



## Levels of polycyclic aromatic hydrocarbons in Canadian mountain air and soil are controlled by proximity to roads

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Soil and air monitoring of PAHs along three transects in the mountains of Western Canada reveals the influence of local emissions.

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### ABSTRACT

Concentrations of polycyclic aromatic hydrocarbons (PAHs) were measured in soil and XAD-based passive air samples taken from a total of 22 sites along three transects (Revelstoke, Yoho, and Observation, 6–8 sites for each transect) in the mountains of Western Canada in 2003–2004. Median concentrations in air (4-ring PAHs: 33 pg/m<sup>3</sup>) were very low and comparable to those in global background regions such as the Arctic. Low median soil concentrations (16 EPA PAHs: 16 ng/g dry weight) and compositional profiles dominated by naphthalene and phenanthrene are similar to those of tropical soils, indicative of remote regions influenced mostly by PAHs from traffic and small settlements. Comparing levels and composition of PAHs in soils between and along transects indeed suggests a clear relationship with proximity to local sources. Sampling sites that are closer to major traffic arteries and local settlements have higher soil concentrations and a higher relative abundance of heavier PAHs than truly remote sites at higher elevations. This remains the case when the variability in soil organic carbon content between sites is taken into account. Both air/soil concentration ratios and fugacity fractions suggest atmospheric net deposition of four-ring PAHs to soils.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and toxic chemicals, which are produced by industrial activities and the incomplete combustion of fossil fuels (Baek et al., 1991). Because of the large capacity of soil for semi-volatile organic compounds, a large portion of PAHs emitted to the atmosphere accumulates in soil via dry and wet deposition. More than 90% of the total PAHs in the UK environment is estimated to be stored in soil (Wild and Jones, 1995). This high capacity also makes soils suitable for investigating the spatial variability in the atmospheric deposition of PAHs (Wong et al., 2004). In urban areas, PAH concentrations are directly affected by proximity to sources and the intensity of emission, resulting in a strong urban-suburban-rural gradient in both air and soil (Motelay-Massei et al., 2005; Wang et al., 2007b). Long-range atmospheric transport has been shown to deliver PAHs to the high Arctic (Patton et al., 1991) and far over the Pacific Ocean (Ding et al., 2007).

High mountains can act as a convergence zone for semi-volatile organic compounds (Blais et al., 1998; Grimalt et al., 2001). Diurnal

winds efficiently link source regions at lower altitude with mountain areas, and wet deposition enhanced by orographic precipitation, low temperatures, and efficient snow scavenging may lead to elevated contamination of higher altitudes (Daly and Wania, 2005). Mechanistic considerations suggest that chemicals differ in terms of their susceptibility for such enrichment at higher altitudes. In particular, model calculations predict that three- and four-ring PAHs should be most susceptible to accumulation in mountains (Daly et al., 2007a).

Investigation of accumulation patterns along altitudinal gradients can shed light on the factors affecting contaminant fate in mountain environments. Several studies have observed enrichment of PAHs at higher altitude: In the Northern Czech mountains, levels of PAHs in forest soils were significantly elevated at higher than at lower altitude (Wilcke and Zech, 1997). Concentrations of total and three-ring PAHs in Himalayan soil were positively correlated with altitude (4700–5600 m), whereas no correlation was found for heavy PAHs (Wang et al., 2007a). On the other hand, heavy PAHs, such as benzo(k)fluoranthene and benzo(a)anthracene, did show a positive correlation with altitude (2636–3820 m) in Himalayan spruce needles (Wang et al., 2006). Detection of PAHs in fish (Escartín and Porte, 1999; Vives et al., 2004) and sediment (Barra et al., 2006; Usenko et al., 2007) from remote mountain lakes further supports that high mountains are convergence zone for PAHs.

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Whereas several studies have reported concentration gradients of organochlorine pesticides in air, snow, vegetation, and amphipods with elevation in the mountains of Western Canada (Blais et al., 1998, 2003; Davidson et al., 2003; Shen et al., 2005), air and soil concentration gradients of PAHs have not yet been reported. A field-sampling campaign conducted in the summers of 2003 and 2004 deployed passive air samplers (PAS) at 22 sites along three altitudinal transects in Western Canada, and sampled soils in the vicinity of the PAS. Concentrations of organochlorine pesticides in those samples have been presented and interpreted in an earlier publication (Daly et al., 2007d). Here we present and discuss the concentrations of PAHs in those same samples with an aim to investigate their levels, patterns, and altitudinal distribution. Air/soil concentration ratios and fugacity fractions were calculated to evaluate air/soil equilibrium status, and principal component analysis was conducted to compare PAHs profiles in different soils.

