



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



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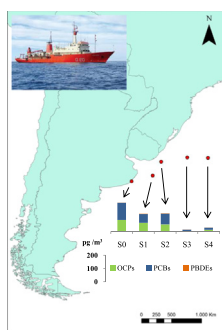
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HIGHLIGHTS

- 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



RV Puerto Deseado – South Atlantic Ocean - October 2014

ARTICLE INFO

Article history:

Received 31 May 2016

Received in revised form 20 July 2016

Accepted 21 July 2016

Available online xxxx

Keywords:

Persistent organic pollutants

South Atlantic Ocean

Active air sampling

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 dioxins 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 \times 7.6 cm). The HVAS was setup above the bridge, facing the wind. The average air volume sampled was 980 m³ 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 N₂ 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).

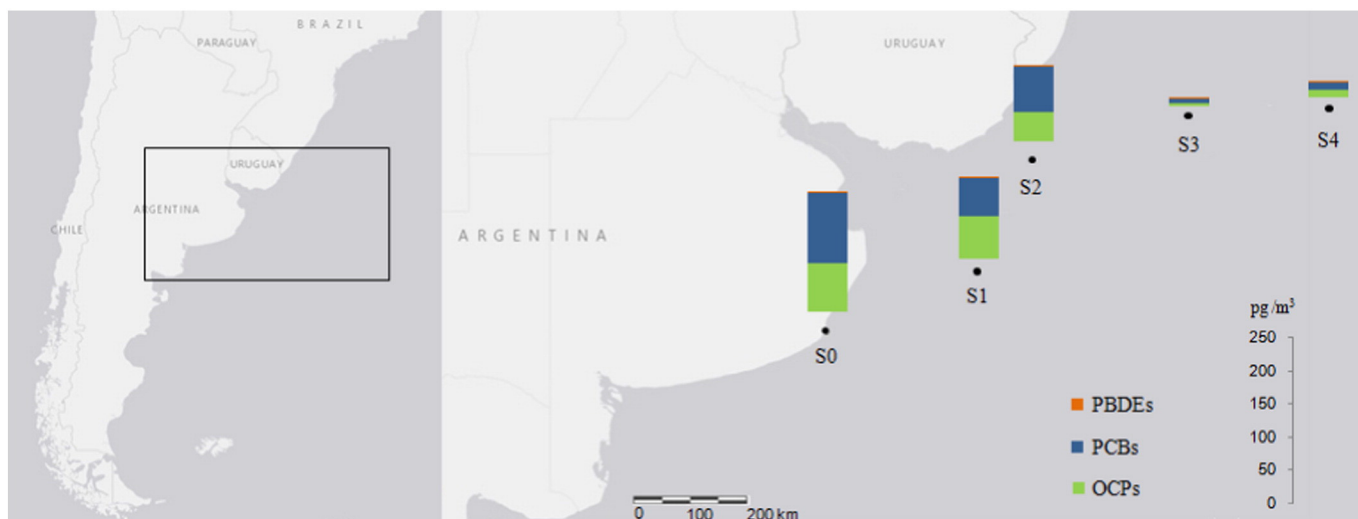


Fig. 1. Concentrations in air (pg/m³) for the targeted POPs classes at the sampling sites.

2.4. Quality assurance, quality control

Average blank values were 160 pg/sample for PCBs, 43 pg/sample for OCPs and 37 pg/sample for PBDEs. All the concentrations were blank corrected. External recoveries for the method in general were >85% for OCPs and PCBs, and >90% for PBDEs except to PBDE-209. The instrument detection limit (IDL), defined as the amount of pollutant that gives a signal to noise ratio of 3:1, was determined by calculating the signal to noise ratio for the compound in the lowest calibration standard. Method detection limit (MDL) was calculated as three times the standard deviation of the blanks determination. More details are shown in the supplementary information.

