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Citation/Publisher Attribution
Khairy, M. A., Luek, J., Dickhut, R., & Lohmann, R. (2016). Levels, Sources and Chemical Fate of Persistent Organic Pollutants in the Atmosphere and Snow along the Western Antarctic Peninsula. Environmental Pollution, 216, 304-313.
Available at: http://dx.doi.org.10.1016/j.envpol.2016.05.092

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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.

0. Capsule

Highest concentrations of organic pollutants were observed in an Antarctic glacier's snow sample, highlighting their importance as a possible secondary source of legacy pollutants.

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; Risebrough 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 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 - 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 to 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 is significantly accelerated nowadays because of the increased effect
of global warming, loads of POPs to the surrounding environment is expected to greatly increase.

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 GFF filters and PUF plugs) during the spring (October 19 – November 11) from Palmer Station (USA) located to the west of Palmer Peninsula (Figure 1). The average volume of air samples was 3082 m³, which was higher than air volumes previously sampled in the Antarctica (Dickhut et al.,
Seven snow samples were collected from five different locations (including two duplicates) during the same air sampling period (Figure 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, oxychlordane, 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 A 5-6). 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):

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

where \( \rho \) is the density of the snow (kg/m\(^3\)). 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):

\[
F (\text{pg/m}^3/\text{day}) = K_m \left( \frac{C_s}{K_{SA}} - C_g \right) \tag{2}
\]

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/m\(^3\)) and \(C_g\) is the gaseous atmospheric concentration of POPs (pg/m\(^3\)). \(C_s/K_{SA}\) 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 observed at Torgerson Island and Old Palmer located to the northwest of...
Palmer Station. The least OCP concentrations were always observed at Jacob Island located to the south of the Palmer Station (Figure 1), whereas the backyard of the research station showed the lowest concentrations of PCBs and PBDEs in the snowmelt samples. In the particulate phase samples, concentrations of HCBz, p,p'-DDT and PCBs at Torgerson Island were 2.0-14 times greater than concentrations detected at all the other locations including the glacier. Torgerson is a rocky Island and could possibly be richer in organic matter compared to the other locations. In contrast, concentration of p,p'-DDE at the glacier was 3.0-16 times greater than concentrations detected at the other samples. Chlordanes and PBDEs showed comparable concentrations at all the locations. Most of the OCPs, and PCBs were found in the snowmelt as was previously observed for OCPs in the Canadian melting glaciers (Blais et al., 2001) due to the poor organic matter in the glacial clay. In contrast, a significant portion of PBDEs was bound to particles indicating either their different emission sources and/or a different particle-snowmelt partitioning behavior than PCBs. Ratios of OCPs confirmed their legacy origin whereas for PBDEs, the existence of possible local sources was indicated (see discussion below and Supplementary data for more details).

3.1.1. OCPs

DDTs (sum of the six isomers) showed the highest concentrations among all the investigated OCPs at all the locations with concentrations ranging from 30 pg/L (Jacob's Island) to 412 pg/L (glacier). Aldrin, dieldrin, oxychlordane, endosulfans, endrin, endrin aldehyde, endrin ketone and methoxychlor were <LOD in all the samples. Snowmelt concentrations (in pg/L water) of OCPs are given in Table A9.
HCBz, trans-chlordane, cis-chlordane, p,p′-DDE, p,p′-DDD and p,p′-DDT were the only detected OCPs in the particulate phase. HCBz showed the highest concentrations among the other detected OCPs in all the samples with values ranging from 10 pg/L (Palmer Backyard) to 46 pg/L (Torgerson Island) followed by p,p′-DDE (3.5 - 55 pg/L), p,p′-DDD (<LOD - 20 pg/L) and cis-chlordane (7.0 - 19 pg/L). Particulate phase concentrations of OCPs in the snow samples are given in Table (A10).

3.1.2. PCBs

Snowmelt PCB concentrations ranged from 300 pg/L (Palmer Backyard) to 1,100 pg/L (glacier) with an average concentration of 770 pg/L (Table A11). The most abundant PCB congeners were PCB 8, 11, 28, 44, 52, 66, 101, 153, 138, 180, 187 and 206 (Table A11). Except for the glacier sample, all the other samples were dominated by tri- through penta-chlorinated biphenyls comprising 63 - 72 % of the total detected snowmelt concentrations (Figure 2A). In the glacier sample, comparable contributions from di- through hepta-chlorinated biphenyls were observed (14 - 20 %).

