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Levels, sources and chemical fate of persistent organic pollutants in the atmosphere and snow along the western Antarctic Peninsula[☆]



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ABSTRACT

The Antarctic continent is among the most pristine regions; yet various organic contaminants have been measured there routinely. Air and snow samples were collected during the austral spring (October–November, 2010) along the western Antarctic Peninsula and analyzed for organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) to assess the relative importance of long-range transport versus local primary or secondary emissions. Highest concentrations of PCBs, PBDEs and DDTs were observed in the glacier's snow sample, highlighting the importance of melting glaciers as a possible secondary source of legacy pollutants to the Antarctic. In the atmosphere, contaminants were mainly found in the vapor phase (>65%). Hexachlorobenzene (33.6 pg/m³), PCBs (11.6 pg/m³), heptachlor (5.64 pg/m³), PBDEs (4.22 pg/m³) and cis-chlordane (2.43 pg/m³) were the most abundant contaminants. In contrast to other compounds, PBDEs seem to have originated from local sources, possibly the research station itself. Gas-particle partitioning for analytes were better predicted using the adsorption partitioning model than an octanol-based absorption approach. Diffusive flux calculations indicated that net deposition is the dominant pathway for PBDEs and chlordanes, whereas re-volatilization from snow (during melting or metamorphosis) was observed for PCBs and some OCPs.

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1. Introduction

Polar regions have been regarded as clean environments with no significant pollution sources. The Antarctic in particular has been considered more pristine since it is far away from any urbanization, and the southern hemisphere is mainly covered by oceans and is less populated. Nonetheless, starting from 1960s, persistent organic pollutants (POPs) were detected in the Antarctic Peninsula (Baek et al., 2011; Bidleman et al., 1993; Montone et al., 2003; Riserbrough et al., 1976, 1968). It was assumed that global cold-trapping, fractionation (Wania et al., 1999) and long range atmospheric transport processes are the major source of POPs to the polar regions (Larsson et al., 1992; Montone et al., 2003; Tanabe et al., 1983). Additionally, research stations have been identified as

local point sources of POPs in the Antarctic (Hale et al., 2008; Larsson et al., 1992).

Due to its large surface area, snow can sorb significant quantities of POPs (Roth et al., 2004). During aging, the snowpack can release scavenged pollutants or take up compounds present in the lower layers of the atmosphere (Roth et al., 2004). The degradation of POPs in the Antarctic is slow due to the low temperatures and winter darkness (Corsolini, 2009). However, trapped POPs in the ice can be released to the environment during spring melt causing them to bioaccumulate in the Antarctic organisms (Geisz et al., 2008). Release of POPs to the atmosphere could also occur when snow melts (Burniston et al., 2007). Accordingly, quantitation of the snow-air exchange is deemed important to better understand the environmental fate of POPs in the polar regions.

The capacity of snow to bind pollutant has also resulted in glaciers accumulating POPs over time. Melting glaciers have hence been identified as potentially important secondary sources of legacy pollutants. For instance, melting of Alpine glaciers have been found to be a major source of OCPs in sediments and mussels (during 2005) of lakes in Italy (Bettinetti et al., 2011, 2008) and

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Switzerland (Bogdal et al., 2009; Schmid et al., 2011). Sediment cores taken from Lake Iseo, Italy and Lake Stein, Switzerland indicated that although DDT was heavily used in the period from 1950 to 1970s, a peak increase was observed at sediment intervals corresponding to 1990s (long after its ban) due to accelerated melting of glaciers. Additionally, melting glaciers supply 50–97% of the OCP inputs to Bow lake in Alberta, Canada (Blais et al., 2001), and were found to be a probable source of DDTs in the Antarctic marine ecosystem (Geisz et al., 2008). As the melting of glaciers accelerates due to global warming, fluxes of legacy POPs to the surrounding environment are expected to increase over time.

Although numerous studies investigated the levels of POPs in the Arctic atmosphere and snow (Baek et al., 2011; Barrie et al., 1992; Bidleman et al., 1989; Eckhardt et al., 2007; Halsall et al., 1998; Herbert et al., 2005; Hung et al., 2005, 2002, 2001), similar studies in the Antarctic are limited (Baek et al., 2011; Bidleman et al., 1993; Dickhut et al., 2005; Kallenborn et al., 1998; Li et al., 2012; Montone et al., 2003). Accordingly, we performed this study to determine concentrations, distribution and potential sources of OCPs, PCBs and PBDEs in the Antarctic atmosphere and snow. The air-snow exchange of the gaseous POPs was also evaluated to determine whether atmospheric deposition is still a major source of POPs to snow or the snow is currently the source of POPs to the atmosphere.

2. Materials and methods

Detailed description of the air and snow sampling, extraction and cleanup, instrumental analysis and quality assurance are given in the Supplementary data. A summary is given below.

