



RESEARCH ARTICLE

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Key Points:

- The atmospheric occurrence of PAHs over the Southern Ocean is mainly the result of long-range atmospheric transport
- The observed gas-particle partitioning of PAHs suggest a modest influence of elemental carbon due to its low concentrations
- Antarctic soils and snow are secondary sources of some PAHs to the terrestrial atmosphere

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Sources and fate of polycyclic aromatic hydrocarbons in the Antarctic and Southern Ocean atmosphere

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Abstract Polycyclic aromatic hydrocarbons (PAHs) are a geochemically relevant family of semivolatile compounds originating from fossil fuels, biomass burning, and their incomplete combustion, as well as biogenic sources. Even though PAHs are ubiquitous in the environment, there are no previous studies of their occurrence in the Southern Ocean and Antarctic atmosphere. Here we show the gas and aerosol phase PAHs concentrations obtained from three sampling cruises in the Southern Ocean (Weddell, Bellingshausen, and South Scotia Seas), and two sampling campaigns at Livingston Island (Southern Shetlands). This study shows an important variability of the atmospheric concentrations with higher concentrations in the South Scotia and northern Weddell Seas than in the Bellingshausen Sea. The assessment of the gas-particle partitioning of PAHs suggests that aerosol elemental carbon contribution is modest due to its low concentrations. Over the ocean, the atmospheric concentrations do not show a temperature dependence, which is consistent with an important role of long-range atmospheric transport of PAHs. Conversely, over land at Livingston Island, the PAHs gas phase concentrations increase when the temperature increases, consistently with the presence of local diffusive sources. The use of fugacity samplers allowed the determination of the air-soil and air-snow fugacity ratios of PAHs showing that there is a significant volatilization of lighter molecular weight PAHs from soil and snow during the austral summer. The higher volatilization, observed in correspondence of sites where the organic matter content in soil is higher, suggests that there may be a biogenic source of some PAHs. The volatilization of PAHs from soil and snow is sufficient to support the atmospheric occurrence of PAHs over land but may have a modest regional influence on the atmospheric occurrence of PAHs over the Southern Ocean.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of semivolatile organic compounds in terms of their toxic effects on humans and ecosystems and because of their geochemical significance. PAHs are distributed globally and ubiquitously found in all environmental compartments. Due to their toxicity and carcinogenic effects [Nisbet and LaGoy, 1992; Hylland, 2006; Plíšková et al., 2005], PAHs are regulated internationally by the United Nations Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution and by several national legislations.

In Antarctica and the Southern Ocean, the occurrence of PAHs has been described in soils and sediments [Cabrerizo et al., 2012; Martins et al., 2010], ice/snow [Cincinelli et al., 2005; Kukučka et al., 2010], and marine and terrestrial biota [Curtosi et al., 2009; Cabrerizo et al., 2012]. The presence of these chemicals in terrestrial and marine compartments in such a remote region suggests that long-range atmospheric transport, with the subsequent atmospheric deposition facilitated by cold trapping [Bengtson-Nash, 2011] could account for the observed levels of PAHs in Antarctica. The atmospheric residence times of the low molecular weight (MW) PAHs, mainly found in the gas phase, are relatively short due to degradation by reaction with OH radicals [Kwok et al., 1994; Dachs et al., 2002], but atmospheric OH concentrations are low at high latitudes [Spivakovsky et al., 2000]. In addition, atmospheric deposition can also result in decreasing concentrations during transport of both gas and aerosol phase PAHs [Del Vento and Dachs, 2007]. These depletion processes of atmospheric levels of PAHs will limit the role of long-range transport to remote regions such as the Antarctica. Local sources of PAHs are feasible in Antarctica due to the following: (i) emissions from human activities (tourism and research) as suggested by high levels of PAHs in soils and sediments collected adjacent

to research stations [Cabrerizo *et al.*, 2012; Aislabie *et al.*, 1999; Mazzera *et al.*, 1999], (ii) emissions from research and tourist vessels and accidental spills of fuel, (iii) secondary sources due to volatilization from soils and snow as recently demonstrated for persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) [Cabrerizo *et al.*, 2013; Galbán-Malagón *et al.*, 2013a, 2013b], and (iv) natural sources of PAHs in Antarctica due to natural losses or seeps of petroleum or coal deposits, meteorites, and biogenic production in soils, sediments, and the water column [Botta *et al.*, 2008; Clemett *et al.*, 1998; Naraoka *et al.*, 2000; Wilcke, 2007; Cabrerizo *et al.*, 2012]. This biogenic production could be related to the degradation of diterpenes from the organic matter pool.

However, despite the multiple potential sources of PAHs to the Antarctic environment, most of the previous studies on organic pollutants have focused on quantifying the presence of legacy POPs, such as PCBs or OCPs, in the various Antarctic compartments [Cabrerizo *et al.*, 2013; Li *et al.*, 2012; Baek *et al.*, 2011; Galbán-Malagón *et al.*, 2013a], while there is a lack of information regarding the presence, transport pathways, and sources of PAHs in the Antarctic atmosphere despite its importance as a primary vector for the introduction of PAHs to remote areas.

The main objectives of this study are (i) to report the largest data set available of PAHs concentrations in the Antarctic and Southern Ocean atmosphere and (ii) to assess the main drivers of the occurrence of PAHs in the atmosphere, such as long-range transport, gas-particle partitioning, volatilization from soils and snow, and the influence of anthropogenic and/or biogenic local sources.