Particulate phase concentrations of PCBs ranged from 78 pg/L (Jacob Island) to 860 pg/L (Torgerson Island) with an average concentration of 270 pg/L. Detected concentrations of PCB congeners at Torgerson Island (Table A12) were significantly higher (Kruskal-Wallis One Way ANOVA on Ranks, p < 0.05) than detected concentrations at the other samples. Samples were dominated by tetra-through hepta-chlorinated biphenyls comprising 67 - 91 % of the total detected concentrations (Figure 2B). Unlike the snowmelt samples, significant contribution from the hepta-chlorinated biphenyls was observed in the particulate samples.
3.1.3. PBDEs

Snowmelt concentrations of PBDEs in the snow samples are given in Table (A13). Concentrations ranged from 20 pg/L (Palmer Backyard) to 470 pg/L (glacier) with an average concentration of 161 pg/L. BDE-2 and 49 were <LOD in the samples. The most abundant PBDE congeners (Figure 2C) were BDE 47 (11 - 293 pg/L) and BDE 99 (3.0 - 106 pg/L). Both comprised 68 - 85 % of the total detected PBDE concentrations in the snow samples.

Particulate phase concentrations of PBDEs are shown in Table (A14). Concentrations generally ranged from 94 pg/L (Jacob Island) to 213 pg/L (glacier) with an average concentration of 180 pg/L. BDE 2, 8 and 15 were <LOD in all the samples. All the samples were dominated by BDE 47 and 99 comprising 74 - 78 % of the total concentrations (Figure 2D). However, in contrast to the snowmelt samples, concentrations of BDE 99 (51 - 89 pg/L) in the particulate phase were higher than BDE 47 (22 - 80 pg/L).

Of the penta BDE congeners, BDE-100 has the longest photodegradation half-life followed by BDE-47 and BDE-99, which is the most photodegradable congener (Dickhut et al., 2012; Eriksson et al., 2004; Fang et al., 2008). Accordingly, calculated ratios for these three congeners could indicate whether the source of PBDE is long range transport or from local emissions. Calculated ratios of BDE-47/BDE-100 (snowmelt: 8.0 - 49; particulate phase: 3.0 - 5.0) and BDE-99/BDE-100 (snowmelt: 4.0 - 13; particulate phase: 5.0 - 8.0) in the snow samples were within or higher than values calculated for the penta BDE commercial formulations (Dickhut et al., 2012; La Guardia et al., 2006) (BDE-...
47/BDE-100: 2.9-5.5; BDE-99/BDE-100: 3.7-5.4) implying that PBDEs were emitted from local sources (research stations) and did not undergo long range transport.

### 3.2. Atmospheric Concentrations of POPs

Gaseous concentrations of OCPs, PCBs and PBDEs detected at the Palmer station sampling site are given in Tables A15, A16 and A17 respectively. Based on average gaseous concentrations, the following descending order was observed: HCBz (34 pg/m$^3$) > ΣPCBs (12 pg/m$^3$) > heptachlor (5.6 pg/m$^3$) > ΣPBDEs (4.2 pg/m$^3$) > cis-chlordane (2.4 pg/m$^3$). All the other detected OCPs showed concentrations < 2.0 pg/m$^3$. Aldrin, dieldrin, methoxychlor, endrin, endrin aldehyde, endrin ketone, DDD (o,p’- and p,p’-isomers), β- and δ-HCH and β- endosulfan were <LOD in all the samples (Table A15).

In the particulate phase, PCBs showed the highest average concentrations among all the investigated POPs at the two sites (S1: 4.2 pg/m$^3$; S2: 3.1 pg/m$^3$) followed by PBDEs (0.8 pg/m$^3$). All the other detected OCPs in both samples showed comparable concentrations (Table A18) with values always < 0.3 pg/m$^3$. Particle-bound concentrations are given in Tables A18, A19 and A20 respectively.

