

PERSISTENT ORGANIC POLLUTANTS (POPs) IN ANTARCTIC LAKES

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Introduction

Persistent Organic Pollutants (POPs) contaminate nearly all environments worldwide and tend to accumulate toward the poles in a global fractionation process¹. Antarctica is affected by POP contamination but there are still large knowledge gaps². There are very few studies regarding organic contaminants in Antarctic terrestrial environment, and in lakes in particular³. Although about 98 % of the Antarctic continent is covered by an ice sheet, during only a few weeks in the austral summer, in limited coastal areas, melting ice and snow flow in small streams and seasonal lakes⁴. As a rule, these have no definite outlets and lose summer meltwater through evaporation or sublimation, becoming sinks for solutes and particulate material from the catchment areas and burying them in the bottom sediments. As a consequence, Antarctic lakes can be considered integrators of the biogeochemical processes taking place in the watershed⁵. Polychlorinated biphenyls (PCBs) were detected in Antarctic lakes since 1982 by Tanabe et al.⁶, who found 48-610 pg L⁻¹ in ice and water from a lake near the Japanese Antarctic station. Recently, further data were reported for POPs in the lakes of Antarctic Peninsula: Klanova et al.⁷ found 0.32-0.83 ng g⁻¹ of PCBs and 1.4-205 ng g⁻¹ of polycyclic aromatic hydrocarbons (PAHs) in lake and river sediments from James Ross Island. Wang et al.⁸ reported total concentrations of 60.1-1436 pg g⁻¹ for PCBs and 2.76-51.4 pg g⁻¹ for polybrominated diphenyl ethers (PBDEs) in soil and sediments from King George Island and Ardley Island. Long-range atmospheric transport and contamination from research bases were hypothesized as sources of POPs. Previous studies investigated the region of Terra Nova Bay (Northern Victoria Land, Antarctica), where some lakes are located, mainly to study the inorganic geochemistry and the ecological features of lacustrine ecosystems^{4,5,9-11}. The only available data about POPs for these lakes refer to sediment samples collected between 1988 and 1992¹², when no significant differences of total PCB concentrations were found among sites. More data are available about POPs in biota¹³ and the atmosphere¹⁴ in this area.

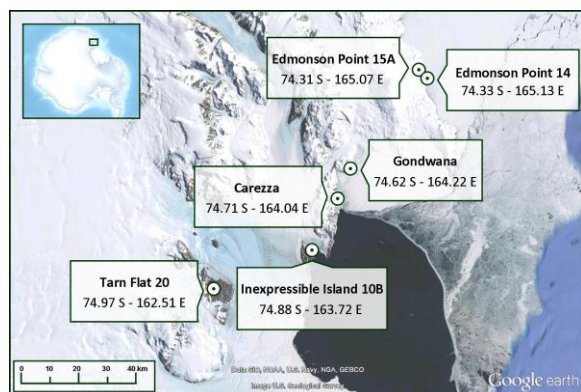


Fig 1: Sampling sites of lake water and sediment in Northern Victoria Land, Antarctica.

In this work we focus on the determination of 127 PCBs (including the non-Aroclor PCB-11), 14 PBDEs and 15 PAHs in lake water and sediment samples collected during the 27th Italian Antarctic Expedition (austral summer 2011–2012). Six seasonal shallow lakes near Terra Nova Bay (Edmonson Point 14, Edmonson Point 15A, Inexpressible Island 10B, Tarn Flat 20, Carezza, Gondwana) were investigated (Fig. 1). These lakes are frozen in winter but ice-free during a few weeks in the austral summer. Runoff from snow and ice melt is the only input of water. The features of each lake are described elsewhere^{5,10,15}. The water of five of the six lakes was sampled twice, at the beginning and at the end of ice melting, in order to highlight possible seasonal changes. It has recently been observed that the release of

POPs is not linear during the melting of a snowpack: on the contrary, pollutants present peaks of concentration, depending on their affinity with particulate matter and phase partition¹⁶. A similar process was observed in the surface seawater of the Ross Sea, Antarctica, with an increase of PCBs of 30-40% after the pack ice melting¹².

