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Assessing levels of POPs in air over the South Atlantic Ocean off the coast of South America

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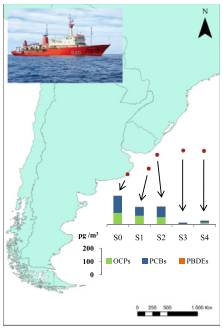
HIGHLIGHTS

- New information is reported on POPs in air over the south Atlantic Ocean off South America.
- Compounds investigated included organochlorine pesticides, PCBs and PBDEs.
- Concentrations were elevated at near-shore sites and dropped at distances >400 km off-shore.
- These results have implications for the environmental fate of POPs in the near-shore environment.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of persistent organic pollutants (POPs) in the atmosphere of the near-coast South Atlantic Ocean was studied. Air samples were collected using a high-volume air sampler (filter and polyurethane foam) on board the Argentinean research cruise R/V Puerto Deseado (CONICET). Samples were analyzed for 50 polychlorinated biphenyl (PCBs), 22 organochlorine pesticides (OCPs) and 14 polybrominated diphenyl ethers (PBDEs). These POPs classes showed a trend of decreasing levels from near-shore to open ocean sites. OCPs and PCBs were in the same order of magnitude (2.71–87.1 pg/m^3 and 9.56–130 pg/m^3, respectively) while PBDEs levels were significantly lower (0.69–2.58 pg/m^3). Dichlorodiphenyltrichloroethanes (DDTs), endosulfans, chlordanes, hexachlorocyclohexanes (HCHs) and heptachlors were between 0.20 and 17.8 pg/m^3, while drines and hexachlorobenzene (HCB) were at lower levels (0.28–3.71 pg/m^3). The most frequently detected PCBs were congeners 32, 28, 44, 52, 95, representing >50% of the total. The PBDEs congener pattern was dominated by congener 209 (70%), followed by 47 and 99 (16% and 7%, respectively). Air parcel back trajectories for the study period provided few insights as trajectories mainly stemmed from the open ocean with limited inputs from continental sources. These results indicate that the concentration of POPs (namely PCBs, OCPs, and PBDEs) in air remain elevated in the near-shore environment and then drop-off substantially beyond a distance of about 400 km. This has implications for the loading of POPs and delivery to the marine environment in the near coastal zone.

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1. Introduction

Human activities introduce into the atmosphere large amounts of pollutants, impacting the air quality on local, regional and global-scales. Some of these compounds can undergo long-range atmospheric transport (LRAT) and deposition from the atmosphere to oceans. This is the major route of introduction of persistent organic pollutants (POPs) to the oceans (Gouin et al., 2004; Jurado and Dachs, 2008).

POPs include organochlorine pesticides (OCPs), industrial chemicals such as PCBs and PBDEs and also unintended by products of industrial processes such as dioxins and furans. International actions have been launched to reduce and eliminate the production of these compounds. In this context, the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the Stockholm Convention on POPs have been entered into force in 2003 and 2004, respectively (Gavrilescu, 2005). Nevertheless, because of their strong persistence and their ability for LRAT, the occurrence of POPs in the environment, even in areas far from emission sources, is still of concern (Jones and De Voogt, 1999).

Only a few studies have reported levels of POPs in the atmosphere of the South Atlantic Ocean. Weber and Montone (1990) measured organochlorine pesticides and PCBs in air between Brazil and the Antarctic Peninsula in 1987. Montone et al. (2005) also reported PCBs and OCPs in the atmosphere of the southwest Atlantic and Antarctic oceans in 1995. Lohmann et al. (2012) analyzed POPs in air and water across the tropical Atlantic far away from the shore. Pozo et al. (2014) measured atmospheric levels of POPs in the Antarctic Peninsula. However, to our knowledge, there are no recent studies that investigate POPs occurrence in the atmosphere of the near-coast (South America) South Atlantic Ocean. The objectives of this study were: i) to investigate the levels of OCPs, PCBs and PBDEs in the atmosphere of the South Atlantic Ocean by collecting air samples on board the Argentinean research cruise R/V Puerto Deseado (CONICET) in October of 2014, during the 10th SAMOC (South Atlantic Meridional Overturning Circulation) expedition, and ii) to assess the extent of the influence of continental sources of these POPs to the atmosphere of the near-coast zone.

2. Material and methods

2.1. Study area

Air samples were collected at five sites (Fig. 1). The first was at the port of Mar. del Plata city, a possible emission source, the second and third were taken at the continental shelf while the fourth and fifth were at the open ocean. Information about sampling sites is detailed in the Supplementary material, Table S1.