Ratios of OCPs calculated for the gaseous and particulate phase samples indicated aged sources, whereas PBDE ratios indicated local sources possibly from the research stations.

#### 3.2.1. OCPs

Concentrations of gaseous HCBz were significantly higher than concentrations of all the other detected OCPs (p < 0.001). A similar finding was previously observed in the Antarctic Peninsula (Dickhut et al., 2005) and at the Norwegian Troll research station (Kallenborn et al., 2013). α- and γ-HCH were the only detected isomers in the gas phase.
No statistical significant difference was observed between detected concentrations of α- and γ-HCH isomers.

Unlike for the Arctic air, few studies have reported concentrations of endosulfans in the Antarctic atmosphere (Baek et al., 2011; Pozo et al., 2006). α-endosulfan was the only detected isomer in the gaseous samples at Palmer station at concentrations ranging from 1.1 pg/m$^3$ to 3.4 pg/m$^3$ (Table A9), which was similar to the finding at King George Island (Baek et al., 2011).

Chlordanes include trans- and cis-chlordane, cis- and trans-nonachlor, oxychlordane, heptachlor and its epoxide. Concentrations of chlordanes ranged from 10 pg/m$^3$ to 18 pg/m$^3$ with an average concentration of 13 pg/m$^3$. Based on average concentrations, heptachlor was the second most abundant OCP in the gaseous samples with concentrations significantly higher than concentrations of trans- and cis-chlordane (p < 0.001) suggesting the use of heptachlor as a pesticide (not as a component of the technical chlordane mixture) (see Supplementary data for comparison with gaseous POP concentrations previously reported for the Antarctic) (Shunthurasingham et al., 2010).

p,p′-DDE, o,p′-DDE and p,p′-DDT were the only detected isomers in the current study. Concentrations of p,p′-DDE (0.3 - 1.4 pg/m$^3$) were significantly higher (p < 0.001) than detected concentrations of gaseous o,p′-DDE (0.05 - 0.2 pg/m$^3$) and p,p′-DDT (0.05 - 0.1 pg/m$^3$) indicating aged DDT sources.

In the particulate phase, only α-HCH, γ-HCH, HCBz, trans-chlordane, cis-chlordane and p,p′-DDE were detected in the samples (Table A18). For sample 1 (S1; gaseous phase
and particulate phase), > 90 % of the total concentrations for the detected OCPs were found in the gaseous phase.

3.2.2. PCBs

$\sum_{29}$ PCB concentrations in the gaseous samples ranged from 5.4 pg/m$^3$ to 16 pg/m$^3$ with an average concentration of 12 pg/m$^3$. Detected concentrations of PCBs in the current study were lower than concentrations previously reported for the Antarctic (see Supplementary data for more details). Gaseous concentrations of PCBs are shown in Table A16.

The most abundant congeners in the gas phase samples were PCB 11 (2.0 pg/m$^3$), PCB 8 (1.4 pg/m$^3$), and PCB 28 (1.2 pg/m$^3$). PCB 11 concentrations (1.1 - 3.1 pg/m$^3$) were the highest among all the detected congeners comprising on average 21 % of the total PCB concentrations. Similarly, PCB 11 exhibited the highest concentrations among the investigated PCB congeners in King George Island during 2005-2007 (Baek et al., 2011), and comprised on average 16 % of the total atmospheric PCB concentrations measured in the Antarctic (Vecchiato et al., 2015). However, contributions in the Arctic were much lower (Baek et al., 2011) indicating that the sources of this non-Aroclor congener may be concentrated in the Southern Hemisphere. PCB 11 is found in paints/pigments (Hu et al., 2008) and has been detected in the atmospheric environments of urban centers and the Great Lakes (Hu et al., 2008; Khairy et al., 2015). PCB 11 can also be generated from the degradation of higher chlorinated PCB congeners such as PCB 77, 12 and 169 (Vecchiato et al., 2015), which were all <LOD in the present study. Accordingly, we assume that PCB 11 is emitted from local sources probably from the research station. More investigation is needed to support our assumption. Gaseous samples were dominated by
di-, tri- and tetra-chlorinated biphenyls (Figure A1A) comprising on average 38, 20 and
15 % respectively of the total PCB concentrations. Penta-, hexa- and hepta-chlorinated
biphenyls showed lower contributions (7.5 - 11 %). Octa-, nona- and deca-chlorinated
congeners were not detected in the gaseous samples. This observed pattern of the
homologue groups indicates that long range atmospheric transport is probably the major
source of PCBs (Gambaro et al., 2005). Dominance of the lower chlorinated PCBs was
previously observed in the Antarctic at Signy Island (Kallenborn et al., 1998), King
George Island (Li et al., 2012), Brazilian Research Station (Montone et al., 2003), Terra
Nova Bay (Gambaro et al., 2005) and the Korean Research Station (Choi et al., 2008).

