Atmospheric Pollution Research

Polycyclic aromatic hydrocarbons in air and snow from Fairbanks, Alaska

Todd Gouin, David Wilkinson, Stephen Hummel, Ben Meyer, Andrew Culley

University of Alaska Fairbanks, Department of Chemistry and Biochemistry, P.O. Box 756160, Fairbanks, AK 99775-6160

ABSTRACT

There has been increasing interest regarding the use of passive air samplers as tools for monitoring organic pollutants in the atmosphere. In this study we report results obtained from passive air samplers that were deployed in both indoor and outdoor environments across the City of Fairbanks, AK, for the polycyclic aromatic hydrocarbons (PAHs) during winter 2009. It is demonstrated that the passive air samplers provide reliable data for the gas-phase PAHs. Results for particulate-phase isomers, however, are more variable and thus likely to be less reliable. For instance, the use of passive air samplers in indoor environments does not appear effective for distinguishing between homes with and without wood stoves, largely due to discrepancies associated with measuring particulate-phase PAHs. Consequently, it is suggested that the passive air samplers should not be used for assessing indoor exposures to particulate-bound pollutants. Nevertheless, air concentrations obtained from active air samplers indicate that PAHs in air are dominated by the gas-phase isomers, resulting in good agreement between the active and passive air samplers for outdoor air. The average passive indoor air concentrations for ΣPAH_{20} are observed to be slightly higher than passive outdoor air concentrations, at 55 and 26 ng m^{-3} respectively. Concentrations in outdoor air for the City of Fairbanks are reported to be an order of magnitude lower during 2009 than during the winter of 1976/77, when they were last reported. Snow data for the PAHs are reported as a complement to the air concentration data, showing similar isomer patterns between air and undisturbed snowpack samples. Snow samples collected from snow dump collection sites are reported to be 25 times greater than nearby undisturbed snow, and are dominated by the particulate-phase PAHs. Recommendations for future monitoring of snowmelt from the snow dump collection sites are suggested.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are produced as a result of incomplete combustion, with significant amounts produced as a consequence of anthropogenic activity (Baek et al., 1991; Zhang and Tao, 2009). Consequently, elevated levels are typically found in urban environments, with strong correlations between levels of PAHs in the environment and population density being frequently observed (Baek et al., 1991; Hafner et al., 2005; Sun et al., 2006; Brandli et al., 2008; Zhang and Tao, 2009; Nam et al., 2009). Whereas automotive and industrial sources tend to strongly influence PAH levels in outdoor environments, observations of PAH concentrations for indoor environments, particularly at higher latitudes, suggest different contributing sources, largely related to human activities, such as domestic heating, smoking and age of the building (Liu et al., 2001; Naumova et al., 2002; Ohura et al., 2004; Li et al., 2005).

In northern communities a combination of long cold winters and reduced ventilation rates can result in poor indoor air quality, which can thus lead to human health problems (Dockery et al., 1993; Johnson et al., 2002; Kovesi et al., 2007; Fuentes-Leonarte et al., 2009). In Fairbanks, Alaska, the formation of a surface inversion with low mixing height and wind speeds, throughout the cold winter months, is believed to significantly contribute to the poor air quality (Bowling, 1986). Unfortunately, however, resources to adequately monitor levels of atmospheric pollutants in remote communities are not readily available. For instance, data pertaining

to PAH levels in Fairbanks air was last reported for a period during the late 1970's by Reichardt and Reidy (1980).

Recently, there has been an increased interest in the use of passive air samplers to monitor levels of organic pollutants in occupational, residential, and remote environments, with an emphasis towards assessing their feasibility of use (Harner et al., 2006; Choi et al., 2007; Esteve-Turrillas et al., 2007; Santiago and Cayetano, 2007; Bohlin et al., 2007; Johnson et al., 2009; Cranor et al., 2009; Bonetta et al., 2009). Of particular note is the recent study by Johnson et al. (2009) who demonstrated the effective use of low cost passive air samplers by individuals in a participant-based exposure epidemiological assessment study. Using a similar approach, the use of passive air samplers in remote northern communities may provide an effective tool for monitoring both indoor and outdoor air quality.

In this study we report levels of PAHs in both indoor and outdoor air samples collected using a combination of passive and active air sampling techniques as well as PAH levels in snow throughout the Fairbanks community during 2008/09 winter. Snow is believed to influence the fate of organic contaminants in the environment in a multitude of ways (Wania et al., 1998; Halsall, 2004). Snowmelt, in particular, could strongly influence the extent and timing of the delivery of organic contaminants to aquatic and terrestrial ecosystems at high latitudes, such as Fairbanks, Alaska. During snowmelt, contaminants are released that have accumulated in the snowpack as a result of wet and dry deposition processes during the winter (Meyer et al., 2006). The combined air

and snow data thus provide an indication of the extent of PAH pollution in the Fairbanks area and potential sources.

2. Method

2.1. Air sampling

Polyurethane foam (PUF) disk passive air samplers (14 cm diameter, 1.35 cm thick, surface area 365 cm^2, density 0.0213 g cm^{-3}, Tisch Environmental) were deployed in duplicate at five outdoor sites in Fairbanks, AK (N 64°50'16", W 147°43'59") for a four-month period, between the end of December 2008 and March 2009. Additionally, eight passive air samplers, of the same type used in the outdoor samples (14 cm diameter, 1.35 cm thick, surface area, 365 cm^2, density 0.0213 g cm^{-3}, Tisch Environmental), were deployed for six weeks, to assess indoor air quality of domestic residences located throughout the City of Fairbanks, between February and March 2009 (Figure 1). PUF-disks were pre-cleaned by Soxhlet extraction for 24 h using acetone, and then for another 24 h using petroleum ether. PUF-disks were then dried under vacuum, before being stored in solvent rinsed, 500 mL amber jars, which were used to store the PUF-disks before and after deployment. Field blanks, which involved inserting the PUF disk into the sample chamber and then returning it to the glass jar, were also collected (n = 3). Indoor samples were deployed in homes that either used (n = 3) or did not use (n = 5) a wood stove as a heating source, to assess the relative difference of wood stove heating with respect to PAH levels in indoor air.