2. Experimental Section

2.1. Study Sites and Sampling Methodology

Three sampling cruises on board R/V *Hespérides* in the Southern Ocean around the Antarctic Peninsula (Weddell, Bellingshausen, and Bransfield Seas) were carried out during the austral summers of 2005 (ICEPOS), 2008 (ESSASSI), and 2009 (ATOS-II). In addition, two terrestrial sampling campaigns at Livingston Island (62°34'S, 61°13'W, Southern Shetlands) were also carried out during the austral summers of 2005 (ICEPOS) and 2009 (ATOS-II). Figure S1 (Annex I) in the supporting information shows the map of cruises' trajectories during each sampling campaign and the sampling locations for the terrestrial field campaigns. The sampling strategy, as detailed below, was not always similar in all the sampling campaigns due to some constraints of performing sampling in the Antarctica. During the oceanic cruises, atmospheric samples (gas + aerosol phases) were sampled using one or two high-volume samplers (High-Vol, MCV, Collbató, Spain) deployed over the bridge, in the top of the front part of the ship to minimize contamination from the ship exhaust. Because of the shape of R/V *Hespérides*, the sampler receives only clean air, as the bow deck is 10 m below the upper bridge. Furthermore, a wind vane was connected to the electric power system in order to allow sampling only when the wind was coming from the bow, avoiding therefore any perturbation of the sample from the ship exhausts. Sampling was performed by first forcing the air to go through a quartz microfibre filters (203 × 254 mm, QM-A, Whatman International Ltd., Maidstone, England), in order to collect the particulate phase, and then through a polyurethane foam (PUF of 100 × 120 mm) to retain PAHs in the gas phase. High-volume samplers operated at a calibrated flow rate of 40 m³ h⁻¹, and the gas and aerosol phase sampled volumes averaged 600 m³, 1000 m³, and 1400 m³ for the 2005, 2008, and 2009 cruises. In total, 22 gas phase samples and 30 aerosol phase samples were taken and analyzed during the oceanic cruises. For the terrestrial campaigns, high-volume samplers, analogous to those used during the oceanic cruises, were deployed at different locations from Livingston Island. Sampling was performed over 24 h for the gas phase, while longer time was needed for sampling the aerosol phase (48–72 h). Gas and aerosol phases volumes averaged 890 m³ and 2300 m³, respectively. At terrestrial sites, a total of 15 gas and 8 aerosol phase samples were collected in 2009 and 12 aerosol phase samples were collected in 2005. The exchange of PAHs between relevant terrestrial Antarctic surfaces (soil and snow) and the atmosphere was measured using four surface fugacity samplers [Cabrerizo *et al.*, 2009] distributed at different sites of Livingston Island (Figure S2, Annex I). The surface fugacity sampler has been previously developed by Cabrerizo *et al.* [2009] and used in both temperate and polar regions [Cabrerizo *et al.*, 2011a, 2011b, 2011c, 2013]. Briefly, the air is forced to flow first into a glass fiber filter (47 mm GF/F, Whatman International Ltd., Maidstone, England) to remove aerosols and then through a polyurethane foam plug

(PUF, 2 cm id × 10 cm), in which compounds from the gas phase are retained. The main advantage of this sampler is that it allows for accurately determining the PAHs surface fugacity by sampling the air which has been previously equilibrated for enough time with the selected surface (soil with vegetation, bare soil, or snow); thus, PAHs soil and snow fugacities can be determined under field conditions. Four of these fugacity samplers were deployed at three sites characterized by having a surface with soil covered by vegetation (sp. *Usnea antarctica*) at Pico Radio Hill (131 m above sea level (asl)), bare soil located near the coast (at Polish Beach, 13 m asl), and snow (at Sofia Mountain, 275 m asl, two samplers). In parallel, another sampler located at 1.5 m (thereafter referred as ambient air fugacity sampler) operated simultaneously with the same conditions and sampling flow rate as the soil fugacity sampler for determining ambient air fugacities. In this case, the sampling of surface and ambient air fugacities measurements were carried out over a 5 day period, giving pair samples of about 70 m³ of air and providing a total of 16 surface fugacity measurements and 16 ambient air fugacity measurements. Top surface soil ($n = 4$) and vegetation samples ($n = 2$) were taken after the surface fugacity sampling by gently collecting the soil surface layer (approximately top 0.5–1 cm) and lichen samples (*Usnea antarctica*) under the sampler device as described elsewhere [Cabrerizo *et al.* 2012].

After sampling, all samples were stored in freezers and transported at -20°C until analysis. Concurrent meteorological data during the oceanic and terrestrial campaigns were continuously monitored with the corresponding meteorological stations.

2.2. Analytical Procedures

All the glassware used for the analysis of samples were carefully cleaned by ultrasonication, cleaned 3 times with Milli-Q water, dried with acetone, and baked during at least 10 h at 450°C . All samples were Soxhlet extracted during 24 h after adding the surrogate standards and further analyzed. Details of the extraction and fractionation scheme for both the high-volume samples, aerosol phases, and surface and air fugacity samples can be found elsewhere [Cabrerizo *et al.*, 2009, 2011c; Galbán-Malagón *et al.*, 2013a, 2013b]. All samples were analyzed for the following PAHs: phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (B(a)ant), chrysene (Cry), benzo(b&k)fluoranthene (B(b&k)f), benzo(e)pyrene (B(e)pyr), benzo(a)pyrene (B(a)pyr), perylene (Pery), dibenzo(a,h)anthracene (Dib(a,h)ant), benzo(g,h,i)perylene (B(g,h,i)peryl), indeno(1,2,3-cd)pyrene (In(1,2,3-cd)pyr), dibenzothiophene (DBT), methyl dibenzothiophenes (ΣMDBT), methylphenanthrenes (ΣMP), and dimethylphenanthrenes (ΣDMPD). The identification and quantification of PAHs was done by an Agilent 6890 gas chromatographer coupled to an Agilent 5973 mass spectrometer with an electron impact source (positive ionization) operating in selected ion mode. Details of the temperature programs and monitored ions are given elsewhere [Cabrerizo *et al.*, 2009, 2011c]. Reference to the sum of PAHs (ΣPAHs) considers the parent compounds only (without the methylated PAHs).

2.3. Quality Control

PUFs were initially precleaned with acetone:hexane (3:1 v/v) before the sampling campaign. The PUFs used in the fugacity samplers were precleaned, handled, and extracted after sampling in a dedicated clean laboratory at Lancaster University which has filtered, charcoal-stripped air, and positive pressure conditions. Quartz microfiber filters used for aerosol sampling were initially precombusted at 450°C during 24 h, preweighed, and wrapped in aluminum foil before sampling. All analytical procedures were monitored using strict quality assurance and control measures. From time to time, the same solvent used for PAHs extraction, without any matrix was also extracted to check any potential contamination of PAHs due to lipid sticky in the glassware. However, solvent analysis resulted in no sign of potential contamination. PUF laboratory blanks and field blanks used to determine surface and air fugacity constituted 30% of the total number of samples processed. The more volatile PAHs were detected in both field and laboratory blanks; however, they accounted between 0.2 and 3% of the levels found in real samples, indicating minimal contamination during sampling and processing. In the same way, PUF laboratory blanks and field blanks used in the high-volume air sampler were also analyzed. In this case, blanks constituted 25% of the total number of samples processed. The more volatile PAHs were also detected in both field and laboratory blanks in the range of 0.1–1.9% of the levels found in samples. In the case of aerosol phase samples, laboratory and field blank filters used in the high-volume air sampler constitute 37% of the total number of samples processed. The more volatile PAHs were also detected at low levels, approximately 1–4% of the mass found in samples, indicating minimal contamination during processing, so samples were not corrected by blanks. Three split PUFs were used to

