PCBs and PBDEs in soil, sediment and moss community from ponds across Victoria Land, Antarctica

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Introduction

The persistence and long-range transport potential (LRT-P) have allowed persistent organic pollutants (POPs) to reach remote areas of our planet, including the polar regions. They are transported to Antarctica mainly by air mass movements through several volatilization-deposition cycles before being finally deposited in cold areas [1], where they can be trapped in the region's snow, ice, ocean and soils [2].

The Victoria Land (East Antarctica) is rich in lakes and ponds characterized by the presence of rare liquid water during the Summer months, when the ice and snow coverage can melt. These ponds are an important resource for migrating seabirds that use them and leave there their excrements and feathers, contributing to enrich the water with organic matter. Moreover, these ponds are also an important freshwater terrestrial ecosystem [3]. In fact, they show peculiar ecological features: they receive nutrients from both the sea (through wind) and seabirds, and host a community of organisms [3,4]. During Summer, the ice and snow melting reveals mat of moss [3,4] and these communities include also bryophytes, cyanobacteria, algae, and lichens [4]. The organic matter is deposited in the pond sediments that are considered as sink for particulate organic matter [3]; thus, they may also be a sink for lipophilic contaminants like POPs.

The terrestrial ecosystems are very rare and poor in the Antarctic continent due to the very low temperature, extreme dryness (absence of liquid water), strong winds; the ponds are rare and precious ecosystems for studying POP accumulation in the Antarctic terrestrial ecosystems. The main aims of this study were to assess the concentration of 21 congeners of polychlorinated biphenyls (PCBs) and 23 congeners of polybrominated diphenyl ethers (PBDEs) in pond sediment, soil and moss community collected close to the ponds.

Materials and methods

Samples were collected in December 2011 – January 2012 in the framework of the XXVII Italian Expedition to Antarctica. The study area was between 74.31°S - 74.97°S, and 165.07°E - 162.51°E and included the following ponds or lakes: Edmonson Point Lake no. 14, Edmonson Point Lake no. 15A, Carezza Lake, Tarn Flat Lake no. 20, Inexpressible Island Lake no. 10B, Enigma Lake. Soil and sediment samples were collected at each lake together with moss community; all samples were wrapped in aluminum foil previously washed with acetone and n-hexane, then stored at -20 °C. The moss community were analyzed as a whole, meaning that, after draining the soil from the mat, different organism species were not identified and separated; therefore, the POP concentrations are referred to all the organisms of the moss community accordingly to the definition found in Borghini et al. [4] and we refer to these samples as moss throughout the text.

All samples were lyophilized for 48 h at 50.1°C and 0.2 mbar in a LIO 5 P (5 Pascal). After grinding of the vegetable matter, an aliquot of about 5 g of each sample was extracted by Pressurized Fluid Extraction (PFE) in an ASE® (Accelerated Solvent Extraction) 200 extractor (Dionex) in compliance with U.S. EPA Method 3545A and finally purified using a Power-Prep™ Multi-Column Sample Cleanup System (Fluid Management Systems Inc.).

The instrumental analyses were performed on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer operating in negative chemical ionization (NCI) and selective ion monitoring (SIM). In particular, PBDEs were separated on a DB-5MS capillary column, 15 m, 0.25 mm i.d., 0.25 μm film thickness because of BDE209 thermolability. The oven program was set to 90 °C for 1 min, increased to 220°C at 20°C/min, and finally increased to 300°C at 10°C/min, where it was held for 7 min. The injection volume was 1μL, the transport gas was He. The mass spectrometer parameters were as follows: the transferline was set to 150 – 270 °C, the quadrupole and source were set to 150 °C. The fragments monitored and used for quantification were: 79, 81, 489. PCBs were separated on a DB-35MS capillary column, 30 m, 0.25 mm i.d., 0.25 μm film thickness. The oven program was set to 70°C for 1 min, increased to 150°C at 20°C/min, to 230°C at 10°C/min, to 308°C at 6°C/min where it was held for 5 min. The injection volume was 1μL, the transport gas was He. The mass spectrometer parameters were as follows: the transferline was set to 150-270°C, the quadrupole and source were set to 150°C.The fragments monitored and used for quantification were: 292, 326, 360, 394, 464, 498. The limit of detection (LOD) ranged 0.0002-0.0005 ng/g for PCBs and 0.001-0.006 ng/g for PBDEs.
The concentrations are given on dry weight (dry wt); please see the legend of Figure 1 for abbreviations of lake names.