Details regarding the operation and theory of the PUF-disk samplers have been described elsewhere (Shoeib and Harner, 2002; Pozo et al., 2004; Gouin et al., 2005; Harner et al., 2006). Briefly, uptake by the PUF-disk sampler is described by Fick's Law of diffusion by linear uptake, integrated over the deployment period of the sampler. PUF-disk sampling rates, based on previous observations, are estimated as 3.5 m^3 d^{-1} for outdoor samples (Shoeib and Harner, 2002; Pozo et al., 2004; Bohlin et al., 2008), and 2.5 m^3 d^{-1} for indoor passive air samplers (Wilford et al., 2004; Bohlin et al., 2008).

In addition to the collection of passive air samples, five 24 hour high-volume air samples were collected (Tisch Environmental, TE-1000 PUF), sampling approximately 350 m^3 d^{-1}. Samples were collected on February 11, 17, 19, and 25, 2009, as well as on March 12, 2009. High-volume air samples were collected to compare with data from the outdoor passive air samplers and were collected on the roof of the Geophysical Institute building at the University of Alaska Fairbanks (denoted as the black star in Figure 1). Briefly, air was aspirated through a glass-fiber filter, which samples the particulate-phase, prior to passing through a PUF plug, which samples the gas-phase. Glass fiber filters and PUF plugs were extracted and analyzed separately, in order to compare concentrations observed in the gas-phase levels from the high-volume air sampler to the passive air samplers, which are believed to sample primarily the gas-phase.
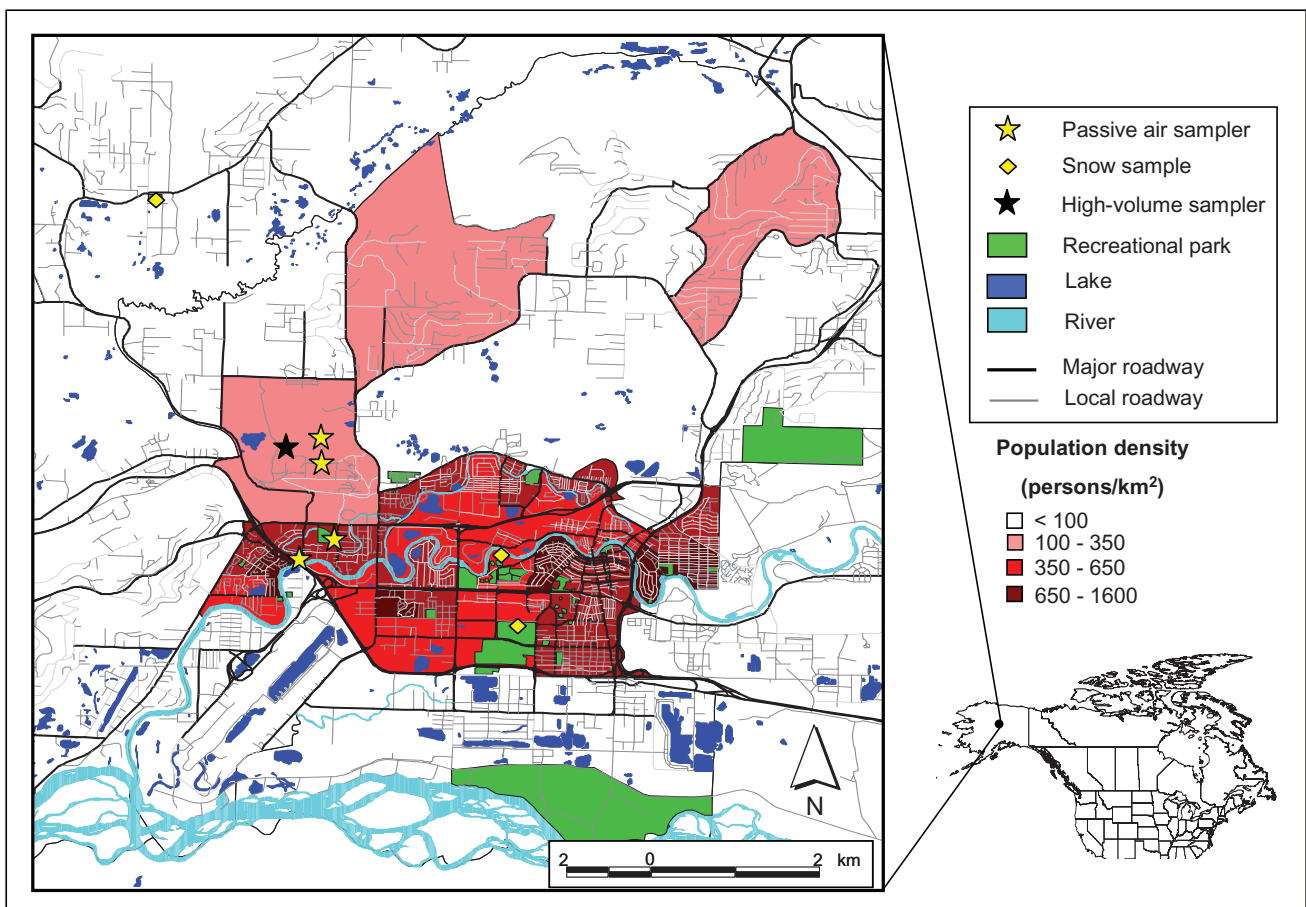