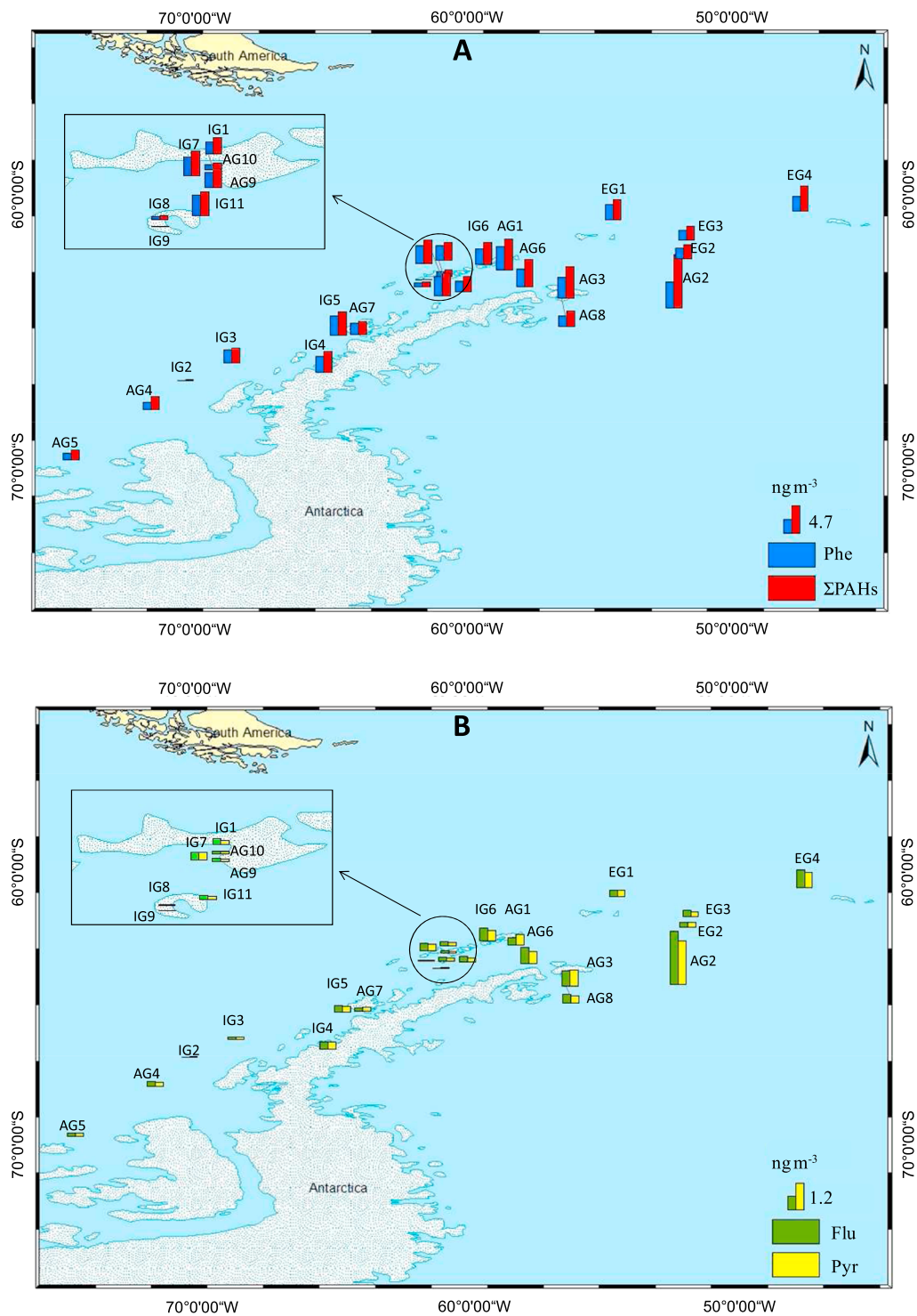


Figure 1. Spatial distribution of gas phase concentrations of (a) Σ PAHs and Phenanthrene (Phe), and (b) fluoranthene (Flu) and pyrene (Pyr) in the Southern Ocean and Livingston Island atmosphere. IG1–IG11 are samples taken during the ICEPOS cruise (2005), EG1–EG4 are samples taken during the ESSASI cruise (2008), and AG1–AG8 are samples taken during ATOS-II cruise (2009). AG9 and AG10 are the mean concentration of samples taken at Livingston Island (Pico Radio Hill and Polish Beach, respectively) during the ATOS-II (2009) terrestrial campaign.

quantify the potential breakthrough of gas phase PAHs. The second half of the split PUFs accounted for between 3 and 7% of the total mass collected on the entire PUF, and thus, there is not a significant breakthrough of PAHs. Method quantification limits for PAHs in air and particulate samples were derived from the lowest standard in the calibration curve and ranged from 0.01 to 0.005 pg m^{-3} for PAHs in air and filter samples. Recoveries were routinely monitored using deuterated PAHs as surrogates in both samples and blanks. Recoveries in samples were in the range between 42–98% (phenanthrene- d_{10}) and 65–113% (crysene- d_{12}) for the PUF used in the fugacities samplers. The surrogate recoveries were 64–105% (phenanthrene- d_{10}), 58–120% (crysene- d_{12}), and 60–118% (perylene- d_{12}) for the PUF used in the high-volume air sampler and between 54–70% (phenanthrene- d_{10}), 71–91% (crysene- d_{12}), and 71–94% (perylene- d_{12}) for the aerosol phase samples. Recoveries in blanks were in the range of 60–90% (phenanthrene- d_{10}), 84–97% (crysene- d_{12}), and 93–120% (perylene- d_{12}). Concentrations were not corrected by recoveries. The organic and elemental carbons in the aerosol phase were determined by Sunset laboratory (EEUU) as described elsewhere [Birch and Cary, 1996]. Statistical analyses to explore the differences between sampling campaigns were performed using SPSS 15.0 for Windows (Inc. Chicago).