In the particulate phase (Table A19), a different pattern was observed. Particulate phase
PCBs ranged from 2.1 - 5.2 pg/m$^3$ and 1.3 - 4.4 pg/m$^3$ at S1 and S2 respectively. In both
samples, PCB 187 (S1: 0.6 - 2.0 pg/m$^3$; S2: 0.4 - 0.9 pg/m$^3$) and 180 (S1: 0.6 - 1.3 pg/m$^3$;
S2: 0.4 - 0.8 pg/m$^3$) were the dominant congeners. As for the distribution of the
homologous groups, both particulate phase samples showed comparable patterns with
slightly higher concentrations of hexa- and hepta-chlorinated biphenyls observed at S1
(Figure A1A). Interestingly, octa-chlorinated biphenyls were <LOD in the gas and
particulate phases. However, PCB 206 and 209 were only detected in the particulate
phase samples. In both samples, hepta-chlorinated biphenyls dominated the profiles
comprising on average 44 % and 39 % of the total PCB concentrations at S1 and S2
respectively. Di- through hexa-chlorinated biphenyls showed comparable contributions in
both samples (Figure A1A), (7.0 % - 12 % at S1 and 8.0 % - 13 % at S2). Nona- and
deca-chlorinated biphenyls had only minor contributions (< 5.0 %).
3.2.3. PBDEs

Gaseous $\Sigma_{12}$ PBDE concentrations ranged from 1.4 - 7.6 pg/m$^3$ with an average concentration of 4.2 pg/m$^3$ (Table A17). BDE-2, 8, 15, 30 and 183 were <LOD in all the samples. > 70% of the detected PBDE congeners in the present study were found in the gaseous phase. Particulate phase concentrations in the present study ranged from 0.4 - 1.3 pg/m$^3$ (average: 0.8 pg/m$^3$) and 0.3 - 1.2 pg/m$^3$ (average: 0.8 pg/m$^3$) at S1 and S2 respectively. BDE-2, 8, 15, 30 and 49 were found <LOD in both samples, whereas BDE-153, 154 and 183 were <LOD only at S1 (Table A20). In the gaseous and particulate phases, BDE-47 was the dominant congener comprising on average 41 - 52% of the total PBDE concentrations followed by BDE-99 (24 - 35%). BDE-100 and 28 showed comparable contributions in the gaseous phase (~7.0% each) and the particulate phase of S2 (~10% each). BDE-153, 154 and 183 showed lower contributions (Figure A1B). BDE-47 and 99 were the dominant congeners detected in gaseous phase of the Arctic air (Shen et al., 2006; Su et al., 2007; Wang et al., 2005), whereas BDE-28 and 17 (not included in the present study) were the dominant congeners at King George, Antarctic (Li et al., 2012). BDE-209 (not included in the present study) was the dominant congener in the particulate phase samples collected at Palmer station in 2001 – 2002 (Dickhut et al., 2012). However, average concentrations (S1 and S2) of particulate phase BDE-47 (0.4 ± 0.1 pg/m$^3$), 99 (0.3 ± 0.1 pg/m$^3$) and 100 (0.07 ± 0.02 pg/m$^3$) were in very good agreement with values observed in 2001 - 2002 (BDE-47: 0.3 ± 0.08 pg/m$^3$; BDE-99: 0.3 + 0.1 pg/m$^3$; BDE-100: 0.06 +0.03 pg/m$^3$) (Dickhut et al., 2012).

