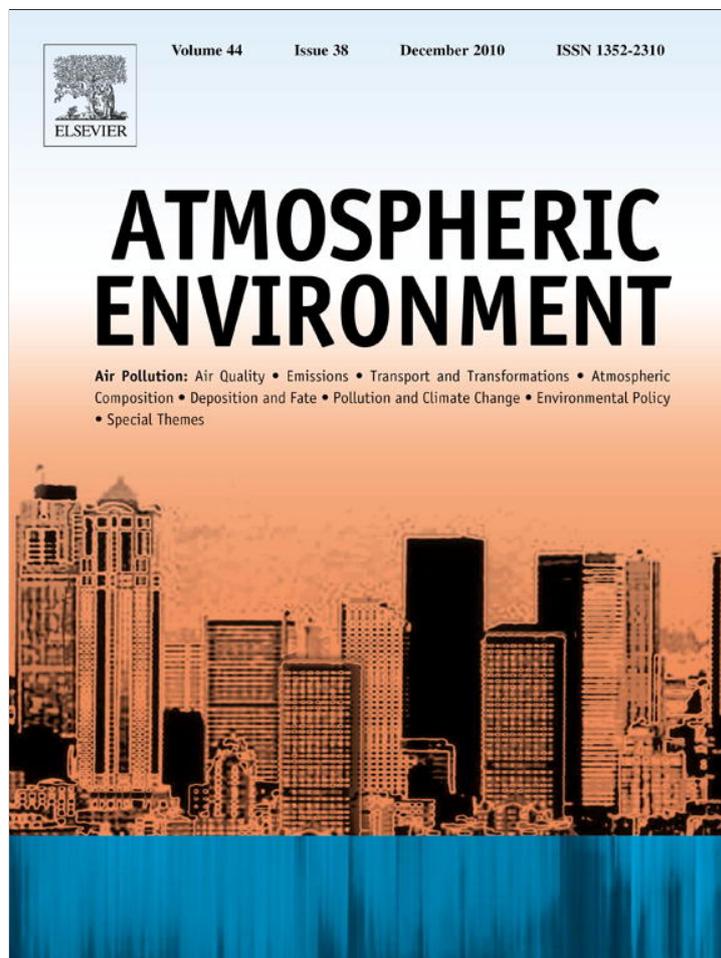


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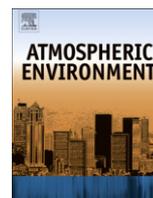
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## The gas/particle partitioning of polycyclic aromatic hydrocarbons collected at a sub-Arctic site in Canada

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## ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) were measured in air samples at a remote air monitoring site established in the Yukon Territory, Canada as part of a global project (International Polar Year; IPY) to study the potential for atmospheric long-range transport of anthropogenic pollutants to the Arctic. Gas- and particle-phase PAH were collected in polyurethane foam plugs and on glass fibre filters respectively from August 2007 to October 2009. PAH concentrations were found to be highest in the winter months and lowest in summer. The gas/particle partitioning coefficients of 3–5 ringed PAH were computed and seasonal averages were compared. In the summer time, lower molecular mass PAH exhibited relatively higher partitioning into the particle-phase. This particle-phase partitioning led to the shallowest slopes being recorded during summer for the log–log correlation plots between the PAH partition coefficients and their sub-cooled vapour pressures. Air mass back trajectories suggest that local impacts may be more important during the summer time which is marked by increased camping activities at camping sites in the proximity of the sampling station. In conclusion, both summer and wintertime variations in PAH concentrations and gas/particle partitioning are considered to be source- and phototransformation-dependent rather than dependent on temperature-driven shifts in equilibrium partitioning.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a class of ubiquitous organic contaminants that are made up of multiple fused benzene rings. They are products of incomplete combustion from both anthropogenic and natural sources. Some PAH are known to be mutagenic and potentially carcinogenic, thus, they could pose adverse health effects to higher organisms (Metcalf et al., 1990; International Agency for Research on Cancer, 2010). Many studies have shown significant correlations between anthropogenic pollution associated with particulate-bound pollutants, increased mortality rates and increased hospitalization rates for respiratory ailments and cardiovascular issues (Pope III et al., 2004, 2002; Jerrett et al., 2005). While there is still debate over whether these health effects are caused by particulate matter alone, the

compounds entrained in them or both (Harrison and Yin, 2000), a lot of knowledge has been garnered regarding the gas/particle partitioning behaviour of some of these pollutants.

PAH have been found in the Arctic and atmospheric long-range transport is believed to be a significant entry process of these contaminants (Halsall, 2004; Halsall et al., 1997). As part of many research activities initiated under the International Polar Year program (IPY), a Canadian project (IPY-INCATPA; INTERContinental Atmospheric Transport of Anthropogenic Pollutants to the Arctic) was created to study the potential for long-range atmospheric transport of a wide range of organic pollutants originating from lower latitudes to the sparsely populated high Arctic (Environment Canada, 2009).

