Study of PCBs and PBDEs in King George Island, Antarctica, using PUF passive air sampling

Yingming Li a, Dawei Geng a, b, Fubin Liu c, Thanh Wang a, Pu Wang a, Qinghua Zhang a, *, Guibin Jiang a

a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
b School of Energy Resources, China University of Geosciences (Beijing), Beijing 100083, China
c National Marine Environmental Forecasting Center, Beijing 100081, China

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ABSTRACT

Polyurethane foam (PUF)-disk based passive air samplers were deployed in King George Island, Antarctica, during the austral summer of 2009–2010, to investigate levels, distributions and potential sources of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Antarctic air. The atmospheric levels of ∑ indicator PCBs and ∑14 PBDEs ranged from 1.66 to 6.50 pg m⁻³ and from 0.67 to 2.98 pg m⁻³, respectively. PCBs homologue profiles were dominated by di-PCBs, tri-PCBs and tetra-PCBs, whereas BDE-17 and BDE-28 were the predominant congeners of PBDEs, which could be explained by long-range atmospheric transport processes. However, the sampling sites close to the Antarctic research stations showed higher atmospheric concentrations of PCBs and PBDEs than the other sites, reflecting potential local sources from the Antarctic research stations. The non-Aroclor congener PCB-11 was found in all the air samples, with air concentrations of 3.60–31.4 pg m⁻³ (average 15.2 pg m⁻³). Comparison between the results derived from PUF-disk passive air sampling and high-volume air sampling validates the feasibility of using the passive air samplers in Antarctic air. To our knowledge, this study is the first employment of PUF-disk based passive air samplers in Antarctic atmosphere.

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1. Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent organic pollutants (POPs) that has been targeted and banned by the Stockholm Convention. These chemicals are toxic, highly persistent in the environment and can undergo long-range atmospheric transport, which means that POPs can be transferred from source regions to the ambient environment in urban, rural and even remote areas, including the Antarctica. Antarctica has been considered as one of the most pristine areas in the world because it is remote from industrial sources and anthropogenic activities. However, increasing tourist visitations and Antarctic research activities have also increased the risk of POPs contamination to the Antarctic environment (Hale et al., 2008). In recent years, POPs have been found in the air (Gambaro et al., 2005; Choi et al., 2008; Baek et al., 2011), soil (Negoita et al., 2003), plants (Park et al., 2010) and animal tissues (Corsolini et al., 2002; Aono et al., 1997; Schiavone et al., 2009; Borghesi et al., 2008; Nash et al., 2008) from the Antarctic environment, further displaying the ubiquity of these pollutants. It was also found that both long-range atmospheric transport (LRAT) and local sources associated with Antarctic research stations can contribute to the occurrence of POPs in Antarctic environment (Choi et al., 2008; Hale et al., 2008).

High-volume air samplers act as the main tool in the air monitoring of POPs in Antarctica. However, these samplers need electricity, which greatly limits their use in truly remote Antarctic areas. Passive air samplers, which adsorb atmospheric POPs on polyurethane foam (PUF) (Shoeib and Harner, 2002; Harner et al., 2004), semipermeable membrane (SPMD) (Bartkow et al., 2004), or XAD adsorbent resins (Wania et al., 2003), have been developed in recent years as complementary tools for monitoring of atmospheric POPs around the globe. Compared to conventional high-volume air samplers, they are economical and do not require electricity. Passive air samples have been successfully used in Asia (Jaward et al., 2005), Europe (Jaward et al., 2004) and other continental areas (Pozo et al., 2006; Gouin et al., 2005). As for the Antarctic air monitoring, however, only XAD-resin based passive air samplers have been used in the vicinity of Korean Antarctic Research Station (Choi et al., 2008; Baek et al., 2011). To our
knowledge, there is no previous report on using PUF-disk based passive air samplers for air monitoring of POPs in Antarctica.

Although the atmospheric monitoring of PCBs in Antarctica has previously been conducted at Signy Island (Kallenborn et al., 1998), Brazilian Antarctic Research Station (Montone et al., 2003), Terra Nova Bay (Gambaro et al., 2005), and the Korean Antarctic Research Station (Choi et al., 2008), data on PCBs contamination in Antarctica air is still scarce. Prior to this study, we have not found any monitoring studies on PBDEs in Antarctic atmosphere. In this work, we deployed PUF-disk based passive air samplers in King George Island, Antarctica, during the XXVI Chinese Scientific Research Expedition to Antarctica in the austral summer of 2009–2010. The objective was to: (1) investigate the atmospheric levels, distributions and potential sources of PCBs and PBDEs in this pristine area; (2) evaluate the feasibility of using PUF-disk based passive air samplers in Antarctic air.