3. Results and Discussion

3.1. Occurrence of PAHs in the Gas Phase

The spatial distribution of gas phase Σ PAHs, Phe, Pyr, and Flu in the Southern Ocean and Livingston Island atmosphere is shown in Figure 1 (complete data set for individual PAHs in Tables S1–S5 (Annex II)). Overall, the PAHs profile over the Southern Ocean and at Livingston Island were dominated by low molecular weight PAHs, such as Phe, Flu, and Pyr, with Phe being the most abundant compound detected for both the oceanic and terrestrial atmosphere. Phe accounted for ~70% of the Σ PAHs in most of the samples. Phe gas phase concentrations were in the range of 0.03–3.49 ng m^{-3} , 1.74–2.67 ng m^{-3} , and 1.22–4.58 ng m^{-3} for the oceanic campaigns carried out in 2005, 2008, and 2009, respectively. The Σ PAHs concentrations were in the range of 0.03–4.17 ng m^{-3} , 2.38–4.36 ng m^{-3} , and 1.68–9.46 ng m^{-3} for the same three oceanic cruises. Phe concentration in the gas phase ranged between 0.78 and 3.65 ng m^{-3} at terrestrial locations of Livingston Island, with a Σ PAHs gas phase concentrations in the range of 1.02 to 4.49 ng m^{-3} . Gas phase Σ PAHs concentrations did not show a latitudinal trend (Figure S3A, Annex I), even though the variability of the concentrations was high in all the subbasins sampled (Weddell, South Scotia, and Bellingshausen Seas), presumably due to the influence of various air masses and processes affecting the occurrence and fate of PAHs. Conversely, the slope of the regression of gas phase Σ PAHs concentrations versus longitude was positive (Figure S3B, Annex I) ($r^2 = 0.21$ and $p < 0.05$), indicating that gas phase PAHs concentrations were higher in the South Scotia and Weddell Seas than in the Bellingshausen Sea. The 24 h air mass back trajectories for the air samples showed three main origins (Figure S4, Annex I): (i) oceanic air masses following the Antarctic circumpolar water current (ACC), (ii) air masses from the Weddell Sea (WS), and (iii) air mass that had “touched” the Antarctic continent or islands (AntC) during the previous 24 h. Despite the differences between the three air masses, there were no significant differences between the PAHs concentrations measured in air samples influenced by the three characteristic air masses (Figure S5, Annex I). A nonparametric Kruskal-Wallis test revealed that the concentrations of Σ PAHs, Phe, and Flu were not different among the different sampling campaigns and thus different years ($p > 0.05$) (Figures S6A and S6B, Annex I), with the exception of samples taken at Polish Beach (Livingston Island), in which the concentration of the more volatile PAHs such as Phe were significantly lower ($p < 0.05$) than the concentrations measured in Pico Radio Hill and in the South Scotia and Weddell Sea cruises. For PAHs with four or more rings, concentrations were not significantly different among the sampling campaigns (Figure S6C, Annex I). The lack of significant differences between the land and ocean atmosphere suggests a minimal or lack of contamination from the ship exhausts.

While PAHs have been detected and reported in Antarctica over the last years in different compartments such as biota [Curtosi *et al.*, 2009], sea water [Stortini *et al.*, 2009], and soils and sediments [Cabrerizo *et al.*, 2013; Klanova *et al.*, 2008; Curtosi *et al.*, 2007], there is a lack of continuous monitoring of PAHs in air either in the Southern Ocean or in the South Shetland Islands. To the best of our knowledge, this study is the first to report the atmospheric occurrence of PAHs in the Southern Ocean atmosphere around Antarctica. The available literature regarding PAHs in the oceanic atmosphere and in the Arctic shows large variability in atmospheric concentrations. Table S6 (Annex II) shows the range of concentration of selected PAHs in this and

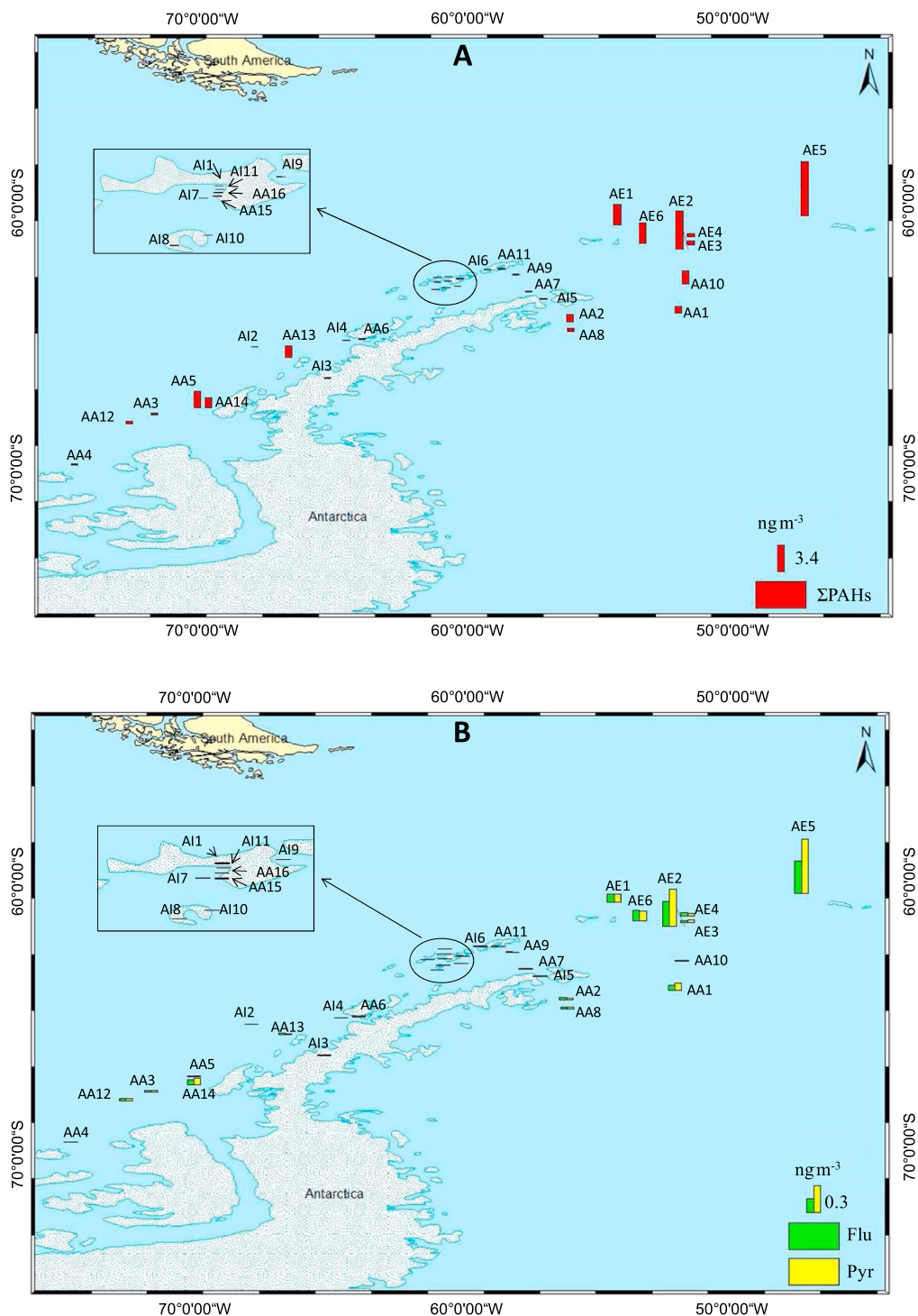


Figure 2. Spatial distribution of aerosol phase (a) Σ PAHs and (b) fluoranthene (Flu) and pyrene (Pyr) in the Southern Ocean and Livingston Island. AI1–AI11 are samples taken during the ICEPOS cruise (2005), AE1–AE6 are samples taken during the ESSASI cruise (2008), and AA1–AA14 are samples taken during ATOS-II cruise (2009). AI12, AA15, and AA16 are the mean concentrations of samples taken at Livingston Island (Pier, Pico Radio Hill, and Polish Beach, respectively) during ICEPOS (2005) and ATOS-II (2009) terrestrial campaigns.