Figure 1. *Map of the City of Fairbanks, AK, showing locations of outdoor passive air samplers and snow samples. Indoor passive air samplers were located in homes within the urban boundaries of the city, i.e. in locations with higher population densities illustrated in red in the map. High volume air sampler is co-located with a passive air sampler, indicated by black star.*

2.2. Snow sampling

Duplicate snow samples were collected from five sites in the Fairbanks area prior to snowmelt during the last week of February, 2009 (February 23 - 25, 2009), thus representing an aged snowpack. Composite snow samples from three of the sites (two urban, one rural) are representative of snow from an undisturbed snowpack, and were collected in open fields used as sports fields during the summer at locations that were at some distance away from intensively used roads, typically >200 m. Snowpack depth for each of the three sites was consistent, at 45 cm. Snow samples were collected in adjacent 3 m x 3 m grids, into 4 L amber bottles, rinsed with dichloromethane. Briefly, a trench was dug to ground level in the center of each quadrant in the grid, and snow was collected in an integrated fashion from the upper two-thirds (30 cm) of the vertical profile using an acetone-rinsed beaker and funnel, into a 4 L amber bottle. The 4 L snow samples consequently resulted in approximately 1 L of melt water for each of the duplicate samples. Samples were stored at 4 °C.

In addition, two snow samples were collected from municipal snow dump sites, located in close proximity (within 400 m) to the two urban snowpack samples. The snow dump sites are used to store snow collected from snow removal operations from roads within the City of Fairbanks. Snow dump samples are thus representative of heavily impacted snow samples. The depth of snow at the snow dump sites was typically about 2.5 m, storing approximately 104 m^3 of snow. Snow pack samples were collected by taking 1 cm plugs of snow, approximately 20 cm in length, using a solvent rinsed PVC pipe, across the frontal face of the snow dump collection site. Snow plug samples were collected approximately 2 m apart in a manner that was sufficient to produce a representative composite 4 L sample. Thus, it is assumed that the levels of PAHs in the snow dump collection site are relatively uniform across the site, and that the collection of the snow samples in this manner is sufficient to characterize the levels in the snow dump. It is notable that the snow stored at the snow dump collection site was densely packed and contained a relatively large amount of particulate material. This is to be expected given that snow collected off of roads has typically been compacted as a result of vehicular traffic and is also regularly treated with gravel to reduce slippery conditions. After collection, all snow samples were subsequently stored at 4 °C, prior to extraction in the laboratory. Snow samples were allowed to melt in their closed storage containers at room temperature, overnight, prior to adding dichloromethane for liquid-liquid extraction. Snow blank samples (n = 2), using 1 L deionized water were also collected, and were used to assess contamination in the laboratory. Deionized water was added to 4 L amber bottles in the lab, stored at 4 °C with the collected snow samples, and then allowed to come to room temperature overnight prior to having dichloromethane added for liquid-liquid extraction, i.e. treated in a manner similar to the snow samples.

2.3. Extraction and quantification

Passive and active air samples were spiked with recovery standards (D_{12}-phenanthrene, D_{12}-chrysene, and D_{12}-benzo[a]-pyrene) and were Soxhlet extracted for 18 h with 250 mL of petroleum ether. Extracts were reduced by rotary evaporation and nitrogen blow-down to 500 μL and solvent exchanged to isooctane. Mirex (100 ng) was added as an internal standard to all samples prior to analysis.

Snow samples were spiked by adding each of the individual recovery standards to the snow sample prior to melting and liquid-liquid extracted with 250 mL dichloromethane, thus providing a combined total of dissolved and particulate loading in the snow. Solvent extracts were isolated from the melt water sample using a

separatory funnel and rotary evaporated to 1 mL. Extracts were next cleaned-up using 1.5 g of 6% activated alumina columns with a solution of 5% dichloromethane in petroleum ether, with the PAHs being eluted from the column with 30 mL. The samples were then reduced to a volume of approximately 1 mL under N_2 and transferred to GC vials, Mirex (100 ng) was added as an internal standard to each sample.

PAH analysis was performed using an Agilent 7890A gas chromatograph with a CTC combiPAL auto sampler and Agilent 5975C inert XL EI/CI MS detector, operated in EI selective ion monitoring mode. An HP-5 MS capillary column (30 m x 0.250 mm i.d. x 0.25 μm film thickness) was used for analyte separation. Oven temperature program was as follows: start at 70 °C (hold 1 minute), 70–90 °C at 10 °C min^{-1}, 90–130 °C at 4 °C min^{-1}, 130–240 °C at 5 °C min^{-1}, 240–300 °C at 4 °C min^{-1}. Carrier gas was helium. A sample of 1 μL was injected under splitless mode. The following PAHs were analyzed: naphthalene (Nap), 2-methyl-napthalene (2Nap), 1-methylnapthalene (1Nap), acenapthylene (Acy), acenaphthene (Ace), fluorene (Flu), dibenzothiophene (diBz), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Per), indeno[1,2,3-cd]-pyrene (IP), and benzo[g,h,i]perylene (BghiP).

2.4. Quality Assurance/Quality Control

Field and method blanks (i.e. solvent blanks) were collected for both the active and passive air samples. The field blanks for the PUF plugs and PUF disks were characterized by higher levels of naphthalene, phenanthrene, fluoranthene, pyrene, and perylene that was found in the method blanks. The mean and standard deviation for the blank values, calculated from the field blanks are reported in Table 1, which also includes the limit of quantification (LOQ), defined as the mean blank value plus 10 x standard deviation. All data have been blank corrected, i.e. the mean blank for individual PAH isomers listed in Table 1 was subtracted from the amount measured in the sample. The LOQ for the passive air samples ranged between 210 pg m^{-3} and 16 ng m^{-3} (assuming an effective air volume of 125 m^3) for the indoor air samples, and 1 and 10 pg m^{-3} (assuming an effective air volume of 420 m^3) for the outdoor air samples. Observed amounts are typically well above the LOQ. Average recoveries for the labeled PAH recovery standards for all samples were >60%, no correction has been made for recoveries.