The Canadian INCATPA air monitoring site is located in a mountainous region near Little Fox Lake (LFL) in Yukon Territory, Canada (61° 21' N, 135° 38' W; 1138 m a.s.l.) and is equipped with a high volume (Hi-Vol) air sampler for the collection of gas- and particle-phase contaminants including PAH. Levels of PAH in high altitude regions may be controlled by the surrounding topography

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(Choi et al., 2009). In the Arctic, the highest levels of PAH are usually observed during the winter months (Halsall et al., 1997). Halsall et al. reported that the haze period (November to April) is usually typified by high levels of anthropogenic aerosols, thus it is particularly important to study the changes that occur in PAH partitioning from summer to winter.

This work focuses on the temporal variation in the partitioning coefficients of common PAH collected in a sub-Arctic environment.

## 2. Experimental section

### 2.1. Air sampling

Weekly air samples were collected at the Little Fox Lake, Yukon site (LFL; see Fig. S1; Supporting Information for a map of all INCATPA sites) from August 2007 to October 2009. Over the course of the project, two daily sampling events were initiated between August 26 – September 08, 2007 and September 15 – September 28, 2008. Most of the weekly sampling was continuous; however, in 2009, three months of sampling were missing due to maintenance issues with the sampler. This study focuses on all samples collected from August 2007 to December 2008. Gas- and particle-phase samples were collected on two inline polyurethane foam (PUF) plugs and on glass fibre filters (GFF) respectively housed in a high volume (Hi-Vol) air sampler. This Hi-Vol air sampler has been previously described (Halsall et al., 1997). The Hi-Vol sampler was fitted with a 10 µm diameter particle size selective inlet and the flow rate was calibrated so that approximately 12000 m<sup>3</sup> of air was collected over a seven-day period. To minimize sample handling and the potential for human error at this fairly remote site, total suspended particulates (TSP) were not sampled or determined at LFL during the course of this project. PM<sub>2.5</sub> were however collected at a National Air Pollution Surveillance Program (NAPS) sampling station (NAPS House, Whitehorse, Yukon) situated relatively close to LFL.

### 2.2. Sample extraction and clean-up

All samples were subjected to Soxhlet extraction in hexane for a period of 24 h. All extractions were carried out by Airzone One Ltd. (Mississauga, ON, Canada). After extraction, a complete sample set comprised raw extracts from one glass fibre filter (GFF) and two polyurethane foam plugs (PUF). Previous studies with the same Hi-Vol sampler model under similar conditions had shown that the potential for breakthrough from the front to the back PUF was very low (Halsall et al., 1997), thus, the PUF raw extracts were combined before further analysis.

**Table 1**

Geometric and arithmetic means, standard deviation (S.D.) and method detection limits (MDL) for 12 PAH (in pg m<sup>-3</sup>) monitored in gas- (PUF) and particle- (Filter) phase samples from Little Fox Lake, Yukon, Canada between August 2007 and December 2008. PAH in boldface are used for gas/particle partition modeling.

PAH	Abbreviation	PUF				Filter			
		Geometric Mean	Arithmetic Mean	S.D.	Mean MDL	Geometric Mean	Arithmetic Mean	S.D.	Mean MDL
<b>fluorene</b>	FLUOR	23	50	61	5.8	0.99	2.5	3.8	1.8
<b>phenanthrene</b>	PHEN	67	92	85	43	5.9	20	31	16
<b>anthracene</b>	ANTH	2.2	5.1	11	3.6	0.41	1.8	3.2	0.39
<b>fluoranthene</b>	FLUORT	14	22	23	12	3.4	9.1	15	2.6
<b>pyrene</b>	PYR	14	25	31	31	5.7	17	32	7.8
retene	RET	34	57	80	13	5.5	18	33	1.1
<b>benz[a]anthracene</b>	BAA	0.59	1.2	1.9	0.22	0.71	2.4	5.8	0.27
<b>chrysene</b>	CHRY	1.5	3.3	4.4	0.84	1.2	3.7	6.6	0.30
<b>benzo[b]fluoranthene</b>	BBF	0.50	0.80	0.68	0.24	1.2	3.8	7.2	0.080
<b>benzo[k]fluoranthene</b>	BKF	0.24	0.52	0.56	0.24	0.87	2.8	4.7	0.080
<b>benzo[e]pyrene</b>	BEP	0.26	0.41	0.37	0.21	0.83	2.5	4.2	0.070
benzo[ghi]perylene	B_GHI_P	0.040	0.10	0.090	0.71	0.80	2.0	3.0	0.14

One half of each raw extract was further cleaned-up at the National Laboratory for Environmental Testing (NLET, Environment Canada, Burlington, ON, Canada) using NLET protocols for pre-existing Arctic sites monitoring programs. Briefly, raw extracts were evaporated to 1 mL under nitrogen and transferred onto a silica gel column (8 g, activated overnight at 160 °C) wet packed with top and bottom anhydrous sodium sulphate plugs (1 cm, fired at 600 °C). Elution with hexane (70–90 mL) afforded Fraction A while elution with hexane/dichloromethane (1:1, v/v 130 mL) afforded Fraction B. Fractions A and B were evaporated, reduced under nitrogen, and solvent-exchanged into iso-octane (1 mL).