Materials and Methods

Pesticide-grade dichloromethane, *n*-pentane, *n*-hexane and acetone (Romil Ltd., Cambridge, Great Britain; Fisher Scientific SAS, Illkirch Cedex - France) were used. All isotope-labelled standard solutions (EC-1434, EC-1426, EC-4187, EC-4188, EC-4189, EO-5100, EO-501A, CLM-2477, CLM-2722, CLM-3757, CLM-2451) were purchased from CIL (Cambridge Isotope Laboratories, Inc., Andover, Massachusetts, USA), as well as

PBDEs native compounds solution (EO-5103). PCBs and PAHs native standard solutions (M-1668-A, PAH Mix 9) were acquired from Accustandard Inc. (New Haven, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). All the tools and glassware were washed with an aqueous 5% (v/v) Contrad® solution, dried and rinsed three times with dichloromethane and three times with *n*-hexane. In the laboratory of the Italian Antarctic Station acetone was used instead of dichloromethane, in order to reduce the use of chlorinated solvents. Water samples were collected in pre-cleaned airtight stainless steel containers and underwent continuous liquid-liquid extraction at the Italian Mario Zucchelli Station (MZS) in Antarctica. Briefly, aliquots of 10 L of sample were extracted with 210 mL of a *n*-pentane-dichloromethane (2:1, v/v) mixture for 24 hours. Extracts were gathered and kept at -20°C until purification in Italy. Surficial sediment samples (topmost 1-2.5 cm) were collected manually using stainless steel scoops at 0.5-1 m depth, where finer sediments accumulated between boulders and stones. Sediments were stored at -20°C in glass containers, dried at ambient temperature and aliquots of about 10±0.01 g were extracted by means of Pressurized Liquid Extractor (PLE, FMS, Fluid Management System Inc., Watertown, MA) using dichloromethane/acetone (1:1 v/v) in presence of anhydrous sodium sulphate, diatomaceous earth and activated metallic copper. For quantification purposes, known amounts of labelled compounds mixtures (21 ¹³C-labelled PCBs at 40 pg μL⁻¹, 7 ¹³C-labelled PBDEs at 2–5 pg μL⁻¹ and 3 ¹³C-labelled PAHs at 500 pg μL⁻¹) were added to samples before extraction. Full analytical details on clean-up stage and instrumental analysis are described elsewhere¹⁴. Cleanup was performed by injecting samples in an automated system (PowerPrep™, FMS) onto a disposable neutral silica column and by eluting it with 30 ml of *n*-hexane and 30 ml of 1:1 *n*-hexane:dichloromethane. Purified samples were reduced to 100 μL under a gentle nitrogen flow at 23 °C (Turbovap II®, Caliper Life Science, Hopkinton, MA, USA) and spiked with a known amount of the recovery standard solution containing ¹³C-PCB 47 and ¹³C-PCB 141 at 40 pg μL⁻¹, ¹³C-PBDE 77 at 20 pg μL⁻¹, ¹³C-PBDE 126 at 30 pg μL⁻¹ and ¹³C-Chrysene at 1000 pg μL⁻¹. A MAT 95XP (Thermo Finnigan) high-resolution mass spectrometer, equipped with a Hewlett–Packard Model 6890 gas chromatograph, was used to analyze PCBs, while instrumental analysis of PAHs and PBDEs was conducted by HRGC-LRMS (7890A-5975C, Agilent Technologies). The gas chromatographic separation was executed on a 60-m HP-5MS

column (0.25 mm I.D., 0.25 μm; Agilent Technologies, Avondale, USA) for PCBs and PAHs, while a 15-m column of the same type was used for PBDEs. Quantification was performed using internal standards and isotopic dilution. Results were corrected using the instrumental response factor. Procedural average recoveries and standard deviations for water and sediment samples were respectively: 68±8% and 70±11% for PCBs, 76±9% and 61±14% for PBDEs and 53±7% and 50±8% for PAHs. Procedural blanks were conducted in parallel with each sample. The LOD (Limit Of Detection) was calculated from the mean blank value plus three times the standard deviation.

