Determination of dioxin-like polychlorinated biphenyls in soil and moss from Fildes Peninsula, Antarctica

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Dioxin-like polychlorinated biphenyls (PCBs) are a class of toxic and persistent chemicals that are often found in the environment. The determination of dioxin-like PCBs in Fildes Peninsula, Antarctica, is reported in this paper. Dioxin-like PCBs were widely distributed in Antarctic soil and moss with concentrations of 2.23–27.2 pg/g in soil and 10.4–812 pg/g in moss. The highest concentrations were found in the Ardley Island area and the lowest concentrations on the west coast. The contribution of PCB-118 to the $\sum_{12}$PCBs ranged from 36.0% to 69.6% in soil, and 17.2% to 43.4% in moss. The congener specific patterns in soil and moss were similar. Long-range atmospheric transport is thought to be the main source of PCBs detected on King George Island. The $\sum_{12}$PCBs toxic equivalent (TEQ) in soil was $0.400 \times 10^{-3}$ to $516 \times 10^{-3}$ pg (TEQ)/g with a mean value of $147 \times 10^{-3}$ pg (TEQ)/g. PCB-126 had the largest contribution (81.1%) to the $\sum_{12}$PCBs TEQ in soil. The $\sum_{12}$PCBs TEQ in moss ranged from $2.90 \times 10^{-3}$ to $1.19$ pg/g with a mean value of 0.482 pg/g. PCB-126 was also the largest contributor (91.4%) to the $\sum_{12}$PCBs TEQ in moss. The mean TEQ in moss was about 40 times that in soil.

Fildes Peninsula, dioxin-like PCBs, concentration, congener distribution

Dioxins are a class of structurally and chemically related halogenated aromatic hydrocarbons. Polychlorinated dibenzodioxins (PCDDs or dioxins), polychlorinated dibenzofurans (PCDFs or furans) and the dioxin-like polychlorinated biphenyls (PCBs) are all dioxins that share similar chemistry and are toxic and persistent in the environment [1,2]. The main sources of dioxin-like polychlorinated biphenyls (dioxin-like PCBs) such as PCB-81, PCB-77, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-189, are commercial products that are used in industrial capacitors and transformers, and oil painting. Dioxins have been detected in a wide range of agricultural and environmental soils and sediments [3–6].

Soils play an important role in the global cycling of persistent organic pollutants (POPs). They store POPs from atmospheric deposition and direct pollution through transformation of the soil organic matter content and type. A series of articles have reported the role of background soils in global POP budgets, air-surface soil exchange, and the influence of soil organic matter on these processes [7–9]. Vegetation is the primary site for bioaccumulation of POPs, which occurs by uptake of lipophilic organic compounds from the air into plant tissues. Soil pollutants can also be taken up by vegetation since both soil and vegetation have a high affinity for hydrophobic organic pollutants and can act as natural sinks [10]. The Polar region is very vulnerable to human activity and POPs, and it is very important to evaluate the risk of contamination of this environment with dioxin-like PCBs and their distribution [11].

While some studies have reported the presence of POPs in the Antarctic region is the result of long-range atmospheric transport [12,13], several other studies have reported that
the pollution comes from local sources around research stations [10,14,15]. There are many reports on the total PCB levels in Antarctic soil, seawater, and sediment [16–18], but information on dioxin-like PCBs in this region is very limited.

In this study, the concentrations of 12 dioxin-like PCB congeners in soil and moss were measured along the Fildes Peninsula, Antarctica. This data will aid understanding of the contribution of this area to the global POP cycle.