The average ratio values of BDE-47/BDE-100, BDE-47/BDE-99 and BDE-99/BDE-100 in the present study were 7.9, 2.1 and 3.7 respectively for the gaseous phase samples, and
5.1, 1.4 and 3.8 for the particulate phase samples. Particulate phase values in the present study were higher than values previously reported for Palmer station during 2001-2002 (Dickhut et al., 2012) (BDE-47/BDE-100: 3.6; BDE-99/BDE-100: 2.5) but were within the range observed in the commercial penta BDE formulations (Dickhut et al., 2012; La Guardia et al., 2006) and the Arctic air (BDE-47/BDE-100: 5.9; BDE-47/BDE-99: 1.1; BDE-99/BDE-100: 5.4) (Dickhut et al., 2012). For the gaseous phase samples, the ratio BDE-47/BDE-100 was higher than the commercial formulation, whereas the other two ratios were within the values of the commercial formulation. Based on our findings, PBDEs detected at Palmer Station were not subjected to significant photodegradation. In other words, PBDEs were emitted from local sources and did not undergo long range transport. Accordingly, we suggest that the station itself is the major source of PBDEs which probably overwhelmed the long range transport source. Research stations have been regarded as possible local sources of PBDEs (Hale et al., 2008) and other POPs (Larsson et al., 1992; Risebrough et al., 1990).

3.3. Gas-Particle partitioning of POPs

Particle-air partitioning coefficients ($K_p$) were calculated in the present study based on the Junge - Pankow adsorption partitioning model (using the subcooled liquid vapor pressure, $P_L$) and the absorption partitioning model (using octanol-air partitioning coefficient, $K_{OA}$) (Finizio et al., 1997; Harner and Bidleman, 1998). Detailed description of the calculations, sources of $K_{OA}$ and $P_L$ and their temperature correction process can be found in the Supplementary data. As concentrations of the total suspended particulates (TSP) and organic matter content were not measured in the present study, we used
literature values measured for Antarctic aerosols (2.4 pg/m$^3$) (Ali et al., 2015; Mazzera et al., 2001).

As shown in Figure (3A), particle-bound fractions of PCBs, OCPs and BDE-28 were much higher than the absorption model predicted values, whereas BDE-47, 99 and 100 were generally in better agreement. Measured particle bound fractions of PCBs, OCPs BDE-28 and 47 showed on the other hand better agreement with the predicted values using the adsorption partitioning model (Figure 3B). In contrast, much lower particle-bound fractions were measured for BDE-99 and 100 (pentabrominated diphenyl ether) compared to the predicted curve. This implies that the adsorptive partitioning model ($P_L$) is generally a better descriptor of particle-air partitioning of POPs in the present study as was previously indicated for some POPs in the UK (Lohmann et al., 2000) (see Supplementary data for more details).

If the major source of POPs in the Antarctic was long range transport, then the gas-particle partitioning should have approached equilibrium [slopes log $K_{OA}$-log $K_p$ and log $P_L$-log $K_p$~1(-1)]. In the present study, slopes (Table A21) were much shallower than -1 (~ -0.2 for PBDEs, ~ -0.4 for PCBs and OCPs). We hypothesize that lower chlorinated PCBs and penta- BDEs were emitted from local sources, which needed to re-equilibrate with the clean background particles or those freshly emitted in the Antarctic. This in turn will alter the established gas - particle partitioning causing the slopes to be shallower. The higher measured particle bound fraction of the lower chlorinated biphenyls and the lower measured values for penta- BDEs compared to the predicted ones could be either the reason of the difference in volatility (lower chlorinated biphenyls will re-equilibrate
faster with freshly emitted particles than PBDEs) or difference in the local sources. As we suggested earlier, the research activities (station, field work) could be a major source of PBDE at the western Antarctic Peninsula (based on the calculated ratios and the photodegradation half-lives of the penta-BDE congeners). For PCBs and OCPs, we suggest that revolatilization from the snow as it ages and/or melt is a secondary source in the Antarctic at Palmer station, especially for the lower chlorinated congeners which are more volatile. This assumption will be further investigated in the air-snow gaseous exchange section (see below).