previous oceanic assessments. As the number of PAHs considered in most studies is usually different, it is difficult to compare the levels between regions. The concentrations reported in this study are generally not significantly different than those reported in the Arctic and surrounding oceans. *Ma et al.* [2013] reported Σ_{18} PAHs in the range 2.15–4.73 ng m⁻³ in the Arctic Ocean (latitudes > 70°N) and between 0.9 and 4.07 ng m⁻³ in the North Pacific Ocean (50°N–66°N). *Ding et al.* [2007] observed concentrations Σ_{15} PAHs in the range of 0.93–92.6 ng m⁻³ over the North Pacific Ocean and the Arctic. A mean concentration of 2.02 ng m⁻³ (Σ_4 PAHs) was reported by *Lohmann et al.* [2009] in the atmosphere of the North Atlantic Ocean and Arctic Ocean. Σ_{10} PAHs levels ranged from 0.023 to 2.56 ng m⁻³ in a North-South Atlantic transect [*Nizzetto et al.*, 2008].

PAHs concentrations in the remote atmosphere over land regions have also been reported for the Arctic [*Ma et al.*, 2013; *Wang et al.*, 2013; *Hung et al.*, 2005; *Halsall et al.*, 1997], and they were lower than those described for the Antarctic Peninsula in this study. For example, Σ_{16} PAH gas phase concentrations in Alert, Nunavut (1993–2000), were in the range 0.113–0.516 ng m⁻³ [*Hung et al.*, 2005] and 0.19–0.25 ng m⁻³ in western Yukon [*Halsall et al.*, 1997].

3.2. Occurrence of PAHs in the Aerosol Phase

The PAHs' patterns in the oceanic and coastal Antarctic aerosol phase are shown in Figure S7 (Annex I), and the complete data set and ancillary data related to them are reported in Tables S7–S12 (Annex II). Overall, the profile was dominated by low to medium molecular weight PAHs, such as Flu, Pyr, Σ MMP, Σ DMP, and Phe, whose contribution accounted for ~60% of the total Σ PAHs, but the contribution of high MW PAHs was higher in the particulate phase than in the gas phase. The spatial distribution of Σ PAHs, Flu, and Pyr is shown in Figures 2a and 2b. Generally, we observed a decrease of Flu and Pyr concentrations ($p < 0.05$) at higher latitude, while no latitudinal gradient ($p > 0.05$) was observed for more volatile PAHs such as Phe. Σ PAHs concentrations in the terrestrial aerosol phase were in the range of 0.013–0.046 ng m⁻³. They were in the same range or slightly higher than those previously measured in the surrounding of the Italian Research station in Terra Nova Bay 0.001–0.050 ng m⁻³ [*Caricchia et al.*, 1993, 1995] and 0.0004–0.014 ng m⁻³ [*Piazza et al.*, 2013], and lower than those reported in field-based stations in the Arctic, ranging from 0.038 to 0.392 ng m⁻³ [*Hung et al.*, 2005]. Concentrations of aerosol phase Σ PAHs over the ocean were in the ranges 0.041–0.089 ng m⁻³, 0.42–6.76 ng m⁻³, and 0.08–2.01 ng m⁻³ for the ICEPOS, ESSASSI, and ATOS-II campaigns, respectively, which are in agreement or slightly higher than previous studies in the Arctic Ocean (0.0002 to 0.360 ng m⁻³) [*Ma et al.*, 2013], or over the North Pacific and Arctic Area (from undetectable level to 4.3 ng m⁻³) [*Ding et al.*, 2007]. A Kruskal-Wallis test was applied in order to study the differences among the sampling campaigns. While there was no statistical difference ($p > 0.05$) for Σ PAHs aerosol phase concentrations for the two campaigns at Livingston Island (2005 and 2009), concentrations measured during the three oceanic cruises were significantly different ($p < 0.05$) (Figure S8, Annex I).

3.3. Gas-Particle Partitioning of PAHs

Gas-particle partitioning is a key process affecting the transport and deposition pathways of PAHs [*Dachs and Eisenreich*, 2000; *Lohmann and Lammel*, 2004]. To the best of our knowledge, this is the first report of simultaneous gas and aerosol phase concentrations of PAHs in the Antarctic atmosphere. The particle/gas partition coefficient, K_p is given by the following:

$$K_p = \frac{C_p}{C_G TSP} \quad (1)$$

where C_p and C_G are the aerosol and gas phase concentrations (ng m⁻³) of individual PAHs, and TSP is the concentration of total suspended particles in air ($\mu\text{g m}^{-3}$). K_p can be parameterized by [*Pankow*, 1994; *Harner and Bidleman*, 1998; *Dachs and Eisenreich*, 2000]

$$K_p = 10^{-12} f_{OM} \frac{\zeta_{OC}}{\zeta_{OM}} \frac{MW_{OC}}{MW_{OM}} K_{OA} + 10^{-12} f_{EC} \frac{\alpha_{EC}}{\alpha_{AC}} K_{EC-Air} \quad (2)$$

where f_{OC} is the unitary mass fraction of organic carbon (organic matter fraction: $f_{OM} = 1.5 f_{OC}$ [*Harner and Bidleman*, 1998]), ζ is the activity coefficients of PAH in organic matter and octanol, MW is the molecular weight of octanol and organic matter, K_{OA} and K_{EC-Air} are the octanol air and elemental carbon air partition coefficients, and f_{EC} is the fraction of elemental carbon in aerosol. The compound specific value of K_{EC-Air} was