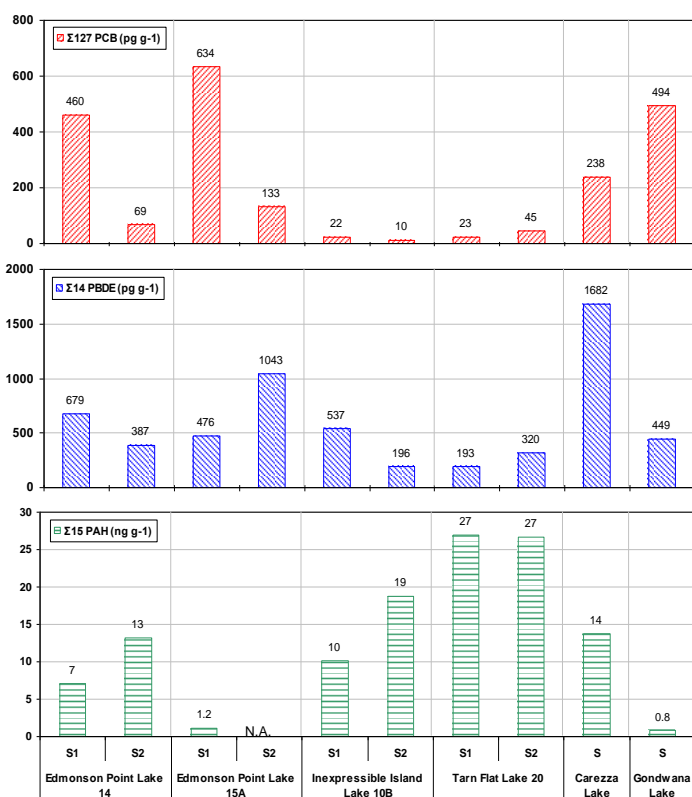


Fig 2: Total concentrations of 127 PCBs (pg g⁻¹), 14 PBDEs (pg g⁻¹) and 15 PAHs (ng g⁻¹) in surficial sediments of the lakes of Northern Victoria Land, Antarctica. PAHs were not analysed (N.A.) in sample Edmonson Point Lake15A S2.

Results and discussion

Total concentrations of PCBs (pg g⁻¹), PBDEs (pg g⁻¹) and PAHs (ng g⁻¹) in sediments are shown in Fig. 2. One or two surficial sediments were analysed for each lake: detected levels are generally low and in some cases close to LOD, with a certain variability even within the same lake. Differences in percentages of organic carbon and fine particles in the sediments cannot fully explain this variability and are

not reported here. Detected values of PCBs ($10\text{-}634\text{ pg g}^{-1}$) are consistent with previous data from 1988-1992 (total mean $120\text{ pg g}^{-1} \pm 87\%$)¹², but appear to be more widespread. Moreover the non-Aroclor congener PCB-11 (3,3'-dichlorobiphenyl) was detected in lake water and sediment samples providing, to our knowledge, the first measurements in lakes outside the Antarctic Peninsula^{8, 14}. PCB-11 was one of the most abundant congeners representing the (l.d.l)-12% and 6-19% of total PCBs in sediment and water samples respectively.

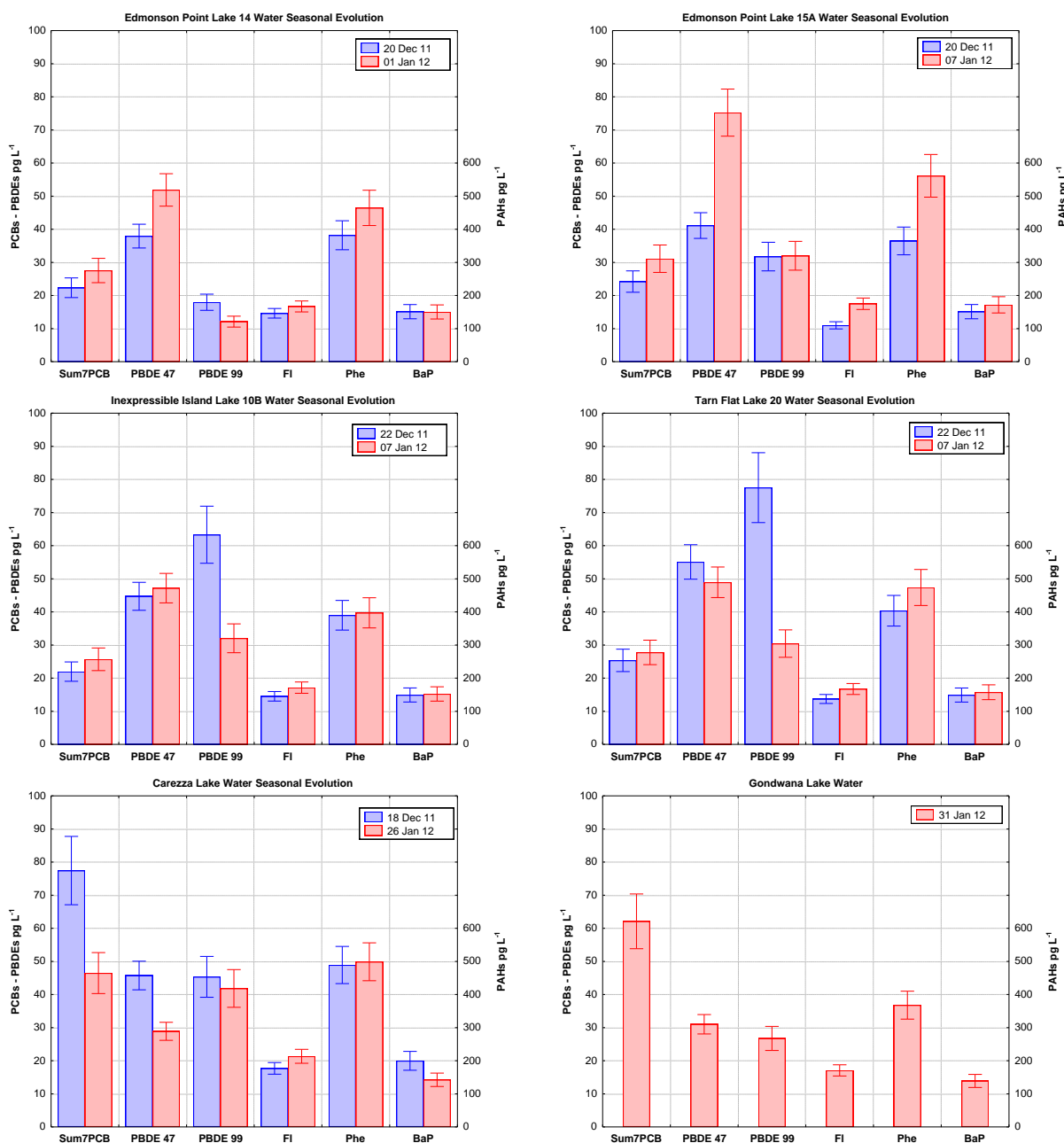
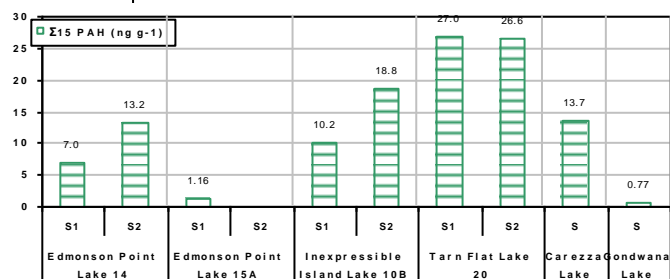