### 2.3. GC/MS analysis and quality control

All GC/MS analyses were performed at NLET and all quality control parameters applied to this study met or exceeded the basic criteria for acceptable data. For PAH analysis, a 100 µL aliquot of each sample was obtained by combining 45 µL each of Fractions A and B and adding 10 µL of internal standard solution containing three deuterated PAH. Relative response factors for each PAH were obtained by running six calibration standards containing the target compounds in concentrations ranging from 10 to 2000 pg µL<sup>-1</sup> on an Agilent 6890 gas chromatograph/5973 mass selective detector system using electron impact ionization (EI<sup>+</sup>) in selected ion monitoring (SIM) mode and equipped with a J&W DB-5ms column (30 m × 0.25 mm internal diameter, 0.25 µm film). Twenty-one PAH and 4 other polycyclic aromatic compounds were routinely quantified by this protocol where possible. Four deuterated PAH surrogates were spiked into the raw extracts and method blanks before silica gel clean-up and recoveries ( $n > 200$  samples) were: naphthalene-d<sub>8</sub>, 93.3 ± 11.4%; fluorene-d<sub>10</sub>, 101 ± 11.7%; pyrene-d<sub>10</sub>, 104 ± 10.9%; perylene-d<sub>12</sub>, 94.2 ± 10.5%. In all a total of thirteen compounds (indene, naphthalene, 1- & 2- methyl-naphthalene, acenaphthylene, acenaphthene, tetrahydronaphthalene, β-chloronaphthalene, dibenzothiophene, perylene, indeno[1,2,3-cd]pyrene, benzo[a]pyrene, dibenz[a, h]anthracene) were excluded from further data interpretation either because their concentrations were consistently below their method detection limits in one or both phases or they had poor sampling efficiencies. Field blanks comprising pairs of GFF and PUF were collected once every 4 weeks for the weekly samples and once a week for the daily samples over the course of a year and were subjected to the same sample preparation and analytical schemes as the real samples. Method detection limits in pg m<sup>-3</sup> (determined as yearly mean concentration of PAH for all field blanks + 3S.D) for PAH of interest can be found in Table 1.

2.4. Data analysis

Data used in this work have been blank corrected. The 12 PAH remaining after initial data screening were used for this work even though benzo[ghi]perylene was almost exclusively found in the particle-phase making its partition coefficient incalculable in > 95% of the samples. Parameters for computing temperature-dependent constants  $\log P_L^0$  were readily available for all compounds except retene and were sourced from the recent reports of Ma et al. (2010) and elsewhere when necessary (e.g. parameters for chrysene, benzo[b]fluoranthene, & benzo[k]fluoranthene were from (Odabasi et al., 2006) and benzo[e]pyrene from (Hinckley et al., 1990)) for log–log relationships with the partition coefficients. All data analyses were performed in a spreadsheet (Microsoft Excel, Microsoft Office 2003).

Five-day air mass back trajectories were obtained from the Canadian Meteorological Centre (CMC) for LFL and were plotted using a GIS mapping program (ArcGIS 9.3).

The partitioning between the gas- and particle-phase for many freely exchangeable organic contaminants may be correlated with their sub-cooled vapour pressure (Pankow, 1987; Lohmann and Lammel, 2004). At equilibrium, in the absence of sampling artefacts, and assuming that the organic compound is completely available for gas–particle exchange from the sorbent material, its partitioning coefficient may correlate fairly well with its vapour pressure by the linear equation below for both adsorption and absorption phenomena (Pankow, 1998).

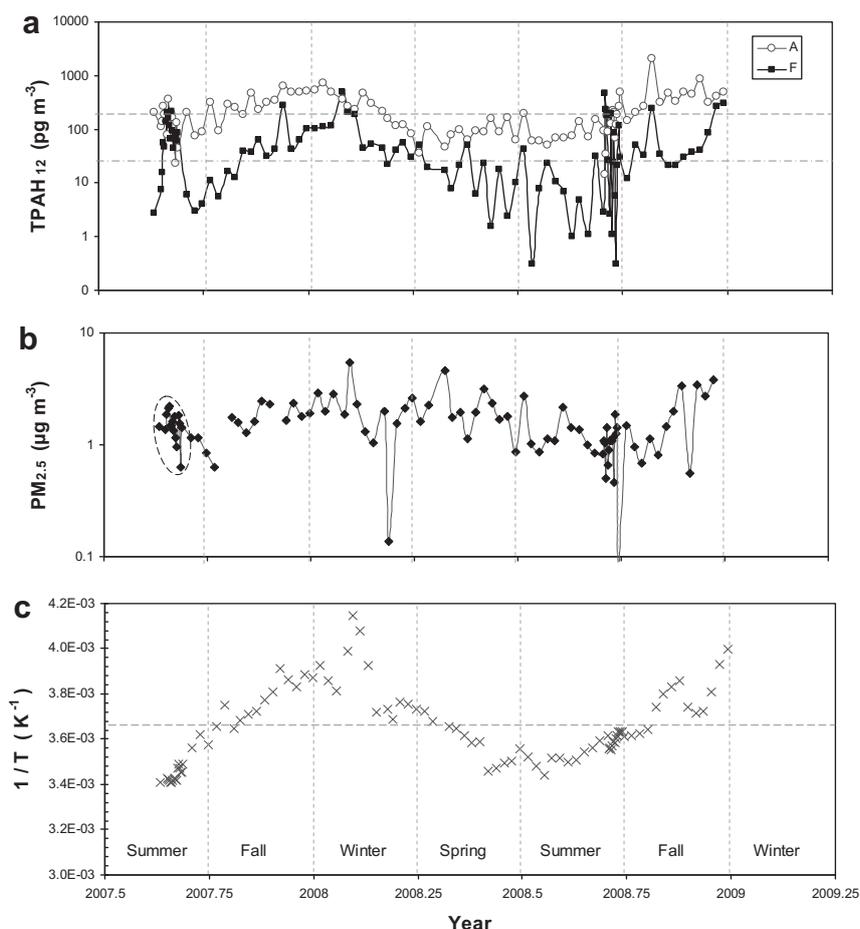
$$\log K_p = m \log P_L^0 + b \quad (1)$$