## 2. Experimental section

### 2.1. Air and soil samples

Air and soil samples were collected along three transects (Revelstoke, Yoho, and Observation) in the mountains of Western Canada (Fig. S1 in the Supplementary information). The Revelstoke transect (R1–R8: 570–1951 m) is located in Mount Revelstoke National Park in southeastern British Columbia. The Yoho transect (Y1–Y6: 1109–2561 m) is located in Yoho National Park on the western slopes of the Canadian Rocky Mountains in British Columbia. The Observation transect (O1–O8: 1402–2902 m) is located in the eastern side of the Canadian Rocky Mountains, in the northern part of Banff National Park, Alberta. Table S1 lists elevations, coordinates, annual mean temperatures, organic carbon fractions in soils, and vegetation covers of the sampling sites. Daly et al. (2007d) provide more detailed information on these transects. All of the sites below the tree line are located in forests.

XAD-resin based PAS, which had previously been used to monitor PAHs in Costa Rica (Daly et al., 2007a), were deployed in duplicate at each site for one year (August 2003–August 2004). Details on sampler preparation and sampling procedures can be found elsewhere (Wania et al., 2003; Shen et al., 2006). Selection criteria for sampling sites and photos of PAS deployed at Revelstoke (R4) and Observation (O7) can be found in Daly et al. (2007d). Annual mean air concentrations ( $\text{pg}/\text{m}^3$ ) were estimated semi-quantitatively from the amounts of chemicals sequestered by the PAS ( $\text{pg}/\text{PAS}$ ) using a sampling rate of  $0.52 \text{ m}^3/(\text{day} \cdot \text{PAS})$  (Wania et al., 2003) and a sampling period of 365 days. The air samplers at Yoho Y6 (2561 m) were damaged by wind and heavy snow, thus air concentrations for this site are not reported. At each sampling site, 10 soil samples (several meters apart from each other) were collected in the vicinity of an air sampler (within 20 m) with a Riverside type auger (7 cm i.d.) and mixed in a steel bucket. Two sub-samples were collected for analysis and stored in a freezer until analysis. Organic carbon fractions ( $f_{\text{OC}}$ ) in the soil samples were determined as described elsewhere (Daly et al., 2007c) and ranged from 1 to 65% (Table S1).

### 2.2. Instrumental analysis

The samples were prepared and Soxhlet-extracted as described in Daly et al. (2007b) for soil and in Wania et al. (2003) for air. The extracts were cleaned up by silicic acid/alumina columns (Su et al., 2006). The 16 EPA priority PAHs listed in Table 1 were analyzed using an Agilent 6890 gas chromatograph (GC)-5973 mass spectrometric detector (MSD) in electron ionization mode. A DB-5MS column (60 m  $\times$  0.25 mm i.d., 0.10  $\mu\text{m}$  film thickness) and helium gas as a carrier gas at a flow rate of 1.0 mL/min were used to separate PAHs. Only four-ring PAHs (fluoranthene, pyrene, benz(a)anthracene, chrysene) with intermediate volatility were quantified in the air sample extracts because two- and three-ring PAHs may reach equilibrium with the sampling resin during the sampling period (one year) and five- and six-ring PAHs are largely associated with atmospheric particles (Daly et al., 2007a). Details on analytical conditions, including GC oven temperature program and quantification procedures for PAHs, have been provided previously (Su et al., 2006). Recoveries of labeled PAHs in the soil samples ranged from 70 to 105%. Eight procedural blanks for the soil samples were extracted, cleaned, and analyzed in the same way as the real samples. Nine procedural blanks and two field blanks for the air samples were also analyzed. Average blank values and coefficient of variations between duplicate samples are given in Tables S2 and S3.

### 2.3. Air/soil concentration ratios and fugacity ratios

Air/soil concentration ratios for four-ring PAHs were calculated from the measured air and soil concentrations ( $C_A$  in  $\text{mol}/\text{m}^3$  and  $C_S$  in  $\text{mol}/\text{kg}$ ) and a site-specific soil density ( $\rho_S$ ):

$$A/S = C_A/(\rho_S \cdot C_S) \quad (1)$$

$\rho_S$  was calculated using:

$$\rho_S = f_{\text{OC}} \cdot \rho_{\text{OC}} + (1 - f_{\text{OC}}) \cdot \rho_{\text{SM}} \quad (2)$$

where,  $\rho_{\text{OC}}$  and  $\rho_{\text{SM}}$  are the density of soil organic carbon ( $1000 \text{ kg}/\text{m}^3$ ) and mineral matter ( $2500 \text{ kg}/\text{m}^3$ ), respectively (Wania and Daly, 2002).