1 Materials and methods

1.1 Sampling and sample preparation

The Great Wall Station (62°13′S, 58°59′W) is located on the Fildes Peninsula, King George Island, Antarctica. This area is affected by polar cyclones and has a cold subantarctic climate, which is dominated by west and northwest winds. The average annual temperature is −1.5°C with a maximum temperature of 8.5°C and lowest temperature of −20.3°C. The average annual wind speed, pressure and relative humidity are 7.1 m/s, 9.91×10⁴ Pa, and 86%, respectively. The annual rainfall in this area is about 630 mm, and mainly in the form of snow. The depth of freeze-thaw soil reaches a maximum of 40–70 cm in late March [19] after increasing from mid-December when surface snow and soil begin to melt. Most of the ice free area is covered by abundant vegetation, which is dominated by cryptogamic species, including two flowering plants, 33 bryophytes, and 62 lichens [19]. The thickness of fine particles and organic clay soil under the lichen moss layer is about 10–15 cm. This kind of soil comes from freezing, thawing, and the root soil’s biogeochemical process [20].

Surface soil samples (upper 5 cm) and moss samples were collected on Fildes Peninsula, King George Island from December 2007 to January of 2008. As illustrated in Figure 1 and Table 1, 15 sampling sites, S1–S15, were selected on Fildes Peninsula. The average temperature during sampling was 2.5°C. All samples were wrapped in aluminum foil and stored at −20°C. Soil and moss samples were freeze-dried, ground, and sieved (80 mesh) before accelerated solvent extraction (ASE-300, Dionex, Sunnyvale, CA, USA) at 185°C and 10.3 MPa. About 20.0 g of a homogenized soil or moss sample was statically extracted using toluene in a 33 mL cell. After cleanup by multi-layer silica gel (pesticide grade, Merck KGaA, Darmstadt, Germany), a basic alumina column (Brockmann I, standard grade, Aldrich Chemical Co., Milwaukee, USA), and gel permeation chromatography (Bio-Beads SX3, Bio-Rad, Hercules, CA, USA), the soil and moss samples were fractionated on a Florisil column (60100 mesh, Riedel de Haen, Seelze, Germany). The desired fraction was concentrated on a rotary evaporator and analyzed on a high-resolution gas chromatography high-resolution mass spectrometer (JMS 700D, JEOL, Tokyo, Japan) equipped with a J&W Scientific DB-5MS column (60 m×0.25 mm I.D., 0.25 μm particle size, Agilent, Santa Clara, CA, USA) in selected ion monitoring mode.

1.2 Reagents

Table 1 Description of the samples and sampling locations

| Serial number | Sites | Sampling time | Sampling location (GPS) | Description |
|---------------|-------|---------------|------------------------|-------------|
| S1            | West Coast | 2007-12-26 | S62°12'56.6" W58°59'35.0" | Dark brown soil. Lichen and moss are abundant. |
| S2            |             |               | S62°12'40.0" W59°00'29.2" | Light brown soil. Fruticose lichens are dominant. |
| S3            |             |               | S62°13'36.5" W59°00'03.1" | Dark brown soil. Lichen and moss are abundant. |
| S4–S6         | Ardley Island | 2008-1-4 | S62°12'44.9" W58°55'34.3" | Dark brown soil. Moss is dominant (wet condition). Frequented by seabirds and penguin. |
| S7–S9         | Mountain Lakes | 2008-1-11 | S62°12'32.5" W58°57'15.2" | Light reddish brown soil in slope. Soil sample was collected from the newly exposed surface. Sea-birds feathers and droppings are common (near the penguin rookery). |
| S10–S12      | Tern Lake   | 2008-1-13   | S62°13'15.0" W58°57'33.2" | Light brown soil. Fruticose lichens are dominant. |
| S13–S15      | Great Wall Station area | 2008-1-14 | S62°13'08.3" W58°57'15.5" | Light brown soil in slope. Fruticose lichens are dominant. |
CVS-JQ (calibration and verification solutions CS1–CS5), MBP-MXS (labeled compound stock solution) and MBP-79 (internal standard spiking solution), were purchased from the Wellington Laboratories (Ontario, Canada). Toluene, hexane, methylene chloride and acetone (pesticide grade) were purchased from Thermo Fisher Scientific (Waltham, MA, USA). Decane (dioxin level) was obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