As noted in Section 2.1 above, TSP were not collected at LFL. Freely available data for  $PM_{2.5}$  collected at a NAPS sampling station situated relatively close (60° 42' N, 135° 3' W, 669 m a.s.l.; <http://www.etc-cte.ec.gc.ca/napsdata/main.aspx?dir=D%3a%5cexternal%5cclients%5cRiver%5cnapsdata%5cDATA>) to LFL were used as TSP surrogates for the computation of  $\log K_p$  in relevant portions of this study. This assumption was made because the bulk of PAH are known to partition to particulate matter with effective diameter < 2.5  $\mu m$  (Chrysikou and Samara, 2009; Kaupp and McLachlan, 1999, 2000; Liu et al., 2006; Venkataraman et al., 1994; Venkataraman and Friedlander, 1994). Furthermore, data from the work of Kaupp and McLachlan at a temperate sampling site show that  $PM_{2.5}$  accounts for  $\geq 70\%$  of all particulate matter collected in February (winter) and August (summer) (Kaupp and McLachlan, 1999).

3. Results and discussion

3.1. Temporal variation of PAH in the gas- and particle-phase

The plot in Fig. 1 is a time series of the sum of the concentrations of 12 PAH (TPAH<sub>12</sub>, see Table 1 for the PAH) in the gas- and particle-phase. As noted above, the other PAH were not included because



**Fig. 1.** (a) Temporal variation of blank-corrected TPAH<sub>12</sub> in the gas- and particle-phase at LFL (A; top line with open circles and F; bottom line with square blocks respectively). Horizontal dashed lines (upper and lower) in (a) represent the geometric means of the TPAH<sub>12</sub> in the gas- and particle-phase respectively. (b) Temporal variation of  $PM_{2.5}$  collected at the closest PM sampling site. The  $PM_{2.5}$  data has been averaged to reflect the same sampling frequency as the PAH measurements. The ellipse is explained later. (c) Variation of temperature at sampling site. Dashed line represents arithmetic mean temperature for period of study (1.24 °C).

their levels were below zero after blank correction or due to poor extraction recoveries stated above. The PAH concentrations at this site are higher in fall-winter than in spring-summer. The gas-phase PAH dominate the entire time series at this sub-Arctic site but the colder period (fall-winter) shows an enrichment of the particle-

phase PAH by a factor of about 2 when compared to the spring-summer of 2008. This is in agreement with the observed trend for a monitoring site at Tagish, Yukon (60° 20' N, 134° 12' W) reported by Halsall et al. (1997); this location is proximate to the Little Fox Lake site but is now decommissioned).