2. Methods and materials

2.1. Sample collection

PUF-disk based passive air samples were collected at five sampling sites in the vicinity of Chinese Great Wall Station (S62°12′59″, W57°52″), King George Island, Antarctica. The Great Wall station is the first Chinese Antarctic scientific research station. It was built in 1985 and located in the King George Island of South Shetland Island, west Antarctica. Sampling site S1 was the nearest site (300 m southwest) from the Great Wall Station in this study. Site S2 was situated close to the south seacoast, southeast of the Great Wall Station. Site S3 was close to the west seacoast, whereas S4 was about 600 m southeast from the Frei (Chile) and Bellingshausen (Russia) Stations. Site S5 was located on the Ardley Island, which situates a large penguin colony. The map of the sampling sites is shown in Fig. 1.

Air samples were collected by using PUF-disk based passive air samplers (Shoeib and Harner, 2002) in the austral summer of December 8th 2009–February 7th 2010, during the XXVI Chinese Scientific Research Expedition to Antarctica. The PUF-disks (diameter, 14 cm; thickness, 1.35 cm; surface area, 365 cm²; volume, 207 cm³) were housed in stainless steel domed chambers that are designed to protect the disks from coarse particle deposition, precipitation and sunlight. To minimize possible contaminations, the PUFs were extracted in sequence with acetone and hexane in an accelerated solvent extraction (ASE) apparatus (Dionex 300, pressure, 1500 psi; temperature, 100 °C; heating, 5 min; static, 8 min; flushing, 60 vol.%; purge, 120 s; 2 cycles) before use. The average temperature and wind speed in the Great Wall Station during the sampling campaign, provided by the National Marine Environmental Forecasting Center of China, was 6.5 °C and 7.3 m s⁻¹, respectively.

2.2. Sample analysis

Analysis of PCBs and PBDEs were respectively performed according to the revised U.S. EPA method 1668A and U.S. EPA method 1614. Briefly, air samples were spiked with 1 ng of isotope-labelled surrogate standards of PCBs (68A-LCS, 27 13C₁₂-labelled congeners) and PBDEs (13C₁₂ -BDE-47, 13C₁₂ -BDE-99 and 13C₁₂ -BDE-153) prior to the extraction in the ASE apparatus. After extraction, the extract was evaporated and cleaned with multilayer silica (1 g neutral silica, 4 g basic silica, 1 g neutral silica, 8 g acid silica, 2 g neutral silica, 4 g anhydrous sodium sulfate) and active carbon columns (containing Carbopack C dispersed on Celite 545). The multilayer silica column (15 mm i. d. × 30 cm) was rinsed with 100 mL hexane before use and eluted with 100 mL hexane after the extract was loaded. The carbon column (15 mm i. d. × 8 cm) was rinsed with 15 mL toluene and 15 mL hexane, respectively, and eluted with 50 mL hexane, which were used for PCBs and PBDEs analysis. The final extract was concentrated to ~20 μL and spiked with 1 ng of 13C₁₂-labelled injection standards (13C₁₂ -PCB-9, 52, 101, 138 and 13C₁₂ -PCB-194).

Fig. 1. Map of sampling sites.
Instrumental analysis was performed on Micromass Autospec Ultima high-resolution mass spectrometer (HRMS) coupled with Agilent 6890 gas chromatography using El ionization at 35 eV. The HRMS was operated in selected ion recording mode (SIR) with a mass resolution of 10,000. Detailed instrumental method can be found elsewhere (Li et al., 2009, 2008). In this study, the concentration of 20 PCB congeners (PCB-77, PCB-81, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-189, PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180, PCB-209 and PCB-11) and 14 PBDE congeners (BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-183, BDE-190 and BDE-209) were reported. Field blank and laboratory blank samples were routinely analyzed and the blank values were in most cases below the limit of detections (LOD). The chromatography peaks were quantified only when the signal/noise ratio was ≥ 3. The sample recoveries of 13C12-labelled surrogate standards ranged from 47 to 107% for PCBs and from 41 to 110% for PBDEs. The LOD, defined as three times of signal/noise ratio, were in the range of 0.2–6.7 fg m⁻³ for PCBs and 2.8–17.4 fg m⁻³ for PBDEs, respectively. The uncertainty of the analytical method was 25%, which was based on the published literature (Quam, 2000).