Fig 3: Lake water concentrations of the sum of the 7 indicator PCBs (PCB-28, -52, -101(+84,+90), -118, -138 (+-164), -153, -180, pg L^{-1}), selected PBDEs (-47,-99, pg L^{-1}) and selected PAHs (Fluorene (FI), Phenanthrene (Phe) and Benzo(a)Pyrene (BaP) pg L^{-1}). Error bars refer to method precision. Water samples were collected at the beginning and at the mid-late austral summer season (dates are shown). Note the different scale for PAH values.

The different classes of PCBs, PBDEs and PAHs exhibit little correlation between their behaviours in sediments (Fig. 2). In particular the samples from Inexpressible Island and Tarn Flat show the lowest levels of PCBs and PBDEs but the highest of PAHs. These two lakes are strongly influenced by katabatic winds coming from the



...e influenced by the sea. An indirect effect of the closeness to the sea is the presence of seabirds that could transport marine-bioaccumulated contaminants and significantly affect freshwater and ponds in terrestrial sites¹⁷. The relevant presence of southern polar skuas and penguins near these lakes could act as a punctual source of contamination at a local scale. Research stations could also constitute a local source of POPs emission in the Antarctic environment. In particular the sample from Lake Carezza, which is the nearest to the Italian MZS station (3 km), presents the highest levels of PBDEs among the analysed samples. Because of dry weather conditions, fire hazards constitute a major concern inside research stations, which contain plenty of flame-retarded materials¹⁸. However, the heavy BDE-209, as in the other lakes, was below LOD, suggesting that PBDE contamination is controlled by a more general process, such as long-range atmospheric transport (LRAT), rather than direct contamination. Moreover lake Carezza was not dramatically affected by PAHs, despite the nearby twin-otter refuelling point, which represents a risk of oil spills during logistics operations.

POPs concentrations in water are rather similar across the lakes despite their different characteristics: total PCBs and total PBDEs range between 46-143 pg L⁻¹ and 60-151 pg L⁻¹ respectively. Total PAHs are one order of magnitude higher (769-1190 pg L⁻¹) and similarly to sediment samples, concentrations in water generally resulted PCBs<PBDEs<PAHs. In order to highlight the seasonal variation, the discussion will be here limited to the sum of the 7 indicator PCBs and to selected compounds of PBDEs and PAHs (Fig. 3, note the caption). Σ₇PCBs increased of about 20% between the beginning and the complete melting of ice, though such increase is little significant when considering method precision. Lake Carezza is an exception with a significant decrease of 40%, probably due to dilution or sedimentation phenomena, and possibly also because of a longer period of time elapsed between samplings. PBDEs evolution is more complex, with the absence of a definite general trend, while PAHs were more constant both during the season and across sites. These results suggest that the lakes of Northern Victoria Land are not significantly affected by POPs amplification phenomena during the melting season. However, more in-depth investigations are required.

Acknowledgements

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