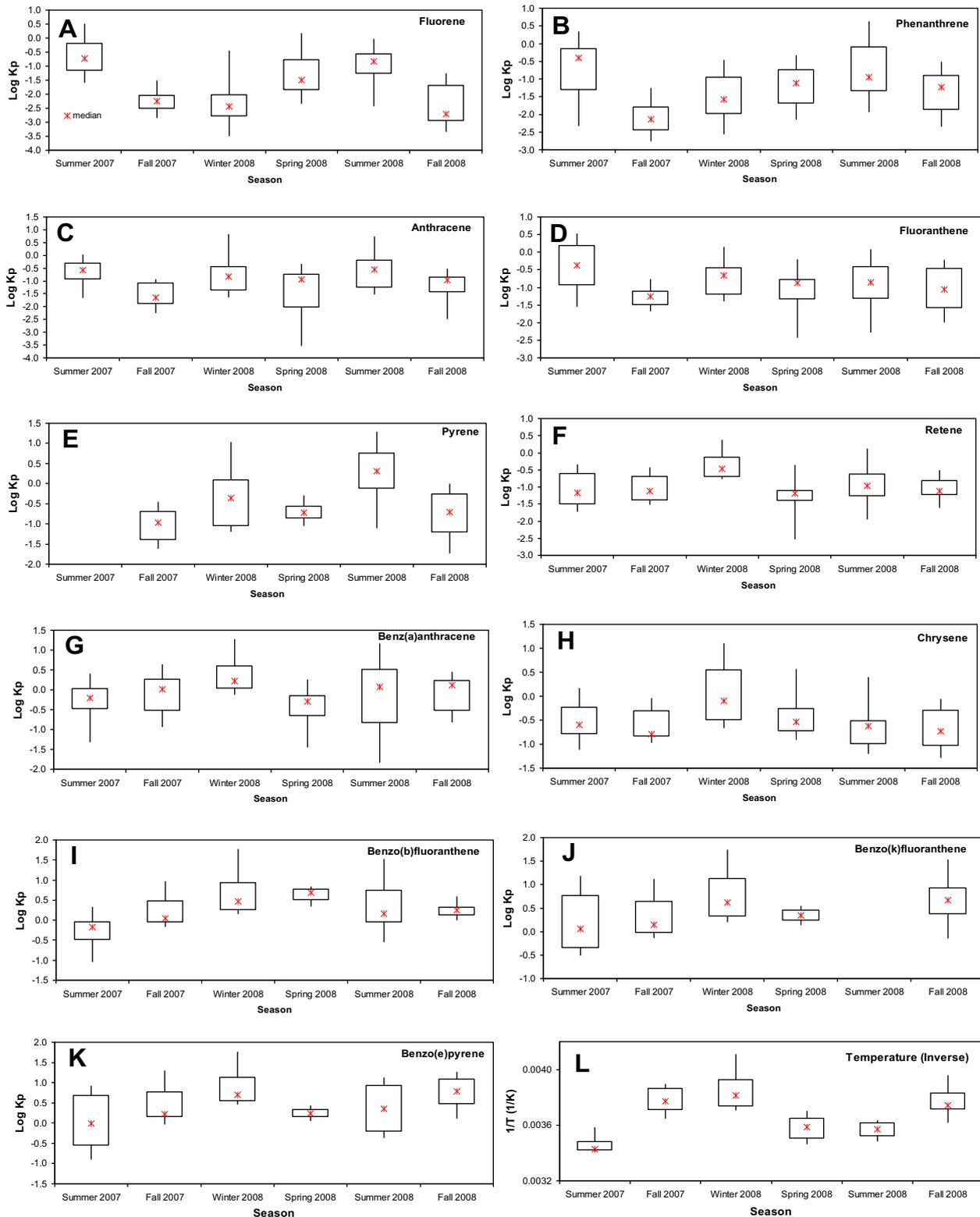
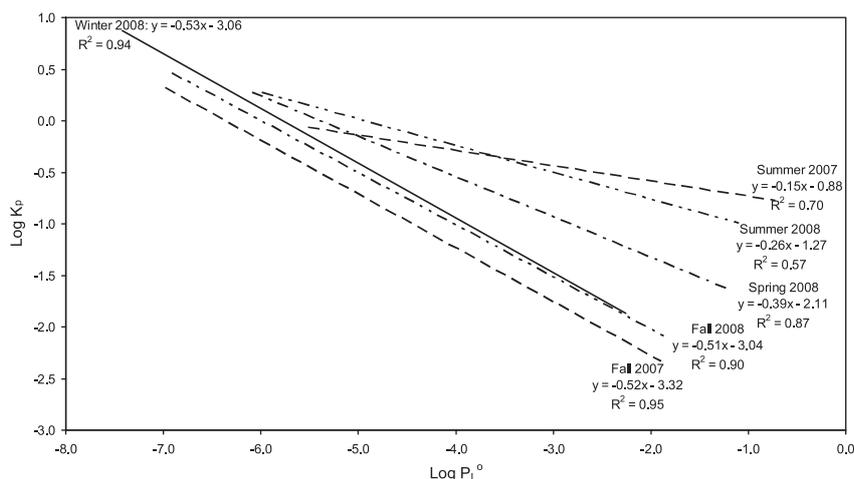


Fig. 2. Box and whisker plots of the seasonal of averages log  $K_p$  for 11 PAH and temperature measured at LFL between August 2007 and December 2008. The error bars represent the 5th and 95th percentiles and the star represents the median value.



**Fig. 3.** Average  $\log K_p$  versus  $\log P_L^0$  for 10 PAH (benzo[ghi]perylene partitioned almost exclusively into the particle-phase; the parameters for computing the temperature-dependent sub-cooled vapour pressure for retene are not readily available) collected at Little Fox Lake classed by seasons between August 2007 and December 2008.

The plots in Fig. S2 reveal that PAH with molecular mass 228–276 Da are the ones getting enriched in the particle-phase in the fall-winter months and are thus responsible for the increase in particle-phase TPAH<sub>12</sub> observed during this period.

The middle plot (Fig. 1b) also reveals the seasonality of PM<sub>2.5</sub> with greatest levels in the winter of 2008, though other 2008 maxima can be found in the spring and summer times. Interestingly, the winter maximum for PM<sub>2.5</sub> does not exactly coincide with the 2008 winter maximum for most particle-bound PAH. This may indicate that the sample with highest PAH levels recorded in winter of 2008 has different source origins from the sample/period with the highest PM<sub>2.5</sub>.

PAH levels were lower in summer than during any other season resulting in some heavier molecular mass PAH diminishing below their method detection limits mainly in the gas-phase. Winter samples on the other hand had the highest total PAH concentrations measured and showed enrichment in particulate phase PAH.