3. Results and discussion

3.1. Air concentration and profile of PCBs

To our knowledge, this study is the first report on the employment of PUF-disk based passive air samplers for POPs monitoring in Antarctic air. The measured air concentrations of PCBs are summarized in Table 1. The uptake rate of passive air sampler has previously been found to mainly be controlled by wind speed (Tuduri et al., 2006). We used the same sampling rate of 14 m⁻³ day⁻¹ as in our previous study (Li et al., 2009) for calculating the air concentrations of PCBs and PBDEs in the Antarctic air, as similar wind speeds were measured in both studies. The atmospheric concentrations of ∑ indicator PCBs (PCB-28, 52, 101, 118, 152, and 180) ranged from 1.66 to 6.50 pg m⁻³, with an average of 4.34 pg m⁻³. The low air concentrations confirm that the Antarctic atmosphere around this area is still in pristine status. However, the sampling sites (S1, S2 and S4) in the vicinity of Antarctic research stations showed higher PCB concentrations than the other sites, reflecting potential local PCB sources from Antarctic research stations. Waste burning and dumping from Antarctic research stations can contribute to PCB emissions in the Antarctic atmosphere (Montone et al., 2003). On the other hand, oil burning, which was used for generating electricity and domestic heating in the Antarctic research stations, could possibly also produce PCBs as a byproduct and emit these to the ambient air. Further evidence of local pollution of PCBs from research stations in the Antarctic atmosphere was demonstrated by Choi et al. (2008).

However, local pollution of PCBs from the Antarctic research stations should be limited and the long-range atmospheric transport in a global scale was still considered as the main influence factor in Antarctic atmosphere (Gambaro et al., 2005).

The PCB levels in this study were similar to previous atmospheric data reported for other Antarctic sites. For example, Choi et al. (2008) found that atmospheric concentrations of ∑ indicator PCBs in the atmosphere of Korean Antarctic Research Station in the range of 0.85–3.12 pg m⁻³ in 2004–2005, based on XAD passive air sampling. Gambaro et al. (2005) studied gas-phase PCBs in Terra Nova Bay, Antarctica, over the austral summer of 2003–2004, by using high-volume air sampling. The atmospheric concentrations of PCB-28 and 52 were found to be 0.088–0.22 and 0.027–0.10 pg m⁻³, respectively. Even earlier, Montone et al. (2003) reported atmospheric concentrations of PCBs (PCB-52: 8.6 pg m⁻³; PCB-77: 0.076 0.032 0.013 0.029 0.014; PCB-81: 0.009 n.d. 0.001 n.d. 0.001; PCB-105: 0.074 0.026 0.017 0.052 0.02; PCB-114: 0.011 0.004 0.002 0.007 0.002; PCB-118: 0.157 0.07 0.042 0.148 0.064; PCB-123: 0.024 0.006 0.004 0.006 0.006; PCB-126: 0.01 0.002 n.d. 0.001 n.d.; PCB-156: 0.012 0.003 0.002 0.008 0.004; PCB-157: 0.004 0.001 n.d. 0.002 n.d.; PCB-167: 0.006 0.001 0.001 0.004 0.002; PCB-169: 0.003 n.d. n.d. n.d. n.d.; PCB-189: 0.002 n.d. n.d. n.d. 0.0003; PCB-28: 3.46 5.53 1.70 5.10 1.17; PCB-52: 0.67 0.52 0.24 0.78 0.2; PCB-101: 0.19 0.10 0.05 0.16 0.05; PCB-138: 0.18 0.05 0.03 0.11 0.06; PCB-153: 0.26 0.07 0.04 0.17 0.10; PCB-180: 0.039 0.009 0.006 0.029 0.019; PCB-209: 0.009 0.009 0.008 0.010 0.006; PCB-209: 12.2 23.9 5.16 31.4 3.60; ∑ indicator PCBs 5.00 6.44 2.10 6.50 1.66; ∑ 15PBDEs 0.43 0.14 0.08 0.26 0.11; WHO-TEQ (fg m⁻³) 1.1 0.17 0.01 0.16 0.01; BDE-17-17 0.87 0.43 0.17 0.50 0.15; BDE-28 0.85 0.45 0.22 0.71 0.16; BDE-47 0.20 0.14 0.09 0.20 0.10; BDE-66 0.03 0.03 0.03 0.03 0.02; BDE-71 0.07 0.04 0.03 0.07 0.03; BDE-85 n.d. n.d. n.d. n.d. n.d.; BDE-99 0.06 0.02 0.01 0.02 0.04; BDE-100 n.d. n.d. n.d. n.d. n.d.; BDE-138 n.d. n.d. n.d. n.d. n.d.; BDE-153 0.10 0.03 0.03 0.05 0.05; BDE-154 0.10 0.02 0.01 0.02 0.03; BDE-183 0.69 0.24 0.1 0.12 0.27; BDE-190 n.d. n.d. n.d. n.d. n.d.; BDE-209 n.d. n.d. n.d. n.d. n.d.; ∑ indicator BDEs 2.98 1.40 0.67 1.72 0.83).