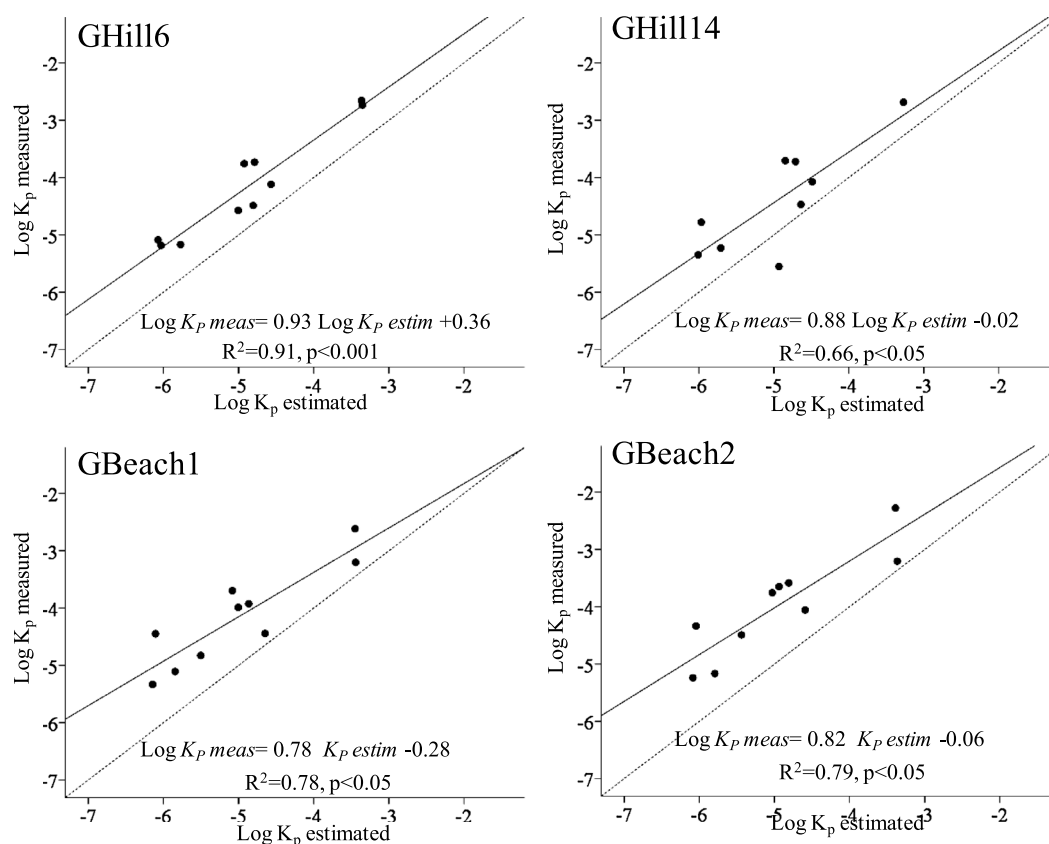


Figure 3. Aerosol-gas partitioning of PAHs. Measured versus estimated particle-gas partition coefficient (K_p) from equation (2) for samples collected at terrestrial site (GHill) and coastal site (GBeach) in Livingston Island (Southern Shetlands).

estimated from the subcooled liquid vapor pressure (p_L^0) and the elemental carbon specific surface areas (α_{EC}) by Van Noort [2003]

$$\log K_{EC-Air} = -0.85 \log p_L^0 + 8.94 - \log(998/\alpha_{EC}) \quad (3)$$

A value of $200 \text{ m}^2 \text{ g}^{-1}$ was used for α_{EC} [Bucheli and Gustafsson, 2000], and the temperature-dependent vapor pressures were estimated following Lei *et al.* [2002]. Measured K_p were calculated using the measured C_p , C_g , and TSP values for Livingston Island. These values were compared with the predicted K_p (Figure 3) obtained by applying equation (2) assuming that the ratio $\text{MW}_{\text{OC}}/\text{MW}_{\text{OM}}/\text{MW}_{\text{OC}}/\text{MW}_{\text{OM}} = \alpha_{EC}/\alpha_{AC} = 1$ [Harner and Bidleman, 1998], an assumption that does not affect the discussion below; f_{OC} and f_{EC} were only measured in the aerosols taken at Livingston Island, and they were in the range below detection limit to $0.31 \mu\text{g m}^{-3}$ for f_{OC} and below detection limit to $0.02 \mu\text{g m}^{-3}$ for f_{EC} . Because of the low concentrations of elemental carbon in the Antarctic atmosphere, as measured in this study and elsewhere [Weller *et al.*, 2013], the value of the first term of equation (2) is larger than the value of the second term, implying that the partitioning process in this remote region may be dominated by the aerosol organic matter fraction. Measured and predicted K_p were significantly correlated (r^2 in the range from 0.66 to 0.91 and $p < 0.05$) in the Antarctic atmosphere (Figure 3). The slopes of the regression between measured and predicted K_p were lower but close to the unity (slope between 0.78 and 0.93). In the remote atmosphere, gas and particle PAHs concentrations are expected to be close to equilibrium conditions because they have been transported over long distances from their sources [Cotham and Bidleman, 1995; Kamens *et al.*, 1995]. This apparent lack of equilibrium at coastal areas of Livingston Island could be driven by recent emissions or losses of PAHs to the atmosphere.

3.4. Temperature Dependence of Gas Phase Concentrations

Temperature (T) is usually considered as a primary controller in the deposition/volatilization processes involved in secondary sources of pollutants and atmospheric concentrations of POPs [Wania and Mackay,