This seasonality was investigated further by the use of a classical phase change relationship at equilibrium. The phase change from liquid or solid to gas for most organic compounds including persistent organic pollutants (POP) can be predicted by their enthalpies of vaporization or sublimation using the thermodynamic relationship in the Clausius–Clapeyron equation (Atkins, 1994) which yields a negative slope (i.e., concentration/partial pressure decreases with temperature) when the natural logarithm of the pressure  $\ln P$  is plotted against the inverse of the absolute

temperature  $1/T$  (see examples of PCB in (Hillery et al., 1997)). The negative slope of the plot is equal to  $-(\Delta_{\text{vap}}H/R)$  and the enthalpy of the phase change is a positive number calculable by multiplying the slope by  $R$ , the gas constant. Using the ideal gas equation, concentrations of the most abundant gas-phase PAH were converted to partial pressures in atmospheres and the plots in Fig. S3 show the temperature dependence of their  $\ln P$ . Only two PAH (phenanthrene and pyrene) yielded negative slopes albeit insignificant at the 95% confidence level for pyrene. The others had statistically significant positive slopes which is anomalous for phase changes predictable due to enthalpies alone. Gas-phase PAH concentrations at this site generally increase with a decrease in average temperature. Clearly, some other mechanism(s) is at work with regards to PAH which cannot be captured by phase change thermodynamics alone. Cortes et al. observed similar phenomena with gas-phase PAH collected near the Great Lakes (Cortes et al., 2000) and suggested that other seasonal sources (e.g. wintertime residential heating) which were not correlated with the ambient temperature may be responsible.

### 3.2. Seasonal variation of gas/particle partitioning behaviour of PAH at LFL

The partitioning of PAH between the gas- and particle-phases also exhibits seasonality for some PAH.

**Table 2**

Particle fraction  $\phi$  for 11 PAH collected from August 25, 2007 to September 08, 2007. Particle fraction values greater than 0.1 have been highlighted for lower molecular mass PAH (166–202 Da). Missing values indicate a mathematically impossible solution.

SAMPLE COLLECTION END DATE	FLUOR	PHEN	ANTH	FLUORT	PYR	RETENE	BAA	CHRY	B_B_F	B_K_F	B_E_P
26/08/2007	<b>0.22</b>	<b>0.060</b>	<b>0.13</b>	<b>0.22</b>		0.0		0.19	0.15	0.0	0.0
27/08/2007	<b>0.18</b>	<b>0.21</b>	<b>0.10</b>	<b>0.25</b>		0.040	0.0	0.17	0.39	0.45	0.45
28/08/2007	<b>0.11</b>	<b>0.17</b>	<b>0.35</b>	<b>0.25</b>		0.17	1.0	0.35	0.60	0.92	0.95
29/08/2007	<b>0.60</b>	<b>0.52</b>	<b>0.32</b>	<b>0.55</b>	<b>1.0</b>	0.28	0.64	0.29	0.31	0.63	0.27
30/08/2007	<b>0.80</b>	<b>0.76</b>	<b>0.33</b>	<b>0.76</b>	<b>1.0</b>	0.50	1.0	0.42	0.53	1.0	1.0
31/08/2007	<b>0.28</b>	<b>0.40</b>	<b>0.28</b>	<b>0.37</b>	<b>1.0</b>	0.070	1.0	0.21	0.40	0.43	1.0
01/09/2007	<b>0.29</b>	<b>0.47</b>	<b>0.40</b>	<b>0.61</b>	<b>1.0</b>	0.070	0.33	0.44	0.52	0.89	0.12
02/09/2007	<b>0.59</b>	<b>0.38</b>	<b>0.19</b>	<b>0.68</b>	<b>1.0</b>	0.12	0.61	0.31	0.79	0.95	1.0
03/09/2007	<b>0.40</b>	<b>0.54</b>	<b>0.57</b>	<b>0.73</b>	<b>1.0</b>	0.24	1.0	0.40	0.53	1.0	1.0
04/09/2007	<b>0.21</b>	<b>0.40</b>	<b>0.50</b>	<b>0.61</b>	<b>1.0</b>	0.17	0.47	0.43	0.49	0.92	1.0
05/09/2007	<b>0.21</b>	<b>0.42</b>	<b>0.25</b>	<b>0.47</b>		0.050	0.0	0.31	0.58	0.47	0.93
06/09/2007	<b>1.0</b>	<b>0.80</b>	<b>0.42</b>	<b>1.0</b>	<b>1.0</b>	0.43	0.49	0.52	0.12	1.0	1.0
07/09/2007	<b>0.29</b>	<b>0.31</b>	<b>0.24</b>	<b>0.55</b>		0.21	0.68	0.50	0.53	0.62	1.0
08/09/2007	<b>0.91</b>	<b>0.73</b>	<b>0.42</b>	<b>0.97</b>		0.26	0.72	0.67	0.52	0.97	1.0

Statistical evaluation of the seasonal  $\log K_p$  averages using the Welch  $t$ -test for comparing arithmetic means with unequal sample sizes and variances (Welch, 1947) shows that the heavier PAH (especially benzo[*k*]fluoranthene and benzo[*e*]pyrene) had partitioning coefficients that were usually not statistically different in the consecutive progression from one season to the next. The lightest PAH fluorene, however, had partitioning coefficients that were statistically different from Summer 2007 to Fall 2007, Winter 2008 to Spring 2008, and Summer 2008 to Fall 2008. Other lower molecular mass PAH (phenanthrene, anthracene, fluoranthene and pyrene) had  $\log K_p$  averages with varying statistically significant differences from Summer 2007 to Fall 2008. In general winter  $\log K_p$  were usually statistically different from the preceding or succeeding season. A summary of the side-by-side comparisons of all the seasons and the summer vs. winter periods can be found in the Supplementary information section and Fig. 2 below shows the seasonal variations in the  $\log K_p$  for 11 PAH in box and whisker plots.