3. Results

Concentrations in indoor air were dominated by the two-ring PAHs, naphthalene, 1-methylnapthalene, and 2-methylnapthalene, with the sum of the average for two-ring PAHs being 44 ng m^{-3}, representing 80% of the total PAH (ΣPAH_{20}) in indoor air (Table 1). In addition to the two-ring PAHs, outdoor air concentrations were also dominated by the three-ring PAH, phenanthrene, at 8 ng m^{-3}, which contributed 32% of the ΣPAH_{20} in outdoor air (Table 1). Observations for the outdoor air samples are seen to be consistent with high-volume air sampling data, for which the average ΣPAH_{20} concentration for the gas-phase, represented by the concentration measured on the PUF plug sorbent, was observed to be 11 ng m^{-3}, with phenanthrene contributing 35% to the ΣPAH_{20} (Figure 2). Particulate-phase concentrations, represented by the concentration measured on the glass fiber filter, were typically enriched in the 4 and 5-ring PAHs, which contributed 90% to the ΣPAH_{20} measured in the particles. Average particle-phase concentrations were an order of magnitude lower than gas-phase concentrations, at 1.6 ng m^{-3}.

Table 1. *Mean and LOQ of PAHs for field blanks, and the mean and standard deviation of indoor and outdoor passive air samples and snowpack and snow dump collection site samples*

| PAH	Blanks (ng)		Passive air samples (ng m^{-3})		Snow samples (ng L^{-1})	
	mean	LOQ	Indoor	Outdoor	Snowpack	Snow dump
Nap	63	202	9.6 ± 16	3.9 ± 2.0	450 ± 517	735 ± 604
2Nap	1.0	18	19 ± 38	4.3 ± 1.9	260 ± 327	1 780 ± 2 120
1Nap	2.7	6.3	15 ± 32	3.4 ± 1.5	157 ± 193	1 150 ± 1 420
Acy	nd	nd	1.0 ± 1.2	0.01 ± 0.02	34 ± 43	131 ± 135
Ace	nd	nd	0.3 ± 0.5	0.9 ± 0.3	13 ± 19	367 ± 382
Flu	0.9	3.0	3.2 ± 3.3	2.5 ± 0.5	71 ± 93	487 ± 480
diBz	0.2	2.6	0.3 ± 0.7	0.3 ± 0.1	23 ± 27	1 080 ± 920
Phe	5.4	27	5.0 ± 3.1	8.2 ± 2.3	377 ± 336	4 280 ± 2 010
Ant	nd	nd	0.2 ± 0.2	0.02 ± 0.06	1.9 ± 4.7	6 630 ± 3 100
Fl	2.9	22	0.7 ± 0.7	1.5 ± 0.5	125 ± 91	7 650 ± 1 590
Pyr	1.3	9.6	0.4 ± 0.5	0.6 ± 0.2	53 ± 45	5 220 ± 403
BaA	nd	nd	0.01 ± 0.002	0.03 ± 0.005	3.7 ± 2.8	2 080 ± 486
Chr	0.2	2.9	0.03 ± 0.03	0.09 ± 0.03	29 ± 16	4 030 ± 806
BbF	nd	nd	nd	nd	12 ± 8.0	1 450 ± 2 050
BkF	nd	nd	nd	nd	7.0 ± 5.0	2 000 ± 1 150
BeP	nd	nd	nd	0.03 ± 0.01	11 ± 9.0	1 540 ± 2 180
BaP	nd	nd	nd	nd	4.8 ± 4.8	5 350 ± 3 310
Per	0.2	3.9	nd	nd	nd	1 890 ± 1 260
IP	nd	nd	nd	nd	3.6 ± 8.0	1 300 ± 1 840
BghiP	nd	nd	nd	0.02 ± 0.02	9.4 ± 21	3 080 ± 422
ΣPAH	78	297	55	26	1 645	52 230
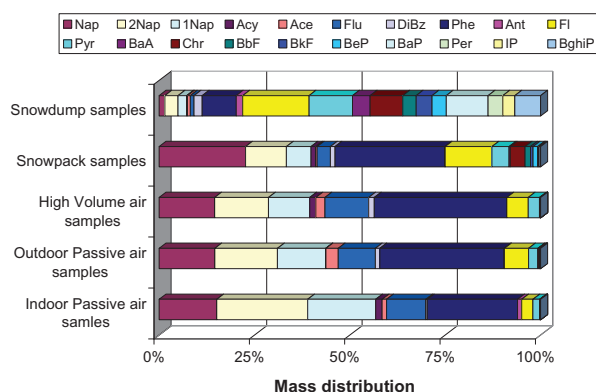
Figure 2. *The average mass distribution of PAH isomers observed in air and snow samples.*

Undisturbed snowpack samples included equal proportions of the two and three-ring PAHs, similar to the results for the outdoor air samples, but were characterized by a higher contribution of the four-ring PAHs (14% to the total PAH in the snowpack) than was observed in the passive air samples (Figure 2). Whereas snow dump collection site samples were dominated by the five-ring PAHs, contributing 46% to the ΣPAH$_{20}$ observed in the snow dump samples (Figure 2). Average concentrations for each individual PAH are reported in Table 1. Average ΣPAH$_{20}$ in the snowpack and snow dump sample were 1.6 µg L^{-1} and 52 µg L^{-1}, respectively.