1.3 Instrumental analysis

For GC the carrier gas flow rate was 1.5 mL/min, and the injection volume was 1 μL. The column temperature was programmed as follows: held at 150°C for 1 min, heated to 185°C at 20°C/min, maintained at this temperature for 3 min, heated to 245°C at 2°C/min, maintained at this temperature for 3 min, and finally heated to 280°C at 6°C/min and held for 5 min. The injector temperature was 280°C. MS was performed under the following conditions: vacuum, <1×10⁻³ Pa; ionization energy, 38 eV; ion current, 500 μA; electron ionization source temperature, 280°C; accelerating voltage, 10 kV; and resolution, >10000. Mass calibration was performed with perfluorokerosene (PFK). The spectra were processed with JEOL Diok V4.02 software (Tokyo, Japan). The total organic carbon (TOC) of the soil was determined using the potassium dichromate method [21].

1.4 Quality assurance and quality control

The stainless steel shovels used for sampling were cleaned with solvent before use. The aluminum foil used to wrap samples was heated at 450°C for 4 h before being placed in a dense vinyl bag and stored at 20°C. Field blank samples were treated in the same way. One procedural blank sample was analyzed for every five soil extracts. All results were blank corrected. The limit of detection (LOD) was calculated as three times the standard deviation of the mean of the blank. The LODs of the congeners ranged from 0.0100 to 0.0630 pg/g. Concentrations of samples that were below the LOD were replaced by a value of half the LOD. All samples were spiked with a labeled recovery standard. The recoveries ranged from 35.0% to 115% (average 89.0%). These recoveries are in line with US EPA 1668 requirements [22].

2 Results and discussion

2.1 Dioxin-like PCB levels

Although there are many reports on PCBs in soils around the world, information on the dioxin-like PCB composition in Antarctic soil is scarce. Concentrations of dioxin-like PCBs in the soil and moss on Fildes Peninsula are displayed in Table 2. Dioxin-like PCBs were detected in all the samples. The summed concentration of all 12 dioxin-like PCBs (Σ12PCBs) in soil ranged from 2.23–27.2 pg/g (average 13.2 pg/g). The highest Σ12PCBs was observed in the Ardley Island area (S4–S6) and the lowest on the west coast (S1). The PCB concentrations in surface soils from Fildes Peninsula (2.23–27.2 pg/g) were much lower than those in soils from Zhejiang (1.52 × 10⁵–318 × 10⁶ pg/g) [23] and Beijing, China (0.390 × 10⁶–13.0 × 10⁶ pg/g) [24], but higher than those from Barton Peninsula, Antarctica (0.893–2.30 pg/g). The Σ12PCBs concentration in moss ranged from 10.4–812 pg/g, with a mean concentration of 385 pg/g, which was about 29 times that of the soil concentration.

Σ12PCBs in soil from the Ardley Island area and the Greatwall Station area were much higher than those in soil

Table 2 Concentrations of dioxin-like PCB congeners (pg/g) and TEQ (pg(TEQ)/g) in soil and moss samples collected from Fildes Peninsula