3.4. Comparison between Atmospheric and Snow Concentrations of POPs

Measured snow concentrations (particulate phase and snowmelt) were compared with the measured atmospheric concentrations in the present study assuming that atmospheric deposition is the major source of POPs present in the snow. To test this assumption, snow concentrations of POPs in the interstitial pore spaces ($C_{is}$), snowmelt ($C_{sm}$) and particulates ($C_{sp}$) were compared to atmospheric gaseous concentrations ($C_g$; dry gaseous deposition), scavenged gaseous POPs by snow (wet gaseous deposition) and scavenged particulate phase POPs by snow (wet particle deposition) respectively. Dry gaseous deposition will be discussed later in the flux calculation section. For the wet gaseous deposition, snowmelt concentrations were predicted ($C_{psm}$) from atmospheric concentrations as follows (equation 1):

$$C_{psm} = W_g \times C_g$$

where,

$W_g$ is the gas scavenging coefficient and $C_g$ is the atmospheric gas phase concentrations of POPs.
$W_g$ is calculated as (equation 2) (Hansen et al., 2006):

$$W_g = K_{ia} \times SSA_{in} \times \rho_w \tag{2}$$

where, $SSA_{in}$ is the specific surface area of fresh snow (0.12 m$^2$/g) (Burniston et al., 2007), and $\rho_w$ is the density of water (10$^6$ g/m$^3$) (Hansen et al., 2006).

Similarly, snow particle phase concentrations ($C_{psp}$) were predicted according to equation 3:

$$C_{psp} = W_p \times C_{sp} \tag{3}$$

where, $W_p$ is the particle scavenging coefficient ($10^5$) (Lei and Wania, 2004).

Results obtained for Palmer Backyard station are shown in Figure (4). Results of the three other locations are presented in the Supplementary Data (Figures A2 - A4).

Snowmelt concentrations of PBDEs predicted from the wet scavenging process of the atmospheric gas phase were significantly higher ($p < 0.001$) than measured concentrations at all the sampling locations (Figures 4A, A2A, A3A, A4A). Additionally, detected PBDE congeners in the atmospheric samples were different from the snowmelt samples. This implies that either the wet scavenging of gaseous PBDEs is probably not highly efficient or that prolonged snow events caused dilution of contaminant concentration in the snow. Additionally, the difference in the congeners patterns suggest different sources affecting the atmosphere and snow. A similar pattern was observed for the majority of OCPs (Figures 4B, A3B, A4B). However at Old Palmer (Figure A3B), some OCPs (o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDD, p,p'-DDT, trans-nonachlor,
heptachlor and its epoxide) were measured in the snowmelt samples but were <LOD in the atmospheric gas phase samples. This finding is another indication of the different sources of POPs in the atmosphere and the snow. We assume that measured OCPs in the snowmelt that were not detected in the atmospheric samples represents old contamination that was probably incorporated in the crystalline structure of snow as it aged and undergone metamorphosis knowing that the detected OCPs were banned more than three decades ago. In contrast to PBDEs and OCPs, measured snowmelt concentrations of PCBs (Figures 4C, A2C, A3C, A4C), were higher than predicted concentrations especially for the lower chlorinated PCB congeners (di- through penta- chlorinated biphenyls). It is important to mention that the snow analyzed in the current study represent a composite sample of various layers at each sampling location to a depth of 15 cm. Snow physical properties (density, specific surface area, porosity) greatly change within hours after snowfall event (Herbert et al., 2005), which will affect the sorbed amount of vapor phase POPs to snow (Herbert et al., 2006). Loss or transformation of analytes in snow could also occur as a result of the photodegradation process (Herbert et al., 2006). Although these processes were not investigated in the present study, it should be considered when comparing between measured and predicted vapor phase POPs in the snow.