The equilibrium status of PAHs between atmosphere and surface can be obtained by comparing  $A/S$  with the air–soil equilibrium partition coefficient  $K_{AS}$ , which can be estimated using:

$$K_{AS} = 1/K_{SA} = 1/(E \cdot f_{\text{OC}} \cdot \rho_S \cdot K_{OA}) \quad (3)$$

where  $E$  is an empirical constant of  $0.00075 \text{ m}^3/\text{kg}$  (Hippelein and McLachlan, 1998, 2000), and  $K_{OA}$  is the octanol-air partition coefficient, which was estimated for the PAHs from vapor pressures adjusted to the mean annual temperature (Lei et al., 2002) and an equation regressing vapor pressure against  $K_{OA}$  (Xiao and Wania, 2003). Another way to express the air–soil equilibrium is to calculate the fugacity fraction  $F$  between air and soil (Daly et al., 2007b):

$$F = f_S/(f_S + f_A) = 1/(1 + E \cdot f_{\text{OC}} \cdot \rho_S \cdot K_{OA} \cdot A/S) = 1/(1 + K_{SA} \cdot A/S) \quad (4)$$

where  $f_S$  and  $f_A$  are the fugacity in soil and air, respectively.

### 2.4. Principal component analysis

Principal component analysis (PCA) was conducted with Simca-P 7.01 (Umetrics) to compare the PAH profiles in the soils from this study with those from other regions. The PAH profiles of Costa Rican soils (Daly et al., 2007a), various types of temperate soils (forest, urban, house garden, gas work site, and roadside) (Wilcke, 2000; Wilcke et al., 2002), and Swiss soil monitoring network (NABO) samples (mostly grassland and forest soils) (Bucheli et al., 2004) were used for comparison. To avoid detection limit artifacts (Meglen, 1992), the more commonly detected PAHs in soil samples (Nap, Ace, Flu, Phe, Flt, Pyr, BaA, and Chr) were included in the PCA. Some concentrations below detection limits were substituted by a value constituting 10% of the minimum concentrations (above detection limit) of the same compounds. Then, the concentrations of all selected PAHs were normalized by dividing by the highest concentrations for each sample, producing data ranging from 0 to 1 (Shen et al., 2006). Finally, these normalized PAH compositions were used as input data for PCA. The traditional normalization method, calculating fractions of each compound to total PAHs, were not used here due to potential propagation of errors in the normalization process (Rietjens, 1995). The first principal component (X-axis: PC1) accounted for 64% of the variance, and the second principal component (Y-axis: PC2) accounted for 15%.

## 3. Results and discussion

### 3.1. PAH concentrations and comparison with other locations

Arithmetic means, medians, and ranges of the blank-corrected air and soil concentrations of individual PAHs are listed in Table 1. As mentioned earlier, we report only air concentrations of four-ring PAHs. Soil (blank-corrected average of two to four sub-samples) and air concentrations (blank-corrected average of duplicates, reported in  $\text{ng}/\text{PAS}$  and  $\text{pg}/\text{m}^3$ ) for each sampling site are provided in the Supplementary Information (Tables S2 and S3). Indeno(123-cd)pyrene, dibenz(ah)anthracene, and benzo(ghi)perylene were not detected in any of the soil samples.

Soil concentrations ( $\sum_{16}\text{PAH}$ ) at all three transects range from 2 to 789  $\text{ng}/\text{g}$  dry weight with a median of 16  $\text{ng}/\text{g}$ , which is very low for temperate regions. Wilcke (2000) reports median concentrations of 216, 194, 410 and 1103  $\text{ng}/\text{g}$  for arable, grassland, forest, and urban soils, respectively. The levels of PAHs in this study are also lower than those in background soils from Western Europe (geometric mean: 640  $\text{ng}/\text{g}$  for the UK and 150  $\text{ng}/\text{g}$  for Norway) (Nam et al., 2008) and rural (mean: 223  $\text{ng}/\text{g}$ ) and mountain (168–595  $\text{ng}/\text{g}$ ) areas from China (Wang et al., 2007a,b). Other alpine soils from the Swiss soil monitoring network (median: 167  $\text{ng}/\text{g}$ ) (Bucheli et al., 2004), remote Austrian forest sites (median: 210  $\text{ng}/\text{g}$ ) (Weiss et al., 2000), and the Holy Cross Mountain region of Poland (geometric mean: 108  $\text{ng}/\text{g}$ ) (Migaszewski, 1999) have generally higher PAH levels than the Western Canadian mountain soils. The PAH levels in this study are comparable to those reported

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