A plot of the seasonal averages of  $\log K_p$  against the temperature-dependent  $\log P_L^0$  using ten PAH (benzo[*ghi*]perylene partitioned almost exclusively into the particle-phase, thus  $\log K_p$  could

not be computed; the parameters for computing the temperature-dependent sub-cooled vapour pressure for retene are not readily available) is shown below in Fig. 3 for representative purposes only while Table S3 in the Supplementary information section contains all the individual  $m$  and  $b$  parameters for each of the weekly and daily samples. In general, the regression lines have steeper slopes in the fall/winter period in comparison with the spring/summer period.

During the spring/summer period, it appears that the lower right end of the plot where lower molecular mass PAH are found experiences a boost in partitioning to the particle-phase. This may arise from filter sorption artefacts in which gas-phase PAH are co-collected on the filters. While filter sorption artefacts were not explicitly investigated in this study, it is not expected to be the main reason for the spring/summer time increase in particle-phase sorption of lower molecular mass PAH because the increasingly warmer temperatures during this time of the year is expected to preferentially favour their partitioning to the gas-phase. Thus, we speculate that these spring/summer deviations may be a case in which the particle-bound lower molecular mass PAH are not totally available for gas-particle exchange but are still largely extractable

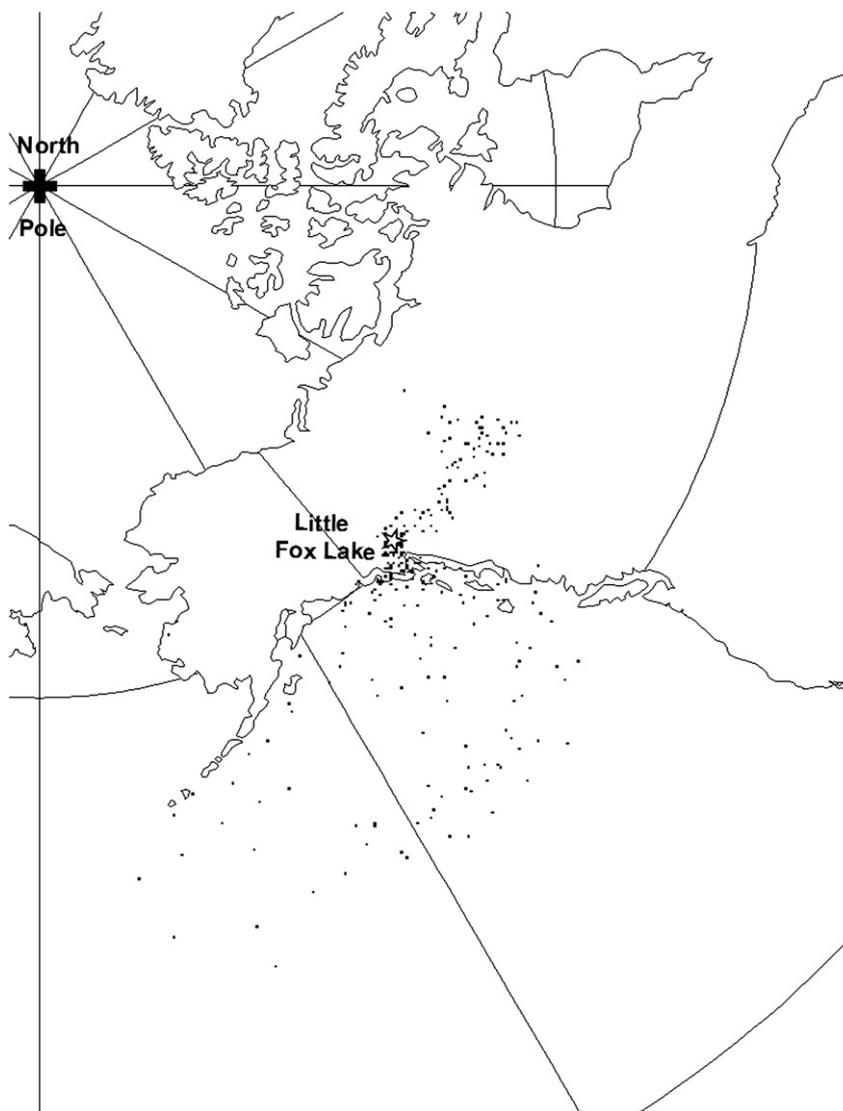


Fig. 4. Five-day air mass back trajectories collected from August 25, 2007 to September 08, 2007 for LFL (depicted approximately by star). The densest aggregation of endpoints occurs around the sampling site indicating the importance of local impacts during this time.

during the extraction step of chemical analysis. Arp et al. reported similar deviations for PAH collected in Europe and suggested a “shell-like” entrapment of PAH to the elemental carbon fraction of particulate matter, thus, leading to slow/non-exchangeability (Arp et al., 2008). Indeed, from theoretical arguments, Pankow and Bidleman had shown that non-exchangeability will affect the partitioning of lower molecular mass PAH more than the heavier ones (Pankow and Bidleman, 1991).