PCB-101: 4.9 pg m⁻³) in the vicinity of Brazilian Antarctic Research Station during the austral summer of 1995–1996. Kallenborn et al. (1998) reported PCB levels in the ambient air at Signy Island, Antarc-tica, during the austral summer of 1994–1995, with ∑ indicator PCBs at 20.67 pg m⁻³.

Reports of dioxin-like PCBs in Antarctic atmosphere are generally scarce. In this study, toxic equivalence (TEQ) of dioxin-like PCBs was calculated using the 1998 World Health Organization Toxic Equivalent Factors. In cases where concentrations were below the LOD, their values were taken as zero. The WHO-TEQ of PCBs varied from 0.01 to 1.08 fg m⁻³, with an average of 0.29 fg m⁻³, similar to the results from the Korean Antarctic Station of 0.17 fg WHO-TEQ m⁻³ (Choi et al., 2008).

Fig. 2 shows the relative distribution of PCB homologues. PCB homologue profiles were dominated by low chlorinated PCB homologues. The di, tri and tetra-PCBs respectively accounted for 38–56%, 20–25% and 11–24% to the total PCB concentrations. In contrast, heavier PCBs contributed to only a small fraction to the total PCBs. Homologues from hepta to deca-PCBs only accounted for 0.07–0.43% of the total PCB concentrations. This result can be explained by the effect of long-range atmospheric transport processes (Gambaro et al., 2005). The predominance of low chlorinated PCBs in ambient air was also found in other Antarctic sites, including Signy Island (Kallenborn et al., 1998), Korean Antarctic Research Station (Choi et al., 2008), Terra Nova Bay (Gambaro et al., 2005) and Bra-ziilan Antarctic Research Station (Montone et al., 2003).
3.2. Observation of PCB-11

The non-Aroclor congener PCB-11 (3,3’-dichlorobiphenyl) has attracted great attention in the recent years due to its specific emission sources to the environment. It is not directly derived from commercial Aroclor and Clophen mixtures (Schulz et al., 1989). However, high levels of PCB-11 could be detected in paint and pigment manufacturing as a byproduct (Hu et al., 2008). PCB-11 has been found in the atmosphere of Chicago (Hu et al., 2008), Great Lakes (Basu et al., 2009), Philadelphia (Du et al., 2009), and even in Arctic and Antarctic air (Choi et al., 2008), suggesting a wide atmospheric distribution of PCB-11 around the world. In this study, PCB-11 was actually found to be the most abundant PCB congener, with atmospheric concentrations in the range of 3.60–31.4 pg m⁻³ (average 15.2 pg m⁻³), lower than the results from Korean Antarctic Research Station (average 60 pg m⁻³) (Choi et al., 2008). Further detailed investigations are needed to explain the sources of PCB-11 in Antarctic atmosphere (Choi et al., 2008).