2.5. Air mass back trajectory analysis

With the aim of examine the influence of air mass origin for the cruise samples back trajectories were performed for each sampling location using NOAA's HYSPLIT model (Draxler and Rolph, 2011). Trajectories were calculated for each day at 300 m above the ground at 10:00 UTC.

3. Results and discussion

3.1. Overview

POPs showed a trend of decreasing levels in air from near-shore to open ocean sites (Fig. 1) demonstrating that sources to air for these compound classes are mainly land-based and that the influence of these land-based sources drops off within the first ~400 km of the near-shore. In general, OCPs and PCBs were in the same order of magnitude (2.71–87.1 pg/m³ and 9.56–130 pg/m³, respectively) while PBDEs levels were lower (0.69–2.58 pg/m³). >90% of the total of OCPs and PCBs (Table S3 and S4) were found in the gas phase, while >60% of PBDEs were associated with the particulate (Table S5).

3.2. OCPs

As shown in Fig. 2, the groups of OCPs were present in air in the same order of magnitude, despite sampling sites showed differences between them, with drines and HCB exhibiting the lowest concentrations in air.

Total concentrations of DDTs in air varied considerably among sites, from 0.23 (S3) to 16.9 pg/m³ (S0). Similar values have been measured in the South Atlantic Ocean by Montone et al. (2005) with concentrations between 8 and 19.7 pg/m³. Lower concentrations were found by Lohmann et al. (2012) (North of Brazil) as Σ_3 DDT (*p,p'*-DDT/DDE/DDD) with values between 0.2 and 0.7 pg/m³ compared with our work where Σ_3 DDT were 0.23 and 2.75 for S3 and S4 respectively.

The ratio *p,p'*-DDT/*p,p'*-DDE > 1 at S2 might suggest new DDT sources in the environment. Nevertheless, this ratio has been suggested to be unsuitable for the evaluation of old and new sources of DDT in

regions where Dicofol has been used. After the use of technical DDT was restricted, the use of Dicofol, which contains DDT as an impurity (mostly >80% as *o,p'*-DDT), has become an important source of DDT in the environment (Qiu et al., 2005). The *o,p'*-DDT/*p,p'*-DDT ratio was used to estimate the relative potential contributions of Dicofol formulation and those of technical DDT to overall environmental DDT, according to Qiu and Zhu (2010). The fraction of DDT from Dicofol formulation (Fd) was 30% for S1, <20% for S2 and S3 while it was close to 50% in S4 and S0. These results suggest that Dicofol could represent an important source to the DDT present in air in this region. Dicofol has been reported for agricultural usage in Argentina fields (Gonzalez et al., 2010).

Endosulfans showed the highest concentration at the urban site (S0 = 17.8 pg/m³), whereas levels were lower at the other sites (0.45–3.16 pg/m³) (Table S3). Endosulfan was heavily used in Argentina on soybean crops and some extremely high concentrations have been reported previously. Pozo et al. (2009), found levels of 57 to 18,739 pg/m³ in the city of Bahia Blanca (Buenos Aires province), while Astoviza et al. (2016) reported endosulfan concentrations in air between 10 and 63,000 pg/m³ in rural and urban sites in the province of Buenos Aires. However, these works were conducted before the Endosulfan prohibition in Argentina in July 2013 (SENASA, 2011) and so it is likely that Endosulfan concentrations in air have declined since 2013. Measurements of Endosulfans in the Southwest Atlantic Ocean were not found in the literature, while higher values were reported for the Southeast Atlantic Ocean 2.2–18 pg/m³ (Gioia et al., 2012) and North Atlantic ocean 16–17 pg/m³ (Bidleman, 1982). More recently a mean value of 1 pg/m³ for α -endosulfan was found in Chukchi Sea-Arctic (Zhong et al., 2012) and 5 pg/m³ in Canadian and Russian Arctic (Weber et al., 2010).