2.2. Sampling

Air samples were collected using a high-volume air sampler (HVAS) (HI-Q USA). The particles were collected on an 11 cm diameter glass fiber filter (GFF) and the gas phase was sampled using a polyurethane foam (PUF, Restek, 6 cm diameter × 7.6 cm). The HVAS was setup above the bridge, facing the wind. The average air volume sampled was 980 m^3 and the duration of sampling was 72 h. Two field blanks (PUF + GFF) and one laboratory blank were analyzed. Field blanks were collected in the same way as real samples but for a very short time (less than a minute). Detailed information about sampling sites is provided in Table S1.

2.3. Analytical procedures

Prior to exposure, PUFs were pre-cleaned by washing with water and then Soxhlet extracted with ethyl acetate for 16 h, followed by hexane-ethyl ether 1:1 for 16 h. Following extractions, the PUFs disks were dried under vacuum for several hours and then kept in pre-cleaned glass jars during storage and transport. GFF filters were baked at 400 °C for 12 h to remove adsorbed organic compounds and then stored in aluminum foil in a desiccator.

PUFs and filters were Soxhlet extracted for 16 h with a mixture of 3:1 hexane:ethyl ether, individually. The extract volumes were concentrated by Kuderna-Danish evaporator and a high purity N_2 to a final volume of 1 mL. Each extract was cleaned using a Pasteur pipette filled with 1 g of sodium sulphate and then fractionated with a Pasteur pipette with 0.6 g of activated silica. The samples were eluted with 15 mL of a mixture of 3:1 hexane:ethyl ether and 15 mL of ethyl acetate. The cleaned extracts were nitrogen blow-down to a volume of 1 mL and solvent exchanged to isooctane. Mirex was added as an internal standard for volume correction to all sample extracts prior to analysis. All the samples and blanks were processed on the ship immediately after sampling.

Samples and field blanks were analyzed for a range of target compounds that included 50 PCBs, 22 OCPs and 14 PBDEs. Target compounds were analyzed by gas chromatography–mass spectrometry (GC–MS) using electron impact (EI) for PCBs and negative chemical ionization (NCI) for OCPs and PBDEs in the selected ion monitoring mode (SIM). Methods are described by Pozo et al. (2004).

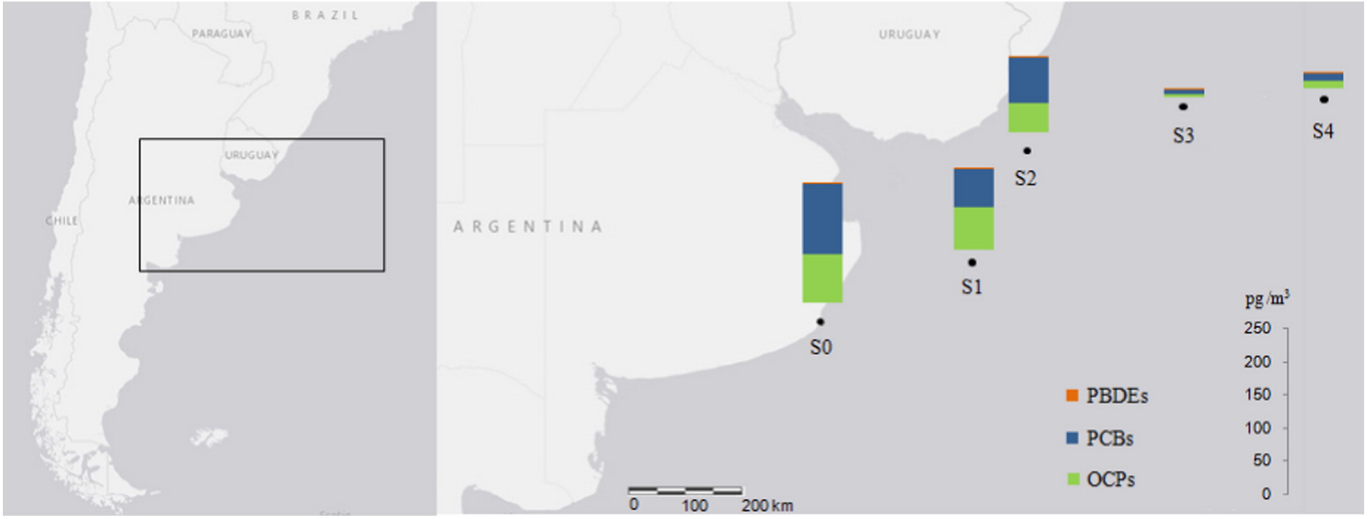

Fig. 1. Concentrations in air (pg/m^3) for the targeted POPs classes at the sampling sites.