Results and discussion

The sum of PCB congeners (∑PCBs) ranged <0.003 – 0.699 ng/g dry wt in moss, <0.003 – 0.807 ng/g dry wt in soil, and <0.003 – 0.775 ng/g dry wt in sediments (Table 1). PCBs were detected in 2 of 3 moss samples (Edmonson Point Lake 14, Carezza Lake) and in 50% of soil and sediment samples. The PCB levels detected in this study were consistent with other reported concentration and of the same order of magnitude than those found in soil samples from other areas in Antarctica, e.g. Hop Island (114-328 pg/g [5]), several sites in the Victoria Land (0.36-0.59 ng/g dry wt [6]), King George Island and Ardley Island (410 pg/g dry wt, with a range of 60.1–1436 pg/g dry wt in soil and sediment [7]). The PCB concentration in mosses from several sites in the Victoria Land other than our sampling areas were 25 - 34 ng/g dry wt [6]; concentrations was 670 pg/g dry wt (406–952 pg/g dry wt) in moss from King George Island and Ardley Island [7].
Of the 21 congeners analyzed, only PCB81, PCB105, PCB114, PCB138, PCB156, PCB167, PCB170, PCB180, PCB187, and PCB204 were detected in our samples. PCB138 was the most abundant congener (40 - 75%) in moss samples from Carezza Lake, in soil from Tarn Flat and Inexpressible Island Lakes, and in sediments from Edmonson Point and Tarn Flat Lakes; PCB114 made up most of the PCB residue in the other samples (Figure 1). The congener abundance in samples from King George Island and Ardley Island was PCB28 (40%) > PCB138 > PCB153 > PCB118 [7].
PBDEs were determined in all soil samples with comparable concentrations, ranging from 0.191 to 0.286 ng/g dry wt except for Carezza Lake and Inexpressible Island Lake no.10B, which showed lower levels (0.09 and 0.117 ng/g dry wt, respectively) (Table 1). PBDEs were detected in 2 of 3 moss samples (Edmonson Point Lake 14, Edmonson Point Lake 15A) and in 4 of 6 sediment samples. PBDEs averaged 2.76 – 51.4 pg/ g dry wt in soil and sediment and 6.54 – 36.7 pg/g dry wt in moss from King George Island and Ardley Island [7], and 0.77 – 33 ng/g in soil samples collected close to the Italian Station Mario Zucchelli [8]. Levels were 818 ± 270 pg/g dry wt in moss collected at King George Island [9].
Only BDE17, BDE28, BDE47, BDE99, BDE100, BDE154 and BDE183 were detected in our samples (Figure 1). Most of the BDE residue was made up by BDE47 (Edmonson Point Lake 15A moss and soil, Edmonson Point Lake 14 soil, Inexpressible Island Lake soil, Enigma Lake sediment), BDE 183 (Tarn Flat Lake sediment), and BDE28 (Tarn Flat Lake soil, Carezza Lake sediment). BDE183 was found only in the sediment samples collected

at Tarn Flat Lake 20 (0.231 ng/g dry wt), moss sample from Edmonson Point Lake 14 (0.031 ng/g dry wt), and soil sample from Enigma Lake (0.017 ng/g dry wt). BDE209 was below LOD in all matrices analyzed, suggesting that PBDE contamination is more related to LRT rather than to local contamination; even the prevalence of lower brominated congeners may confirm the potential long-range transport. Comparing our results with literature data, BDE99, 47 and 100 were also the most abundant congeners in moss samples from King George Island [9], and BDE47 and 99 in moss, soil, and sediment from King George Island and Ardley Island [7]. BDE 47 and 99 were the most abundant congeners in soil collected close to the Italian Station Mario Zucchelli [8], in agreement with our results, being these congeners the most abundant soil samples from Carezza Lake, which was the sampling site nearest to the Italian Station.