The low levels of the β -isomer could be attributed to the isomeric irreversible conversion β - to α - (Rice et al., 1997; Schmidt et al., 2001) and to the fact that β - is easily removed from the atmosphere by dissolution into sea water and wet deposition (i.e. due to a higher aqueous solubility and lower Henry's Law constant). The technical mixture of endosulfan contains α and β -isomers in the ratio of about 2.3 (Hayes and Laws, 1991). Therefore, the higher α/β ratio observed at S0 (~5) might be the result of the higher reactivity of the β - isomer as well as the presence of aged inputs or the influence of LRAT.

Chlordanes concentrations in air were in the range 0.24 (S3) to 10.1 pg/m³ (S0). These values are similar to the range of published results, including: Southern ocean (4.8–7.5 pg/m³) (Kawano et al., 1985) and South of New Zealand Sea (1.7–2.8 pg/m³) (Bidleman et al., 1993). Lower concentrations of chlordanes in air were reported in the North Atlantic and Arctic Ocean (average mean: 0.54 pg/m³) (Lohmann et al., 2009), in agreement with our values for the open ocean S3 and S4 (0.31 and 0.53 pg/m³ respectively). *cis*-Chlordane (0.61–7.94 pg/m³) was more abundant than *trans*-chlordane (0.24–1.82 pg/m³). The ratio *trans/cis*-chlordane varied from 0.17 to 1.54 (mean 0.54), which differs from the ratio of 1.56 in the technical mixture (Bidleman et al., 2002). This deviation from the technical mixture may be associated with the greater reactivity of *trans*-chlordane in the environment, indicating the influence of secondary sources to air of an aged/degraded technical chlordane.

HCHs levels were in the range 0.59 (S3) to 14.6 pg/m³ (S1). γ -HCH was the dominant isomer in all the samples (0.59–13.4 pg/m³). α -HCH/ γ -HCH ratios showed a mean of 0.12 \pm 0.09, which is indicative of ongoing lindane (γ -HCH) usage (Li et al., 2003; Zhang et al., 2007). Similar γ -HCH concentrations (<20 pg/m³) and α -HCH/ γ -HCH ratios (average mean: 0.14) were found at the South Atlantic Ocean (West Africa) (Jaward et al., 2004a). α -HCH values found in this work (0.45–1.27 pg/m³) were similar to those reported by Jantunen et al. (2004) for the South Atlantic (0.38–1.7 pg/m³).

Heptachlors concentrations in air ranged from 0.20 to 16.2 pg/m³. Tombesi et al. (2014) found similar values for Heptachlors (average mean: 18 pg/m³) in Bahia Blanca city (Argentina), located at approximately 460 km from Mar. del Plata city (S0). Heptachlor epoxide levels

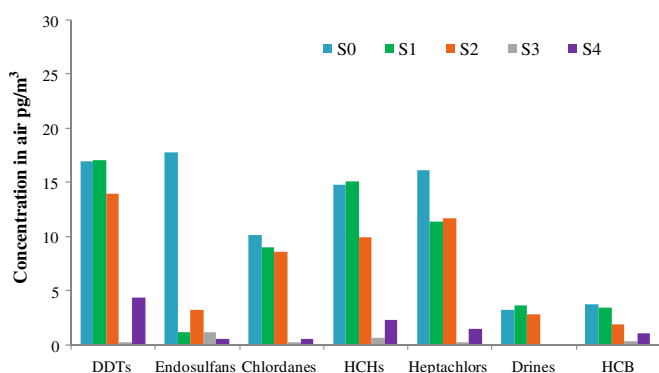


Fig. 2. Concentrations in air for OCP groups (pg/m³).

were significantly lower than its precursor heptachlor. These average heptachlor epoxide/heptachlor ratios in the current study are low (0.08) compared to the Antarctic air samples (0.46) (Dickhut et al., 2005), indicating a recent use of heptachlor.

