries have adopted any regulatory guidance applicable to alkyl-substituted PAHs in the environment.

8. IMPLICATIONS FOR ENVIRONMENTAL MANAGEMENT

Alkyl-substituted PAHs, like their unsubstituted PAH counterparts are virtually ubiquitous in the global environment, and collectively are derived from a wide variety of anthropogenic and natural sources. Where source inputs to a given environmental compartment are primarily petrogenic (of a petroleum-based origin), as in the case of hydrocarbon spills to soils and water, the concentrations of alkyl-substituted naphthalenes, phenanthrenes and anthracenes are generally expected to be far greater than the concentrations of the analogous unsubstituted PAHs in the same sample.

Limited data suggest that alkyl-substituted PAHs cannot be dismissed as less toxic (e.g., carcinogenic or acutely lethal) than the more commonly regulated sixteen unsubstited PAHs. Given the apparent absence of regulatory guidance anywhere in the world, there is an obvious problem.

Under Canadian regulations, one possible interim solution in the conductance of a preliminary (CCME type II) risk assessment of contaminated soils or water would be to sum all of the alkyl-substituted and unsubstituted isomers of a PAH group; e.g. summed concentrations of C0- through C5-naphthalenes (C6-homologues and up have not been investigated to any great extent and the analytical methods have yet to be devised or modified), and to use the existing CCME interim soil, sediment or water quality criteria. The CCME Residential/Parkland Soil Remediation Criterion for naphthalene is 5,000 ng/g. In the absence of a detailed risk assessment, if the summed concentrations of all unsubstituted and alkyl-substituted naphthalenes was greater than 5,000 ng/g, then one approach would be either to remediate samples exceeding that trigger

concentration, or conduct more detailed studies of risk assessment. Similar approaches could be applied for phenanthrenes (CCME R/P Remediation Criterion = 5,000 ng/g) or other PAHs as well as for other contaminated matrices such as groundwater or drinking water.

The approach whereby criteria promulgated for unsubstituted PAHs are applied to alkyl-substituted forms is not very satisfactory, but may serve as interim guidance pending the availability of more knowledge. Whereas limited data suggest that some individual C1-, C2- and C3- PAHs may pose a similar risk to unsubstituted PAHs (Section 6), the same cannot be said for most C4-, C5- and higher alkylated PAHs. The weathering of hydrocarbons in the environment substantially alters PAH composition, with a progressive loss of unsubstituted and lower-substituted PAH relative to more highly alkylated forms (Section 5). Clearly, more information is needed.

In many investigations, PAHs are not measured at all. Instead, surrogate measures of hydrocarbon contamination, such as "oil and grease" (O&G) or "total petroleum hydrocarbons" (TPH) are used to devise and monitor the effectiveness of remedial measures. Because these surrogate measures include an extremely broad range of aliphatic, heterocyclic and aromatic hydrocarbons, which collectively exhibit an extreme range in toxicity, O&G or TPH cannot be credibly linked to environmental or human risk. These surrogate measures could be useful if they were strongly correlated with individual compounds for which the toxicity was known; however, any such correlations are likely to disappear over time and between different samples or areas: Different fractions of a complex hydrocarbon mixture are differentially partitioned between different environmental compartments and are degraded or removed at vastly different rates due to extremely large differences in aqueous solubility, volatility, lipophilicity and resistance to degradation. The net result is a substantial change in hydrocarbon composition and relative toxicity over space or time that would not be accompanied by a comparable change in 'TPH' concentration.

Some interim guidance can be provided, taking into account likely routes of exposure and ecological receptors on a site-specific basis. There is no *a priori* reason, for example to believe that alkyl-substituted naphthalenes or other PAHs are any less deleterious to fish than

unsubstituted forms where exposure concentrations are of similar magnitude. Under Canadian law, therefore, evidence of substantial inputs of alkylated PAHs to fish-bearing waters would have roughly the same implications under the Federal Fisheries Act as for unsubstituted PAHs. Conversely, where isolated hydrocarbon spills on surface and sub-surface soils are not accompanied by any plausible exposure pathway to major biological receptors, or where the spill is historical - provided no new impacts are expected and a reasonable rate of environmental recovery is occurring - the associated lack of evidence for human health or ecological risk would dictate only a limited requirement for remedial action.

Finally, what additional knowledge is required to appropriately regulate alkyl-PAHs in the future? Research is needed in at least two main areas: these are -

- establishment of the relative toxicities (acute and chronic lethality, carcinogenicity, sub-acute effects, *etc.*) of individual alkyl-substituted PAHs relative to unsubstituted PAHs, and as a function of the numbers and positions of substituent groups; and
- comparative studies of the environmental fate - especially associated with biodegradation - of alkylated PAHs.

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