Wet scavenging of particulate phase PBDEs were found to partially account for the PBDEs found in the snow (particulate phase) as measured concentrations were an order of magnitude higher than predicted values for the majority of the congeners (Figures 4D, A2D, A3D, A4D). Additionally, some PBDEs (BDE-30, 49, 153, 154 and 183) were only found in the snow samples, which as observed in the snowmelt imply the existence of
another source other than atmospheric deposition that contributes to the levels of PBDEs in the snow. In contrast, predicted particle bound OCP (except HCBz) (Figures 4E, A2E, A3E, A4E) and PCB concentrations (Figures 4F, A2F, A3F) were significantly higher (p < 0.05) than measured particle bound concentrations. Predicted HCBz concentrations were in good agreement with measured ones. At Torgerson Island, measured particle bound PCBs in snow were higher than predicted concentrations (Figure A4F). Wp was not measured in the present study and estimates available in literature varies greatly (Franz and Eisenreich, 1998; Wania et al., 1999). The process of repartitioning of POPs to particles in snow and the fate of particle bound POPs in snow is also unknown (Herbert et al., 2006). These two points should be considered when performing the comparison between measured and predicted particle bound POP concentrations in snow.

3.5. Diffusive Fluxes of Gaseous POPs

Calculated diffusive fluxes (pg/m²/d) for gaseous POPs are shown in Figure (5). Calculated fluxes for PBDE (Figure 5A), chlordanes, α-endosulfan (Figure 5C) were negative indicating that these contaminants are depositing from the atmosphere.

All the PCBs (Figure 5B), HCBz, heptachlor and DDTs (Figure 5C) showed positive fluxes indicating re-volatilization from snow (when it melts or undergo metamorphism) to the atmosphere implying that the Antarctic snow is acting as a source of PCBs and OCPs to the atmosphere. The highest net volatilization flux was calculated for HCBz (200 – 1040 pg/m²/d), followed by PCB 28/31 (340 – 900 pg/m²/d), PCB 5/8 (200 – 580 pg/m²/d) and PCB 11 (120 – 460 pg/m²/d), whereas the highest net depositional flux was calculated for trans-nonachlor (-5.0 to -15 pg/m²/d) followed by cis-chlordane (-3.5 to -
7.0 pg/m²/d). All the other contaminants that showed net depositions fluxes had values < -5.0 pg/m²/d. Except for BDE-47, and 99, calculated fluxes for the other congeners were within the uncertainty range, and hence treated as being at or near equilibrium (between snow and air). No great variations (in magnitude and directions) were observed for fluxes calculated for POPs at the four sampling locations (Figure 5). For PCBs (Figure 5B), volatilization fluxes for the lower chlorinated congeners (di- through tetra-) were much higher than fluxes calculated for the higher chlorinated ones (penta- through deca-), which is expected when considering the volatility (vapor pressure) of the PCB congeners.

4. Conclusions

We investigated the concentrations of PBDEs, OCPs and PCBs in the atmosphere and snow from the western Antarctic Peninsula. Our results indicated that PBDEs were probably emitted from the research station (local source). However, the atmospheric samples were collected only at one location, which is not enough to support our assumption. Seasonal samples should be collected to have a better image about the temporal variations and chemical fate of POPs in the atmosphere. Due to the difficulties associated with the conventional active sampling technique, the use of passive samplers would be a cost effective way to conduct a long term monitoring of POPs in the Antarctic atmosphere. Although only a few snow samples were investigated in this study, we tried to investigate the wet and dry deposition of gaseous and particle bound POPs and to quantify the diffusive gaseous fluxes of POPs between the air and the snow. Based on the difficulties experienced, the following should be considered in the future studies: a) the fate of POPs in snow should be investigated directly after the snowfall. Additionally, temporal variations in the snow physical properties and the sorbed levels of POPs should
also be considered; b) Snow sampling should be performed seasonally in parallel with the atmospheric sampling due to the great variation in the expected levels of POPs both in the atmosphere and snow due to the temperature variations; c) wet scavenging should be investigated with more details to obtain better estimates of the scavenging coefficients; d) Snow cores should be considered in the future studies to investigate and quantify (magnitude and direction) the diffusive transport of POPs in snow.

Supplementary material

Supplementary data associated with this article can be found in the online version.

ACKNOWLEDGMENTS

We acknowledge funding from the National Science Foundation (ARC 1203486) to study the transport of POPs into the Arctic Ocean. We acknowledge Hugh Ducklow and the Palmer LTER for intellectual and logistical support, and thank Rebecca Dickhut for her prior leadership on this grant.

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