Drines exhibited the lowest concentrations in air among the OCPs with values in the range BDL–3.65 pg/m³. Dieldrin concentrations were similar in S0, S1 and S2 (3.54, 3.65 and 2.83 pg/m³, respectively). These values are similar to those reported for background regions in Chile between 0.98 and 3.80 pg/m³ (Poza et al., 2004). Endrin was only detected at S0, while aldrin was below the detection limit in all the samples.

HCB levels decreased slightly from S0 to S4. Concentrations in the gas phase (0.28–3.71 pg/m³) were comparable to those reported by Lohmann et al. (2012) in samples collected at the South Atlantic Ocean (North Brazil samples: 0.8–4.1 pg/m³). Nevertheless, levels were significantly lower than values registered by Montone et al. (2005) (<0.6–25.3 pg/m³) along a transect between the Southwest Atlantic and Antarctic Oceans and the values reported by Gioia et al. (2012) in the Southeast Atlantic Ocean (0.8–22 pg/m³). This may be due to the fact that HCB because of its high volatility tends to breakthrough in high volume air samples collected using PUFs, leading to an underestimation of air concentrations (Melymuk et al., 2014; Hung et al., 2016).

Pentachloroanisole is a biodegradation product of pentachlorophenol. Concentrations of Pentachloroanisole were 1.99 ± 1.71 pg/m³, similar values have been measured in Arctic stations (4.9 ± 4.8 pg/m³; Su et al., 2008) and higher results have been reported in air samples in the North Sea (0.3–43 pg/m³; Zhong et al., 2012).

3.3. PCBs

PCB concentrations in air are shown in Fig. 1. Concentrations of Σ PCBs ranged between 131 and 9.60 pg/m³. PCBs have been previously measured in the South Atlantic Ocean with values between 75 and 242 pg/m³ (Montone et al., 2005) during a Brazilian expedition in 1995. Moreover, Σ PCB determined by Schreitmuller and Ballschmiter (1994) during north-south cruises across the Atlantic Ocean (1990–1991) were in the range 136–261 pg/m³ (South Brazil–North Argentinean Sea). These previously reported values are of the same order of magnitude as those observed in the current study.

Air concentrations of dioxin like PCBs (dl-PCB) have been reported in the South Atlantic Ocean (Morales et al., 2014). The congeners 77, 81, 105 and 118 represented >70% of the total and the values were between 0.87 and 4.37 pg/m³, being in good agreement with our values (2.84–4.45 pg/m³).

Recent studies reporting Σ_7 PCBs (28, 52, 101, 118, 138, 153 and 180) have shown mean values of 16 ± 14 pg/m³ and 20 ± 19 pg/m³ in the South East Atlantic Ocean (Gioia et al., 2012, 2008) and 8 ± 3 pg/m³ in the South West Atlantic Ocean (Lohmann et al., 2012). These results are in good agreement with Σ_7 PCBs values registered in this work (15 ± 14 pg/m³). The time trends of PCBs in the Atlantic Ocean atmosphere did not show any decline in a ten years period (Gioia et al., 2008). Nevertheless the decline in background air concentrations of PCBs has been reported in Europe and the Arctic (Hung et al., 2010; Schuster et al., 2010). This would imply that surface waters have buffered declining atmospheric concentrations for PCBs (Nizzetto et al., 2010).

As might be expected, the highest PCB concentrations were detected at the urban site S0 and the levels in air drop-off away from the coast. This result is in agreement with other studies from South America with values of 40–360 pg/m³ in Bahia Blanca–Argentina (Tombsi et al., 2014), 160 pg/m³ Concepcion–Chile (Poza et al., 2012) and higher values (215 and 395 pg/m³) were found in Teresopolis–Brazil (Meire et al., 2012). These results are also comparable with those of the GAPs network (~10 to ~100 pg/m³) reported for South America (Poza et al., 2006).