3.3. Air concentration of PBDEs

The air concentrations of ∑₁₄ PBDEs ranged between 0.67 and 2.98 pg m⁻³, with an average value of 1.52 pg m⁻³ (Table 1). To our knowledge, this is the first report on PBDE levels in Antarctic air. As for the PBDE levels in Arctic atmosphere, Shen et al. (2006) reported the sum concentrations of PBDEs (BDE-47, -99, -100, -153, -154) in the Canadian Arctic in 2000–2001 in the range of 0.3–68 pg m⁻³, based on XAD-resin passive air sampling. Su et al. (2007) analyzed high-volume air samples over the period 2002–2004 at Alert, Nunavut, in the Canadian High Arctic. The concentrations of ∑₁₁ PBDEs ranged from 0.40 pg m⁻³ to 47 pg m⁻³. In an expedition cruise from the Bohai Sea to the high Arctic, the average concentration of ∑₁₁ PBDEs in airborne particulates in the Arctic were found to be 17.3 pg m⁻³ (Wang et al., 2005). In comparison, the atmospheric concentrations of PBDEs in Antarctica from this study were lower than those in the Arctic air.

The tri-BDEs of BDE-17 and BDE-28 were predominant and respectively contributed in average to 27% and 31% of the total PBDE concentrations (Fig. 3), contradicting the results from the Arctic air that BDE-47 and BDE-99 were the dominant congeners (Shen et al., 2006; Su et al., 2007; Wang et al., 2005). Among the fourteen analyzed PBDE congeners, BDE-85, BDE-100, BDE-138, BDE-190 and BDE-209 were not detected in any air samples. However, the high contribution of BDE-183 (19% of total ∑ PBDEs), a primary component of technical octa-BDEs products (Wit et al., 2010), indicates that local PBDEs pollution might exist. The atmospheric concentrations of PBDEs in the sites (S1, S2 and S4) close to Antarctic research stations were significantly higher than the other sites, supporting the premise of local PBDE sources. Furnishings, facilities and electronic equipments in the Antarctic research stations may contain PBDEs as flame retardants, which can volatilize and be emitted to the atmosphere. Further evidence of local PBDE pollutions from Antarctic research stations were reported by Hale et al. (2008), which found PBDEs in the indoor dust and wastewater sludge from the U. S. McMurdo and New Zealand-operated Scott Antarctic research bases.

3.4. Comparison with high-volume sampling data

In order to evaluate the feasibility of using PUF-based passive air samplers in Antarctic atmosphere, we compared the PUF-derived air concentrations of PCBs and PBDEs with those from high-volume sampling (Fig. 4). The combination of chemicals in gaseous phase and particulates from high-volume sampling were used for comparison, as suggested by Melymuk et al. (2011) in their evaluation of PUF passive air sampler calibrations. The two sampling methods were deployed during the same sampling period at the site S1. Each high-volume air sample was collected on a weekly basis with a sampling volume close to 2000 m³.

The ratio of concentrations from the PUF passive sampler versus high-volume sampler varied from 1.9 to 5.4 for PCBs, whereas it varied from 0.57 to 2.6 for PBDEs, except for a high deviation of BDE-17. Therefore we could deduce that the results of PCBs and PBDEs from the PUF sampling were reliable and in agreement with the high-volume sampling data. Melymuk et al. (2011) and Gouin et al. (2005) also found good agreements between passive air sampling and active air sampling when sampling rates are based on bulk (gas + particle) air concentrations, consistent with the results from this study. Because of the strong dependence of sampling rate on wind speeds (Tuduri et al., 2006), it was uncertain whether PUF-disk passive air samplers could be used in Antarctic air in high wind conditions. The results from this study, however, have validated the feasibility of using PUF-disk passive air samplers to investigate concentrations and distributions of POPs in Antarctic air. It should be noted that appropriate sampling rates should be used for PUF air sampling in Antarctic air due to high wind velocities.
4. Conclusions

In this study, we employed PUF-disk based passive air sampling in King George Island, Antarctica. The atmospheric concentrations and distributions of PBDEs were reported for the first time in Antarctic air. Both the PCBs and PBDEs could be detected in the air samples. However, the atmospheric concentrations of PCBs and PBDEs were at very low levels, reflecting the pristine status of the Antarctic air. Long-range atmospheric transport and local sources from the research stations were suspected to contribute to the pollution of PCBs and PBDEs in this pristine area. The observation of PCB-11 in the air samples reflects its global distribution in the atmosphere. Comparison between the results from passive air sampling and those from high-volume sampling in this study also demonstrated the feasibility of using PUF-disk passive air samplers in the Antarctic air.

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