These results suggest that seasonal differences in impacting sources may be responsible for the seasonal variation in the gas/particle partitioning of lower molecular mass PAH.

We speculate that summer samples collected at LFL were generally more affected by fresh local emissions containing slowly exchanging or non-exchangeable low molecular mass PAH; summer camping activities at camping grounds relatively close to the monitoring site may lead to an increase in PAH from vehicular transportation, fuel and wood combustion. To investigate this possibility further, we computed the particle fraction ( $\phi$ ) for PAH in the fourteen daily samples (August 25, 2007–September 08, 2007) collected in the summer of 2007 (Table 2) and examined their 5-day air mass back trajectories collected at 0000, 0600, 1200 and 1800 h UTC and obtained for a starting height of 1138 m a.s.l. (the Hi-Vol sampler elevation) at LFL (see Fig. 4).

Clearly, the endpoints for the back trajectories for all 14 days have their densest population in the proximity of the receptor site and in general, the farthest reaches of these 5-day trajectories are either – 1. still in the Yukon, 2. arriving from the Northwest Territories, 3. arriving from the northern portions of British Columbia, or, 4. arriving from within the Pacific Ocean with straying endpoints from Alaska. In other words, the back trajectories seem to originate in regions that are relatively close to the sampling site even at their farthest. This would suggest that the sources of PAH at LFL during this period in the summer are most likely related to local activities. The ellipse in Fig. 1b also indicates that the PM<sub>2.5</sub> collected around the LFL receptor site were relatively high during this 14-day period. Thus, we believe that summer activities at camping grounds close to the sampler may yield sooty particles which cause the slow/non-exchangeability of lower molecular mass PAH and result in the shallower slopes for the summer samples in Fig. 3. Stabilization of PAH by sooty particles has been reported by previous researchers (Behymer and Hites 1988; Gustafsson et al., 1997) and it may result in PAH being unavailable for true equilibrium gas/particle partitioning.

PAH may also be more susceptible to photolytically-initiated transformation reactions in the atmosphere in the summer compared to wintertime due to increased sunlight. The UV-photolysis of ozone yields hydroxyl radicals and homogeneous atmospheric reactions of organic compounds with the OH radical is considered the most significant atmospheric loss process for these organic compounds including PAH (Atkinson and Arey, 1994; Cooper, 1996; Brubaker and Hites, 1998). Low molecular mass PAH typically found in the gas-phase will be more affected by these atmospheric transformation reactions. Kim et al. have recently investigated and compiled the half-lives obtained upon direct irradiation of PAH sorbed to representative environmental substrates and their study shows that low molecular mass PAH are the least stable on these environmental surfaces (Kim et al., 2009). The combined effect of these processes may cause a greater depletion in gas-phase concentrations of lighter PAH leading to their relatively higher summer log  $K_p$  values and may also be a contributory factor in the shallower slopes observed in Fig. 3. We note that all these are speculative assumptions at this point and suggest that one of the goals for future studies at this sub-Arctic site should be the proper determination of the actual causal factors of the summer time increase in log  $K_p$  (i.e., source- and/or photolytic

transformation-dependent) of low molecular mass PAH by conducting carefully designed field and control experiments. This would help determine the seasonal and overall importance of local sources in outcomes of long-range studies.

#### 4. Conclusion

At Little Fox Lake which is a sub-Arctic site, the colder periods showed the highest levels in PAH concentrations and PM<sub>2.5</sub>. An enrichment of particle-associated PAH (see Fig. 1) was also observed during the winter season while the warmer periods were marked by low PAH concentrations and lower levels of heavier molecular mass PAH normally associated with the particle-phase. This is consistent with studies by other researchers who have observed that the highest concentrations of anthropogenic particulates in the Arctic which arrive via long-range atmospheric transport occur during winter and the lowest concentrations occur during summer (Halsall et al., 1997; Polissar et al., 1999). The wintertime increase in gas- and particle-phase PAH concentrations observed at this sparsely populated sub-Arctic site may be generally reflective of the increased residential heating requirements in the northern hemisphere occurring during this time.

In the summer time, the partitioning of lower molecular mass PAH seems to exhibit some non-exchangeability though the potentially significant effect of photolytically-initiated atmospheric transformations on gas-phase PAH during this period could not be ruled out. Air mass trajectories suggest that local sources may be more important than long-range source regions during this time. Local summer sources that could give rise to this phenomenon may include summer camping activities at camping grounds close to the receptor site. Our accompanying article explores factor analysis and air mass back trajectories to identify and quantify the underlying sources of PAH impacting this site (Sofowote et al., submitted for publication).

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#### Appendix. Supplementary Information

Supplementary information including partitioning coefficients for samples collected at LFL during the course of this work can be found in doi:10.1016/j.atmosenv.2010.08.028.

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