| Congener | Soil (pg/g) | Moss (pg/g) | Air²(fg/m³) |
|----------|------------|------------|-------------|
|          | S1 | S2 | S3 | S4–S6 | S7–S9 | S10–S12 | S13–S15 | S1 | S2 | S3 | S4–S6 | S7–S9 | S10–S12 | S13–S15 | F |
| PCB-77   | 0.280 | 0.520 | 0.570 | 3.69 | 3.35 | 0.300 | 1.17 | 0.00 | 10.9 | 0.560 | 43.2 | ND | 5.89 | ND | 40.0 |
| PCB-81   | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| PCB-105  | 0.220 | 0.240 | 0.790 | 4.76 | 4.32 | 0.720 | 3.30 | 82.8 | 7.42 | 1.89 | 137 | 99.8 | 7.14 | 130 | 50.0 |
| PCB-114  | 0.000 | 0.020 | ND | ND | ND | ND | ND | 1.32 | ND | ND | 4.09 | 10.4 | ND | 13.5 | ND |
| PCB-118  | 0.800 | 0.950 | 2.73 | 14.3 | 13.0 | 2.34 | 13.7 | 194 | 25.5 | 5.70 | 393 | 375 | 20.4 | 488 | 180 |
| PCB-123  | 0.0200 | 0.140 | ND | ND | 2.05 | 1.87 | ND | 1.95 | 1.70 | 0.600 | 54.2 | 23.1 | 2.10 | 30.0 | ND |
| PCB-126  | 0.120 | 0.270 | ND | ND | ND | 0.450 | ND | 6.78 | 3.64 | 0.160 | 9.39 | 8.14 | 1.43 | 10.6 | ND |
| PCB-156  | 0.120 | 0.100 | ND | 1.44 | 1.31 | ND | 3.07 | 37.7 | 4.57 | 0.680 | 63.0 | 50.1 | 1.99 | 65.1 | 10.0 |
| PCB-157  | 0.150 | 0.0700 | ND | 0.0200 | 0.0200 | ND | 0.550 | 11.4 | 1.79 | 0.240 | 18.4 | 15.1 | 1.08 | 19.7 | 60.0 |
| PCB-167  | 0.200 | 0.110 | ND | 1.36 | 1.24 | ND | 1.52 | 17.9 | 3.20 | 0.440 | 46.9 | 38.8 | 1.30 | 50.4 | 20.0 |
| PCB-169  | 0.320 | 0.170 | ND | ND | ND | ND | 0.310 | ND | ND | ND | ND | 46.9 | 38.8 | 1.30 | ND |
| PCB-189  | ND | ND | ND | ND | ND | ND | 0.520 | ND | ND | ND | ND | ND | ND | ND | ND |
| Σ12PCBs  | 2.23 | 2.59 | 4.09 | 27.7 | 25.1 | 3.36 | 27.2 | 372 | 59.4 | 10.4 | 775 | 624 | 41.3 | 812 | 370 |
| TEQ(x10⁻³) | 158 | 28.5 | 0.400 | 3.20 | 2.90 | 0.300 | 51.6 | 733 | 372 | 17.0 | 1050 | 902 | 148 | 1170 | 162 |

F, TEQ(a)/(fg/m³)

| TOC (g/kg dry weight) | 25.7 | 28.4 | 30.1 | 65.4 | 60.8 | 15.5 | 45.4 |

a) ND, not detected.

2.2 PCBs in moss

The PCB levels in moss are also high, showing a decreasing trend along the coastline. The concentrations of individual congeners ranged from 0.0700–46.9 pg/g. PCB-126 and PCB-157 were the most abundant congeners in moss. The concentrations of Σ12PCBs in moss varied from 10.4–812 pg/g, with a mean concentration of 385 pg/g, which was about 29 times that of the soil concentration.

2.3 PCBs in air

The PCB levels in air are much lower than those in soil and moss. The concentrations of individual congeners ranged from 0.0100–5.94 pg/g. PCB-157 and PCB-126 were the most abundant congeners in air. The concentrations of Σ12PCBs in air varied from 10.4–180 pg/m³, with a mean concentration of 385 pg/m³, which was about 30 times that of the soil concentration.
samples from other sites in this study. Similar results were found for $\sum_{13}$PCBs in moss. These higher concentrations might be caused by local contamination because of human activity at the research stations in these areas and animal activity. Choi et al. [25] reported that PCB levels in atmospheric samples decreased with increasing distance from the main building of King Sejong Station, Barton Peninsula, Antarctica. Hyun et al. [10] found that soil samples collected near the research station had elevated concentrations of chlorinated homologues compared to other samples, which implies that local pollution influences the concentrations in this area. Many studies have suggested that animal activity and TOC can have a large cumulative effect on the distribution of POPs [26–28]. The dry weight TOC contents in soil samples from sites S1–S15 are shown in Figure 2. The TOC values ranged from 15.5–65.4 g/kg. Correlation analysis showed a high correlation coefficient between $\sum_{12}$PCBs and TOC content in soil samples ($r^2=0.828$, $P \leq 0.05$).