4. Discussion

4.1. Indoor versus outdoor air concentrations

In their study investigating differences between homes with and without woodstoves, Gustafson et al. (2008) observed elevated levels of several of the 4 and 5-ring PAHs in homes that used a woodstove. In this study, passive air samplers were similarly deployed in homes with (n = 3) and without woodstoves (n = 5).

The observed differences in PAH levels between homes in this study, however, was not found to be significant, which may be attributed to the relatively small sample size, but may also reflect the efficiency of the wood stoves used in the homes. An alternative explanation may also be due to the limited ability of the passive air samplers to sample the 4 and 5-ring particulate-phase PAHs (Klanova et al., 2008). Consequently, it is suggested that the use of passive air samplers to assess differences regarding particulate-bound pollutants, such as those that might be derived as a result of using a wood stove for domestic heating, is likely to be of limited value. It is notable that the levels of the 3-ring PAHs in homes with and without woodstoves are found to be consistent between this study and those reported for the reference homes by Gustafson et al. (2008), and are within the lower range reported for indoor air in homes across the U.S. (Naumova et al., 2002; Li et al., 2005).

It is notable that the majority of studies reporting indoor air concentrations rely on the use of active air sampling, and that few studies report indoor air concentrations for PAHs using passive air samplers. Recently, however, Bohlin et al. (2008) reported levels of PAHs in indoor and outdoor environments using passive air samplers in three cities with very different climates; Mexico City, Gothenburg (Sweden), and Lancaster (UK). The data observed in this study for the three and four-ring PAHs in both indoor and outdoor air are in the lower range of values reported by Bohlin et al. (2008). For the four and five-ring PAHs, however, there is some discrepancy between the studies. This is not surprising since, as suggested above, uncertainties regarding how the passive air samplers sample particle-bound contaminants may result in variable results. It is thus recommended that caution be used in the interpretation of passive air sampling data for contaminants associated with particles.

The observation that levels of the predominately gas-phase PAHs in Fairbanks tend to be consistently low compared to other cities, for both indoor and outdoor air, is of interest. We suggest that a possibility for the lower PAH levels is a consequence of the successful implementation of technologies to reduce emissions in the Fairbanks area (Mulawa et al., 1997), which is also observed to

be consistent with the likely cause of a decline in concentrations observed in the UK (Meijer et al., 2008). Indeed the sum of seven PAHs (phenanthrene, fluorene, pyrene, chrysene, benzo[a]pyrene, benzo[e]pyrene, and benzo[g,h,i]perylene) reported by Reichardt and Reidy (1980) during the winter of 1976-1977 in Fairbanks had an average concentration of 44.1 ± 45.2 ng m^{-3}. For the same seven PAHs, the passive and active air samples collected in this study displayed an average concentration of 10.9 ± 2.7 ng m^{-3} and 4.2 ± 3.0 ng m^{-3}, respectively, indicating a decrease in PAH levels by about an order of magnitude.

Figure 3 reports the range of PAH concentrations observed in indoor and outdoor passive air samples, as well as the observed indoor/outdoor (I/O) ratios. Information about the ratio between indoor and outdoor PAH concentrations, as reflected in the I/O ratio, can be an effective tool for assessing human exposure (Freijer and Bloemen, 2000), where a ratio >1.0 implies indoor sources, and a ratio <1.0 implies outdoor sources. It is notable that the samplers deployed indoors show considerable variability, particularly for the two-ring PAHs, but the concentrations for the outdoor air samples are much less variable. This observation implies that levels of PAHs in outdoor air in the Fairbanks area are evenly distributed across the city during the winter. This can be attributed to the formation of a surface inversion, with low mixing height and wind speeds, characteristic of the interior of Alaska throughout the cold winter months (Bowling, 1986). This is further supported by Figure 4, which reports the temperature and wind speeds observed during the sampling period, in which the average wind speed for the period is observed to be relatively low, 1.4 m s^{-1}. Indeed, outdoor passive air samplers were deployed along an altitudinal gradient across the city to investigate the extent of mixing. Results, however, indicate that levels of PAHs in the air are consistent, and that limited mixing appears to occur. It is also notable that the I/O ratios of the two-ring PAHs tend to be >1.0, which likely represents a significant indoor source that appears to be highly variable between the homes studied.
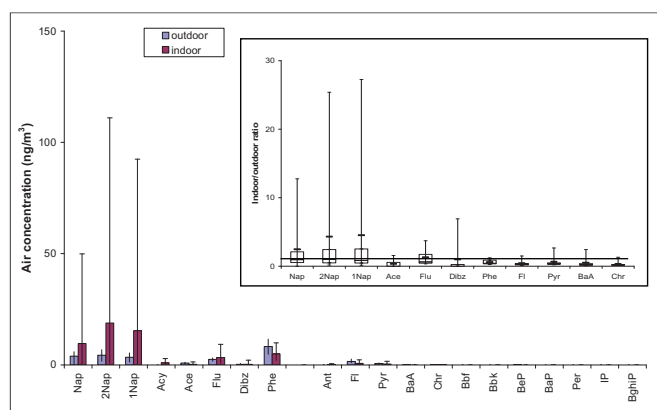

Figure 3. *Average concentrations for individual PAH isomers in indoor and outdoor air samplers, and indoor/outdoor ratios (inset).*