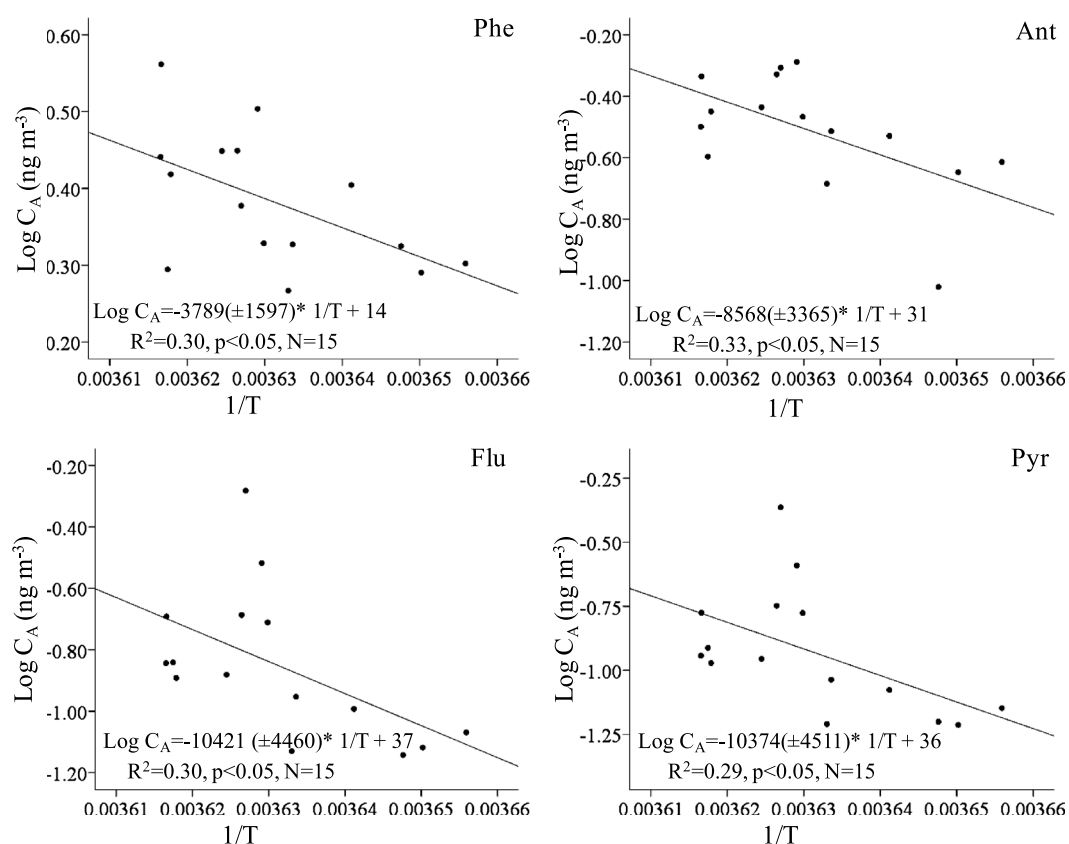


Figure 4. Temperature dependence of atmospheric concentrations. Gas phase concentration of individual PAHs ($\log C_A$) (ng m^{-3}) phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), and pyrene (Pyr) versus the inverse of temperature ($1/T$) for the atmospheric samples taken at Pico Radio Hill (Livingston Island).

1996; Cabrerizo *et al.*, 2011a, 2013]. Temperature dependence of atmospheric PAHs does not always follow the same trends as for other semivolatile compounds, since PAHs are not persistent and there are sources with strong seasonality [Gigliotti *et al.*, 2000]. The gas-phase concentrations of individual PAHs were plotted against $1/T$ to investigate the influence of ambient air temperature (Figure 4). Although the range of ambient temperatures measured at the coastal area of Pico Radio Hill during the sampling campaign was narrow ($0.5\text{--}3.5^\circ\text{C}$), the atmospheric concentrations of low MW PAHs were significantly correlated ($p < 0.05$, $r^2 = 0.29\text{--}0.33$) with ambient air temperature (Figure 4). Conversely, there was a lack of correlation for those samples collected at the coastal site of Polish Beach (directly exposed to oceanic air masses) and for the samples taken on the research vessels accounting for the oceanic atmosphere. The increase of gas phase concentrations for the more volatile PAHs at Pico Radio Hill during warmer periods suggests the presence of local/regional sources of PAHs and their revolatilization or production from local/regional sources. Potential local sources might be (i) emissions from scientific stations [Cabrerizo *et al.*, 2012], (ii) volatilization from reservoirs of PAHs in soils and snow which will be larger at higher temperatures, (iii) local biogenic reservoirs of PAHs in soil [Wilcke, 2007; Cabrerizo *et al.*, 2011c], mainly from the degradation of organic matter (diterpenes), and (iv) enrichment of PAHs in soil after snow melting due to a solvent depletion process [Macdonald *et al.*, 2002]. The lack of temperature dependence of the gas phase PAH concentrations over the Southern Ocean and at the coastal site (Polish beach) is consistent with (i) atmospheric concentrations being supported by long-range atmospheric transport [Wania *et al.*, 1998; Galbán-Malagón *et al.*, 2013b].

3.5. Antarctic Soils and Snow as a Secondary Source of PAHs

The presence of local/regional sources of PAHs at land was elucidated by studying the direction of the soil-air and snow-air exchange of PAHs by comparing the PAHs ambient air fugacity (f_A , Pa) and the PAHs snow or soil

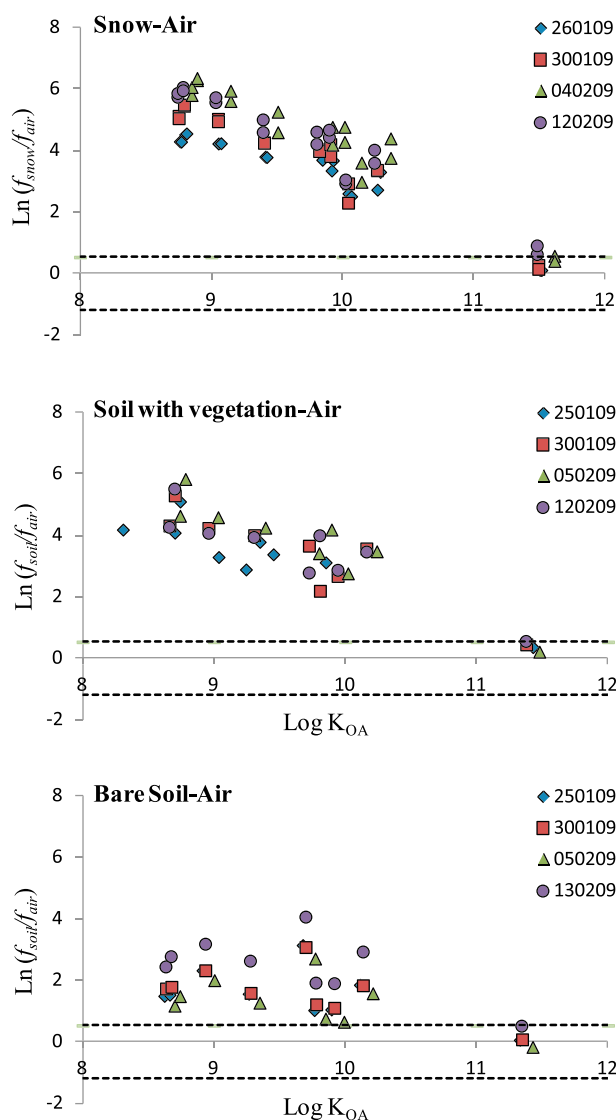


Figure 5. Surface to air fugacity ratios ($f_{\text{snow}}/f_{\text{air}}$ and $f_{\text{soil}}/f_{\text{air}}$) versus $\log K_{\text{OA}}$ for individual PAHs at the three sampling sites, covered by permanent snow, soil + lichens, and bare soil, respectively. Dash lines indicate the equilibrium interval. Initial sampling dates are also indicated in the figure (day/month/year) as 250209 (blue diamond), 300109 (red square), 050209 (green triangle), and 130209 (purple circle), depending on the selected compartment.