2.1. Air and snow sampling

Two air samplers were used to collect 12 air samples (using glass fiber filter, GFF, and polyurethane foam, PUF, plugs) during the spring (October 19 – November 11) from Palmer Station (USA) located to the west of Palmer Peninsula (Fig. 1). The average volume of air samples was 3082 m³, which was higher than air volumes previously sampled in the Antarctica (Dickhut et al., 2005; Galbán-Malagón et al., 2013; Piazza et al., 2013). Seven snow samples were collected from five different locations (including two duplicates) during the same air sampling period (Fig. 1) from Palmer Station (n = 4), Jacob's Island, and Torgerson (n = 2). See Supplementary data, Tables A1 and A2 for more information about sampling periods and volumes.

2.2. Extraction, instrumental analysis and quality assurance

PUF plugs and GFF filters (both air and snow) were separately extracted in a Soxhlet extractor after spiking with surrogates, and purified on a glass chromatographic column as described in (Khairy and Lohmann, 2012). The breakthrough of the analytes from the upper to the bottom PUF was corrected using the PUF-Air equilibrium partitioning approach as detailed in (Zhang et al., 2012).

Extraction of the XAD-2 resin was done according to (Dickhut et al., 2005) and cleanup was performed as described above for the PUFs and filters.

Twenty nine PCB congeners (PCB-8, 11, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209), and 27 OCPs (hexachlorobenzene (HCBz), α -, β -, γ - and δ -hexachlorocyclohexane (HCH), heptachlor and its epoxide, aldrin, dieldrin, oxychlorodane, trans- and cis-chlordane, trans- and cis-nonachlor, α - and β -endosulfan, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, methoxychlor, o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD and p,p'-

DDT), and 12 PBDE congeners (BDE-2, 8, 15, 28, 30, 47, 49, 99, 100, 153, 154, 183) were investigated in the current study. Detailed description of the instrument operational conditions can be found in the Supplementary data.

Procedural blanks and matrix spikes were included with each sample batch and were carried throughout the entire analytical procedure in a manner identical to the samples.

Recoveries of the surrogate standards in the air filters, PUFs, snow filters and XAD-2 resin generally ranged from 68 to 96%. Matrix spikes recoveries were always >90% and relative standard deviation < 20% (Tables A5–6). Results of the replicate analysis of the snow samples indicated that the reproducibility of the analysis ranged from 6.0 to 15% for PCBs, 9.0–19% (OCPs), and 4.9–12% for PBDEs. Method detection limit calculations are detailed in the Supplementary data and Tables A7–8. The majority of the congeners were not detected in the lower PUF of the air samples. Accordingly, these PUFs were used as the field blanks (Dickhut et al., 2005), and this indicates that no cross contamination occurred during the transportation and storage of the samples.

2.3. Snow properties

Snow specific surface area (SSA) was calculated (Table A2) according to the following equation (Burniston et al., 2007) (equation (1)):

$$SSA (\text{m}^2/\text{kg}) = 2030 \exp(-4.1 \times \rho) \quad (1)$$

where ρ is the density of the snow (kg/m³). Density was calculated according to the weight and volume of the snow samples (Table A2).

2.4. Air-snow gas exchange flux

The dry gas exchange flux at the surface was derived as follows (equation (2)) (Hansen et al., 2006; Thibodeaux and Mackay, 2010):

$$F (\text{pg}/\text{m}^2/\text{day}) = k_m \left(\frac{C_s}{K_{SA}} - C_g \right) \quad (2)$$

where k_m is the overall mass transfer coefficient (m/day), K_{SA} is the snow-air partitioning coefficient (dimensionless), C_s is the measured snow concentration (pg/m³) and C_g is the gaseous atmospheric concentration of POPs (pg/m³). C_s/K_{SA} calculates the concentration of POPs in the snow pore space. See Supplementary Data for more details on the flux calculations.

3. Results and discussion

3.1. Concentrations of POPs in the snow samples

Two fractions were analyzed for the snow samples – particle-bound POPs, and the 'snowmelt' fraction (melting the snow and passing the snow melt on XAD-2 resin column). The latter combines POPs adsorbed to the crystal surface of the snow, absorbed in the quasi liquid layer or incorporated in the solid ice.

Overall, concentrations of all POPs in the snowmelt samples were significantly higher in the glacier sample (Kruskal-Wallis One Way ANOVA on Ranks, $p < 0.05$). Concentrations of HCHs, HCBz, DDTs, PCBs and PBDEs were 1.4–23 times greater than at the other locations. This confirms earlier suspicions that melting glaciers could have become an important secondary source of legacy pollutants to the western Antarctic Peninsula. For the other locations, higher concentrations (after the glacier sample) of POPs were

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