4.2. Snow samples

Concentrations of the three-ringed PAHs in the undisturbed snowpack are generally consistent with levels observed near Minneapolis/St. Paul, MN, reported by Franz and Eisenreich (2000). A notable difference between the data reported in this study and those reported by Franz and Eisenreich (2000), however, relates to the smaller proportion of particulate-bound PAHs observed in the snowpack in this study. In this study, the isomer composition of PAHs in the snowpack is observed to be dominated by the two- and three-ring PAHs (Figure 2), whereas Franz and Eisenreich (2000) observed a larger contribution of the four and five-ring PAHs, which are typically associated with particles. Thus, it appears that the dominant process influencing PAH levels in the snowpack in this study may be by gas scavenging, which is contrary to

observations by Franz and Eisenreich (1998). Unfortunately, information regarding levels of PAHs in falling snow, the dissolved versus the particle-phase concentration in the snowpack, or the concentration of particles in the snowpack is not available. Consequently, a quantitative assessment of the relative importance of the particulate fraction in the snow is not possible.
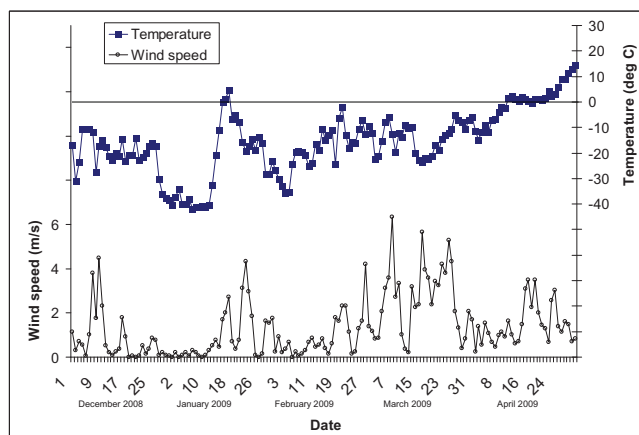

Figure 4. *Meteorological data, daily temperature and windspeed, for Fairbanks Alaska between December 2008 and April 2009 (data obtained from the National Climate Data Center website (www7.ncdc.noaa.gov).*

The potential for a concentration gradient in undisturbed snowpack samples with distance from the centre of Fairbanks was also investigated by collecting one sample at a rural location. The average concentration for the ΣPAH_{20} for the two urban samples collected was 2 150 ng L^{-1}, whereas the rural sample collected had a concentration for ΣPAH_{20} of 154 ng L^{-1}, or about 14 times lower than those observed in the undisturbed urban snowpack samples. This suggests a significant urban-rural gradient in PAH levels, which is consistent with the observation that population density and PAH concentrations are closely related (Hafner et al., 2005). It is also notable that the levels of the four and five-ring PAHs in the rural snowpack sample represent a much lower contribution of the total PAH loadings than that observed for the urban samples.

Levels of PAHs in snow collected from the snow dump sites are significantly greater than those observed in the nearby snowpack samples. Whereas the average ΣPAH_{20} for the two urban samples collected was 2 150 ng L^{-1}, the average ΣPAH_{20} for the two snow dump site samples was 52.2 µg L^{-1}, or 25 times greater. The distribution of PAHs in the snow dump samples was dominated by the particulate bound, i.e. four and five-ring PAHs (Figure 2), implying different sources to those influencing the PAH loading in the undisturbed snowpack samples.

Concern regarding the environmental fate of PAHs in the snow dump site samples following snow melt is likely to be higher than that for PAHs in the undisturbed snowpack samples, particularly given the elevated levels of PAHs observed. Meyer et al. (2006), for instance, assessed the release of PAHs from snow under controlled conditions. They observed a relatively uniform release of phenanthrene and a much slower release of the particulate-bound PAHs, with the latter being released with particles at the end of the experiment (Meyer et al., 2006). Under field conditions, however, the release of particles into waterways may be enhanced during the early periods of snowmelt, as a result of rapid melting, which can result in large surface runoff events. This release, however, may be complicated by other loss processes influencing the fate of PAHs, such as photodegradation. During the month of March in Fairbanks the total number of daylight hours increases significantly from a minimum of 3.7 h at the winter solstice to 12.0 h at the spring equinox. Consequently, PAH losses due to photodegradation in the snow may be enhanced prior to snowmelt (typically occurring during the month of April in Fairbanks). This is based on

recent observations demonstrating relatively rapid photo-degradation of PAHs in snow (Ram and Anastasio, 2009). To better understand the relative importance of these various processes (i.e., volatilization, runoff, deposition to soils, and degradation) with respect to the environmental fate of PAHs, a detailed assessment of the fate of PAHs in snow dump sites is recommended.

4.3. Potential sources and implications

In their study investigating levels of PAHs in spruce needles across Alaska, Howe et al. (2004) suggested that Fairbanks is a source of phenanthrene, fluoranthene, pyrene, benzo[a]-anthracene, and chrysene. Conversely, it was suggested that Fairbanks appears to be a limited source of anthracene (Howe et al., 2004). Observations regarding the PAH isomer composition for the outdoor air samples from this study are generally consistent with those observed in the spruce needles collected at Fairbanks (Howe et al., 2004). Thus, consistent with Howe et al. (2004), it is likely that a combination of petrogenic and combustion based sources of PAHs influence PAH levels in Fairbanks, which is consistent with local activity.