In general, PCB and PBDE levels were higher in moss samples from Carezza Lake (nearest to the Italian Station Mario Zucchelli) and Edmonson Point Lake 14 (near to penguin and skua colonies): both these lakes are close to penguin rookery or are hanged out by South Polar skuas nesting in the areas. Levels in soil and sediment were higher in samples from Inexpressible Island and Edmonson Point 14 Lakes. PCB and PBDE levels were similar or lower to those reported in samples from Arctic regions [10]. The PCB presence in the lake sediments and surrounding soil and moss community may be due to the nature of Antarctic lakes, which melt during the Summer season and receive contaminants from the melted ice and snow coverage, which are rich in atmospheric particulate matter trapped into the ice during its formation. Moreover, they receive also the seabird and penguin droppings and other organics material deriving from bird grooming activity. The LRAT can be confirmed as the most important source of POPs in Antarctica, although the scientific stations and seabirds may contribute to contaminant release [2].

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Table 1: Latitude (Lat) and longitude (Long) of the sampling sites, and concentrations of the sum of PCB (∑PCBs) and BDE (∑PBDEs) congeners (ng g^{-1} dry wt; na = not available).

		∑PCBs			∑PBDEs		
Sampling site	**Lat, Long**	**Moss**	**Soil**	**Sediment**	**Moss**	**Soil**	**Sediment**
Edmonson Point no. 14	74°33'S, 165°13'E	0.353	<0.003	0.623	0.218	0.191	<0.017
Edmonson Point no. 15A	74°31'S, 165°07'E	<0.003	<0.003	<0.003	0.089	0.259	<0.017
Carezza Lake	74°71'S, 164°04'E	0.699	0.113	<0.003	<0.017	0.09	0.169
Tarn Flat no. 20	74°97'S, 162°51'E	na	0.807	0.775	na	0.286	0.504
Inexpressible Island no. 10B	74°88'S, 163°72'E	na	0.686	0.365	na	0.117	0.211
Enigma Lake	74°72'S, 164°03'E	na	<0.003	<0.003	na	0.241	0.152

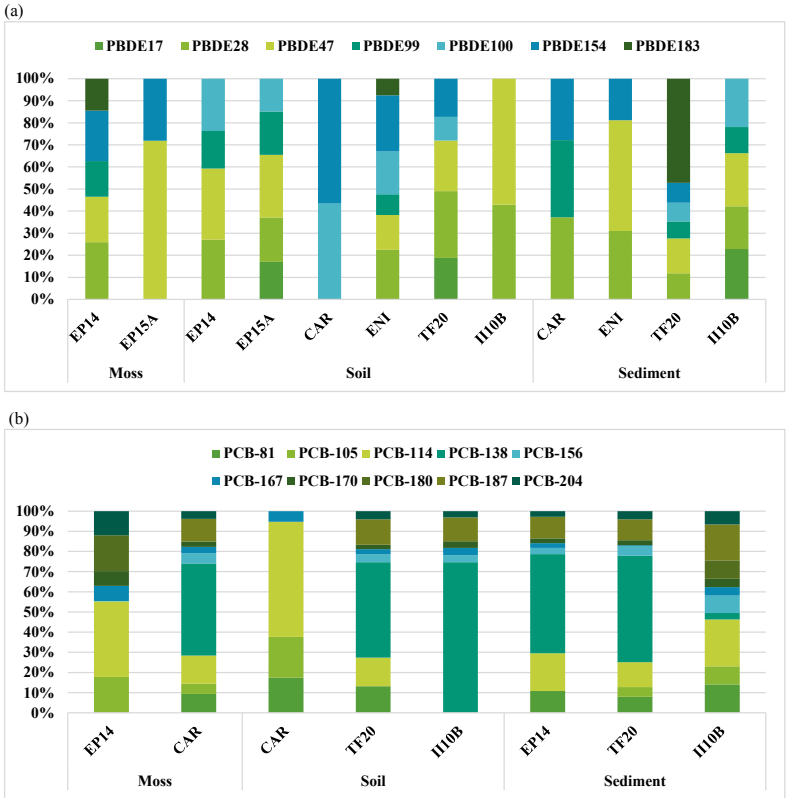

Figure 1: Percentage contribution of the detected BDE congeners (a) and of the detected PCB congeners (b) in soil, sediment and moss of the Antarctic lakes (EP = Edmonson Point, CAR = Carezza, ENI = Enigma, TF = Tarn Flat, II = Inexpressible Island).