2.2 Congener patterns in soil and moss samples

The percentage contribution of each of the 12 dioxin-like PCBs to the $\sum_{12}$PCBs in soil and moss are presented in Figure 3. The congener specific patterns were similar in the soil and moss samples. The most abundant congeners in these samples were PCB-118, PCB-105, and PCB-77. These congeners accounted for 51.9% (PCB-118), 15.6% (PCB-105) and 10.7% (PCB-77) of the $\sum_{12}$PCBs in soil and 38.4% (PCB-118), 11.9% (PCB-105), 5.70% (PCB-77) of the $\sum_{12}$PCBs in moss. Among the 12 congeners, PCB-118 was predominant in both soil and moss samples. The contributions of PCB-118 to the $\sum_{12}$PCBs at the different sample sites ranged from 36.0%–69.6% in soil, and 17.2%–43.4% in moss.

Pearson correlation of the 12 congeners among the soil and moss samples was examined (Table 3). Significant correlations were observed among all the sites, which implies that the sources of dioxin-like PCBs in soil and moss are the same. The large proportion of PCB compounds found in Antarctica could be attributed to atmospheric transport and deposition. Hyun et al. [10] reported the distribution of dioxin-like PCB in soil and lichen on Barton Peninsula, King George Island. It is interesting to note that the dioxin-like PCB congeners found in the Barton Peninsula soil samples have a good correlation with those found in the Fildes Peninsula. This suggests that the dioxin-like PCB congeners found in the Barton Peninsula soil samples have a good correlation with those found in the Fildes Peninsula. This suggests that the dioxin-like PCB congeners in the Greatwall Station area and the Korean Station area likely come from same source. Further comparison of the PCB congener concentrations in air samples from Fildes Peninsula and Barton Peninsula [25] showed a strong correlation.

3 Conclusions

Dioxin-like PCBs was found in all the Antarctic soil and moss samples examined in this study. The concentrations of $\sum_{12}$PCBs ranged from 2.23 to 27.7 pg/g in soil and 10.4 to 812 pg/g in moss. The highest concentration of $\sum_{12}$PCBs...
was observed in the Ardley Island area. Bioaccumulation and biologically mediated transport of PCBs could increase contamination on a local scale.

The contribution of PCB-118 to $\sum_{10}$PCBs ranged from 36.0% to 69.6% in soil, and 17.2% to 43.4% in moss. The congener specific patterns in soil and moss were similar, which suggests that the dioxin-like PCBs in soil and moss come from the same source.

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Table 3  Pearson correlation coefficients of the dioxin-like congeners among the different samplesa)

|       | S1     | S2     | S3     | S4–S6  | S7–S9  | S10–S12 | S13–S15 |
|-------|--------|--------|--------|--------|--------|----------|----------|
| Moss  | 0.831† | 0.962† | 0.979† | 0.984‡ | 0.958‡ | 0.984‡   | 0.986‡   |
| Soil  | 0.881† | 0.873† | 0.934† | 0.936‡ | 0.936‡ | 0.922‡   | 0.841‡   |
| Air–soil | 0.908‡ | 0.858‡ | 0.944‡ | 0.923‡ | 0.923‡ | 0.942‡   | 0.903‡   |
| Air–moss | 0.903‡ | 0.917‡ | 0.934‡ | 0.925‡ | 0.923‡ | 0.938‡   | 0.923‡   |

a) *P<0.05; **P<0.01; *** Choi et al. [25].

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