fugacity (f_s , Pa), obtained using the soil fugacity sampler [Cabrerizo *et al.*, 2009, 2013]. Fugacities f_A and f_S were calculated by the following:

$$f_A = 10^{-9} C_A RT / MW \tag{4}$$

$$f_S = 10^{-9} C_{SA} RT / MW \tag{5}$$

where C_A is the measured ambient air concentration at 1.5 m height (ng m^{-3}), R is the gas constant ($8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$), MW is the chemical molecular weight (g mol^{-1}), T is the temperature (K), and C_{SA} (ng m^{-3}) is the gas phase concentration in equilibrium with the soil or snow surface as measured using the soil fugacity sampler (Tables S13–S16, Annex II). When the PAH's fugacity at the surface (soil or snow) is higher than in ambient air, net volatilization occurs. In contrast, if the fugacity in ambient air is higher than in soil, there is net deposition. Due to measurements uncertainty, it is assumed that equilibrium would be reached when the ratio $\ln f_s/f_a$ is in the range of +0.53 and -1.20 , as assessed elsewhere [Cabrerizo *et al.*, 2011a, 2011b, 2013]. Values of $\ln f_s/f_a$ for individual PAHs were generally higher than 0.53 indicating net volatilization but decreased with increasing hydrophobicity (Figure 5). Therefore, both snow and soils are

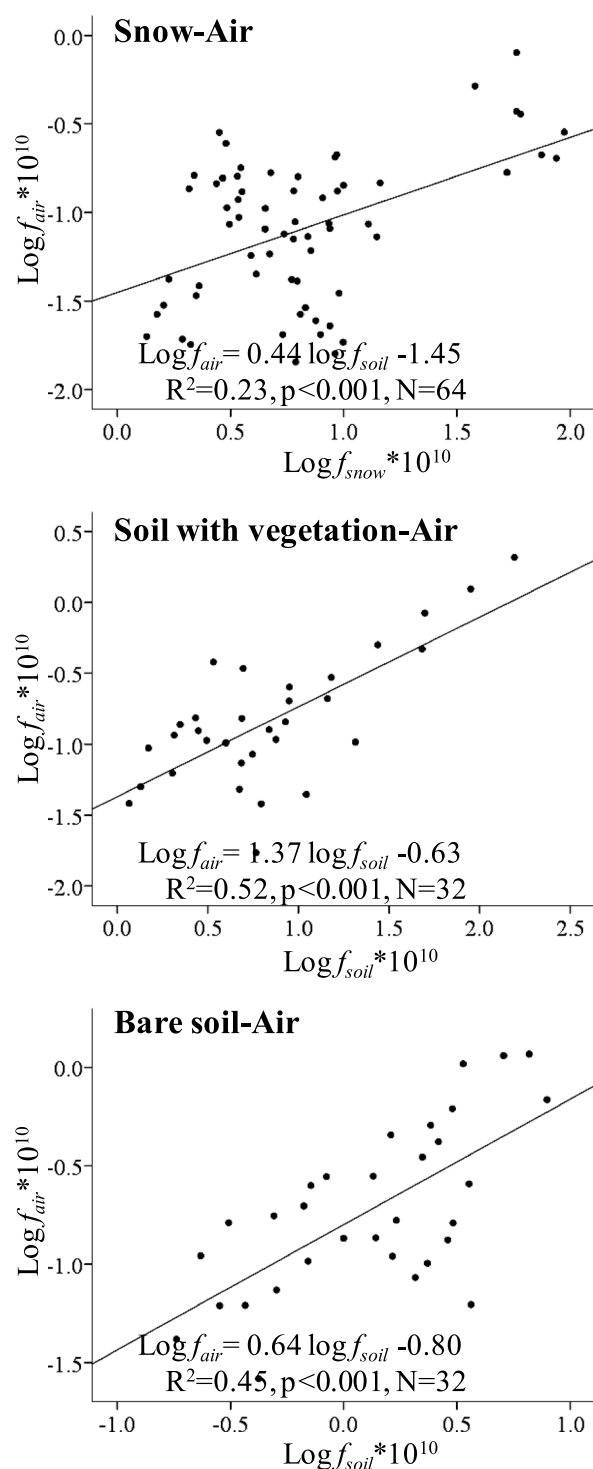


Figure 6. Secondary emissions control of atmospheric concentrations. PAH's fugacity in ambient air versus fugacity in soil or snow for the three sites at Livingston Island that were covered by snow, soil + lichens, and bare soil, respectively.

which may be related to degradation of diterpenes, as suggested in other studies [Cabrerizo *et al.*, 2011c; Wilcke, 2007] or due to an enhanced digestion of SOM by fungal acids which could unbind more easily the PAHs. It is unclear whether secondary emissions of the more volatile PAHs from snow are mediated by snow

significant sources of the lighter PAHs (three to four rings) to the atmosphere during the austral summer. The magnitude of f_s/f_a for the three ring PAHs (Phe, MPhe, and DMPhe) shows a positive significant correlation with soil organic matter (SOM) (Figure S9, Annex I); thus, the volatilization flux is larger when SOM is higher. The opposite trend was observed for synthetic compounds as reported in a companion paper [Cabrerizo *et al.*, 2013] for PCBs (discussed below). If reemission of the more volatile PAHs from soil and snow is a significant source of PAHs to the terrestrial atmosphere, then this process may control ambient atmospheric levels of PAHs over land. This scenario, confirming that local sources can explain the temperature dependence of atmospheric concentrations, can be tested by comparing PAHs' ambient air fugacities and soil/snow fugacities, which are a descriptor of the tendency of PAHs to escape from soil/snow. Figure 6 shows that PAHs fugacities in soil and snow are usually higher than adjacent ambient air fugacity, but a close air-soil and air-snow coupling was observed and confirmed by the significant correlation between the ambient air and the soil/snow PAH fugacity. Indeed, the mixture of PAHs escaping from the soil is significantly correlated ($r^2 = 0.23-0.52, p < 0.001$) with the mixture of PAHs found in the atmosphere, elucidating the potential of Antarctic soils and snow, at least during austral summer, as a source of the more volatile PAHs to the atmosphere. This volatilization flux is enhanced at high temperatures and for high soil organic matter content, as higher f_s/f_a values for the more volatile PAHs were found at higher SOM (Figure S9). This contrasts with the trend previously observed for PCBs in both temperate and polar areas [Cabrerizo *et al.*, 2011a, 2013]. Higher SOM was measured for soils covered by vegetation (lichens, mosses, and grass) [Cabrerizo *et al.*, 2012]. Reemission of the more volatile PAHs (mainly three rings) was higher in soil covered by vegetation than in bare soil. This suggests a potential biogenic generation of the more volatile PAHs from SOM degradation,

melting amplification of fugacities [Macdonald *et al.*, 2002] during the Antarctic summer, or it is due to biogenic processes occurring in the snow pack. It has been suggested by Thomas and Dieckman [2002] that the snow lies a unique habitat for a group of bacteria and microscopic plants which have been suggested to potentially modify the organic carbon concentration deposited in snow from marine or coastal influences [Antony *et al.*, 2011]. However, these potential biogenic sources could not be discerned in this study as the profiles of PAHs derived from degradation of diterpenes are still unknown and further research is needed on biogenic sources of PAHs.

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