Isomeric ratios are often used to assess the relative importance of various sources. For instance the ratio of Benzo[a]anthracene to chrysene (BaA/Chr) can indicate relative importance of automobile versus coal combustion sources, whereby a ratio of about 1.0 can indicate a coal combustion source, and a ratio of about 0.5 implying an automotive source. Figure 5 illustrates the BaA/Chr ratios for samples collected in this study compared to those reported by Howe et al. (2004). It is notable that the air and snow dump site samples all show ratios that are about 0.5, implying automotive sources as having a dominate influence, but the snowpack and spruce needle samples show ratios of about 0.1. We suggest that the reason for this, however, is not related to differences in source contributions but rather is due to the relative importance of the influence of removal processes on the individual PAH isomers. Given that both benzo[a]anthracene and chrysene are associated with particles, their uptake and subsequent accumulation by spruce needles, as well as by the winter undisturbed snowpack will thus be strongly influenced by the mobility of particles. Consequently, due to various competing processes, it is likely that only limited information regarding potential sources of the PAHs by assessing their isomeric ratios will be obtained (Galarneau, 2008). Thus, it can be generally concluded that a combination of automotive, coal, and wood combustion sources influence PAH levels in Fairbanks, consistent with local activity.
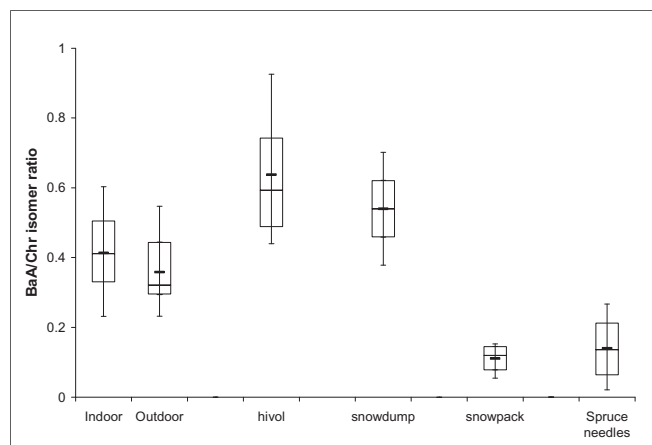
Figure 5. *Box and whisker plots for the PAH isomer ratio results for BaA/Chr for various environmental samples collected in Fairbanks, AK. Spruce needle data obtained from Howe et al. (2004).*

5. Conclusion

Generally, the use of the passive air samplers to assess PAH levels in indoor and outdoor air is promising, particularly for the gas-phase PAHs. Given the variability and uncertainty associated with using the passive air samplers for measuring the particle-bound PAHs, however, the ability to measure differences between homes with and without wood stoves, for instance, proved to be problematic. The observation that concentrations of PAHs in Fairbanks air appear to be an order of magnitude lower during this study (2008/09 winter) than during the late 1970's implies that emission reduction efforts in the city are resulting in significantly lower exposures to PAHs than was previously experienced.

Observations from the snow samples collected suggest that future work be directed towards better assessing the fate of PAHs stored in snow at the various snow dump collection sites in the city. Since PAH levels in the snow at these sites were seen to be significantly higher than those in nearby undisturbed snowpack samples, it is highly probable that these storage sites represent significant local sources to the environment. The fact that the snow dump sites act as storage sites for snow collected off roads that are dispersed across the city, and concentrate it at one location, however, provides an opportunity to implement effective controls to limit the release of pollutants.

Acknowledgements

References

Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic-hydrocarbons - sources, fate and behavior. *Water Air and Soil Pollution* 60, 279-300.

Bohlin, P., Jones, K.C., Tovalin, H., Strandberg, B., 2008. Observations on persistent organic pollutants in indoor and outdoor air using passive polyurethane foam samplers. *Atmospheric Environment* 42, 7234-7241.

Bohlin, P., Jones, K.C., Strandberg, B., 2007. Occupational and indoor air exposure to persistent organic pollutants: A review of passive sampling techniques and needs. *Journal of Environmental Monitoring* 9, 501-509.

Bonetta, S., Carraro, E., Bonetta, S., Pignata, C., Pavan, I., Romano, C., Gilli, G., 2009. Application of semipermeable membrane device (SPMD) to assess air genotoxicity in an occupational environment. *Chemosphere* 75, 1446-1452.

Bowling, S.A., 1986. Climatology of high-latitude air-pollution as illustrated by Fairbanks and Anchorage, Alaska. *Journal of Climate and Applied Meteorology* 25, 22-34.

Brandli, R.C., Bucheli, T.D., Ammann, S., Desaules, A., Keller, A., Blum, F., Stahel, W.A., 2008. Critical evaluation of PAH source apportionment tools using data from the Swiss soil monitoring network. *Journal of Environmental Monitoring* 10, 1278-1286.

Choi, S.D., Baek, S.Y., Chang, Y.S., 2007. Influence of a large steel complex on the spatial distribution of volatile polycyclic aromatic hydrocarbons (PAHs) determined by passive air sampling using membrane-enclosed copolymer (MECOP). *Atmospheric Environment* 41, 6255-6264.

Cranor, W.L., Alvarez, D.A., Huckins, J.N., Petty, J.D., 2009. Uptake rate constants and partition coefficients for vapor phase organic chemicals using semipermeable membrane devices (SPMDs). *Atmospheric Environment* 43, 3211-3219.

Dockery, D.W., Pope, C.A., Xu, X.P., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E., 1993. An association between air-pollution and mortality in 6 United-States cities. *New England Journal of Medicine* 329, 1753-1759.

Esteve-Turrillas, F.A., Pastor, A., Yusa, V., de la Guardia, M., 2007. Using semi-permeable membrane devices as passive samplers. *Trac-Trends in Analytical Chemistry* 26, 703-712.

Franz, T.P., Eisenreich S.J., 2000. Accumulation of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in the snowpack of Minnesota and Lake Superior. *Journal of Great Lakes Research* 26, 220-234.

Franz, T.P., Eisenreich, S.J., 1998. Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota. *Environmental Science and Technology* 32, 1771-1778.

Freijer, J.I., Bloemen, H.J.T., 2000. Modeling relationships between indoor and outdoor air quality. *Journal of the Air & Waste Management Association* 50, 292-300.

Fuentes-Leonarte, V., Tenias, J.M., Ballester, F., 2009. Levels of pollutants in indoor air and respiratory health in preschool children: A systematic review. *Pediatric Pulmonology* 44, 231-243.

Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment. *Atmospheric Environment* 42, 8139-8149.

Gouin, T., Harner, T., Blanchard, P., Mackay, D., 2005. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes basin. *Environmental Science and Technology* 39, 9115-9122.

Gustafson, P., Ostman, C., Sallsten, G., 2008. Indoor levels of polycyclic aromatic hydrocarbons in homes with or without wood burning for heating. *Environmental Science and Technology* 42, 5074-5080.

Hafner, W.D., Carlson, D.L., Hites, R.A., 2005. Influence of local human population on atmospheric polycyclic aromatic hydrocarbon concentrations. *Environmental Science and Technology* 39, 7374-7379.

Halsall, C.J., 2004. Investigating the occurrence of persistent organic pollutants (POPs) in the arctic: their atmospheric behaviour and interaction with the seasonal snow pack. *Environmental Pollution* 128, 163-175.

Harner, T., Pozo, K., Gouin, T., Macdonald, A.M., Hung, H., Cainey, J., Peters, A., 2006. Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environmental Pollution* 144, 445-452.

Howe, T.S., Billings, S., Stolzberg, R.J., 2004. Sources of polycyclic aromatic hydrocarbons and hexachlorobenzene in spruce needles of eastern Alaska. *Environmental Science and Technology* 38, 3294-3298.

Johnson, M., Hudgens, E., Williams, R., Andrews, G., Neas, L., Gallagher, J., Ozkaynak, H., 2009. A participant-based approach to indoor/outdoor air monitoring in community health studies. *Journal of Exposure Science and Environmental Epidemiology* 19, 492-501.

Johnson, R., Schmid, J., Seifert, R., 2002. Assessment of indoor air quality in interior Alaskan homes. *Journal of Cold Regions Engineering* 16, 218-229.

Klanova, J., Eupr, P., Kohoutek, J., Harner, T., 2008. Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. *Environmental Science and Technology* 42, 550-555.

Kovesi, T., Gilbert, N.L., Stocco, C., Fugler, D., Dales, R.E., Guay, M., Miller, J.D., 2007. Indoor air quality and the risk of lower respiratory tract infections in young Canadian Inuit children. *Canadian Medical Association Journal* 177, 155-160.

Li, A., Schoonover, T.M., Zou, Q., Norlock, F., Conroy, L.M., Scheff, P.A., Wadden, R.A., 2005. Polycyclic aromatic hydrocarbons in residential air of ten Chicago area homes: Concentrations and influencing factors. *Atmospheric Environment* 39, 3491-3501.

Liu, Y.J., Zhu, L.H., Shen, X.Y., 2001. Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China. *Environmental Science and Technology* 35, 840-844.

Meijer, S.N., Sweetman, A.J., Halsall, C.J., Jones, K.C., 2008. Temporal trends of polycyclic aromatic hydrocarbons in the UK atmosphere: 1991-2005. *Environmental Science and Technology* 42, 3213-3218.

Meyer, T., Lei, Y.D., Wania, F., 2006. Measuring the release of organic contaminants from melting snow under controlled conditions. *Environmental Science and Technology* 40, 3320-3326.

Mulawa, P.A., Cadle, S.H., Knapp, K., Zweidinger, R., Snow, R., Lucas, R., Goldbach, J., 1997. Effect of ambient temperature and E-10 fuel on primary exhaust particulate matter emissions from light duty vehicles. *Environmental Science and Technology* 31, 1302-1307.

Nam, J.J., Sweetman, A.J., Jones, K.C., 2009. Polynuclear aromatic hydrocarbons (PAHs) in global background soils. *Journal of Environmental Monitoring* 11, 45-48.

Naumova, Y.Y., Eisenreich, S.J., Turpin, B.J., Weisel, C.P., Morandi, M.T., Colome, S.D., Totten, L.A., Stock, T.H., Winer, A.M., Alimokhtari, S., Kwon, J., Shendell, D., Jones, J., Maberti, S., Wall, S.J., 2002. Polycyclic aromatic hydrocarbons in the indoor and outdoor air of three cities in the US. *Environmental Science and Technology* 36, 2552-2559.

Ohura, T., Amagai, T., Fusaya, M., Matsushita, H., 2004. Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations. *Environmental Science and Technology* 38, 77-83.

Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S., 2004. Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environmental Science and Technology* 38, 6529-6537.

Ram, K., Anastasio, C., 2009. Photochemistry of phenanthrene, pyrene, and fluoranthene in ice and snow. *Atmospheric Environment* 43, 2252-2259.

Reichardt, P.B., Reidy, S.K., 1980. Atmospheric polycyclic aromatic-hydrocarbons - An aspect of air-pollution in Fairbanks, Alaska. *Arctic* 33, 316-325.

Santiago, E.C., Cayetano, M.G., 2007. Polycyclic aromatic hydrocarbons in ambient air in the Philippines derived from passive sampler with polyurethane foam disk. *Atmospheric Environment* 41, 4138-4147.

Shoeib, M., Harner, T., 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental Science and Technology* 36, 4142-4151.

Sun, P., Blanchard, P., Brice, K.A., Hites, R.A., 2006. Trends in polycyclic aromatic hydrocarbon concentrations in the Great Lakes atmosphere. *Environmental Science and Technology* 40, 6221-6227.

Wania, F., Hoff, J.T., Jia, C.Q., Mackay, D., 1998. The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals. *Environmental Pollution* 102, 25-41.

Wilford, B.H., Harner, T., Zhu, J.P., Shoeib, M., Jones, K.C., 2004. Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environmental Science and Technology* 38, 5312-5318.

Zhang, Y.X., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmospheric Environment* 43, 812-819.