The PCB profile was dominated by 3-Cl ($41 \pm 7\%$), 4-Cl ($25 \pm 6\%$) and 5-Cl ($18 \pm 6\%$) homologues. The most frequently detected PCBs were congeners 32, 28, 44, 52, 95, representing >50% of the total. It is well known that lower molecular weight congeners of PCBs are more easily transported in air while the higher molecular weight congeners partition to surfaces and aerosols and tend to be deposited near sources. This is evident from Fig. 3 where the 6- and 7-Cl congeners are only detected at sites close to the continent (S0, S1 and S2) demonstrating a “continental” or “near-shore fractionation effect” analogous to the urban fractionation effect proposed for urban sources of PCBs (Harner et al., 2004). Therefore, sites S1 and S2 seem to be showing some influence from continental air masses where PCBs are elevated compared to the open ocean. In the same way, Schreitmuller et al. (1994) discerned a particular marine air pattern for PCBs, with a high proportion of lower chlorinated congeners. These lower molecular weight PCBs once deposited to ocean waters do not partition strongly to settling biogenic particulate matter and are therefore more susceptible to re-emission to air (Jurado et al., 2004).

3.4. PBDEs

Concentrations in air of Σ PBDEs were between 0.7 and 2.6 pg/m³, with an average concentration of 1.8 ± 0.8 pg/m³, showing little variation between sampling sites (Table S5). These results are similar to other studies in the South Atlantic Ocean near the West African coast for Σ_9 PBDEs (0.4–1.3 pg/m³; Xie et al., 2011) and Σ_{21} PBDEs (0.3–2.9 pg/m³; Li et al., 2011). However, this comparison should be interpreted with caution as different PBDE congeners were reported in the different studies and the analysis of PBDEs is challenging and prone to blank issues, since PBDEs are commonly used in commercial products, including laboratory equipment (Poza et al., 2009).

It is noteworthy that the urban site S0 exhibited lower Σ PBDEs concentrations than sites S1 and S2, which is opposite to the trend shown for OCPs and PCBs. PBDEs are typically elevated in air near urban sites (Harrad and Hunter, 2006; Jaward et al., 2004b).

The PBDEs congener pattern was dominated by congener 209 (70%) followed by 47 and 99 (having 16% and 7% respectively of the total concentration). These profiles resemble a combination of the commercial deca-BDE mixture (with >91% of 209) and the penta-BDE formulation that is dominated by congeners 47 and 99 (La Guardia et al., 2006). The higher proportion of 209 in the air samples may reflect reduced emissions associated with the recent listing of penta-BDE under the Stockholm Convention while deca-BDE continues to be used, although it is a candidate for listing under the Convention (UNEP, 2013).

3.5. Air mass back trajectory analysis

Trajectory analysis provided limited insights for source attribution, due to lack of events exhibiting substantial land-based contributions

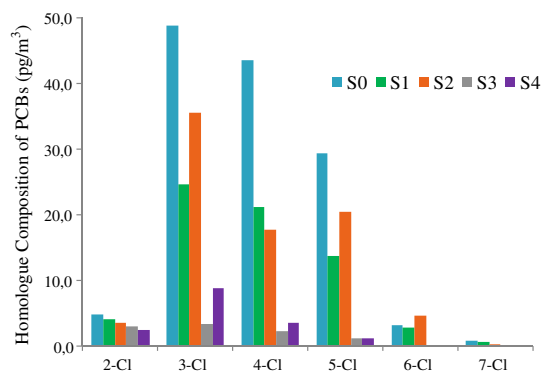


Fig. 3. Homologue composition of PCBs (pg/m³).

to the air masses that were sampled in this study. For most of the air samples, air parcel back trajectories (Fig. S1) stemmed from the open ocean (both southerly and northerly directions) with only limited inputs from continental sources (e.g. for samples S1, S2 and S4). The low concentrations of target compounds in sample S3 are consistent with the fact that all of the air trajectories for this sample stemmed from the open ocean.

4. Conclusions

Ship-based air samples collected in the Southern Ocean off the coast of South America provide new information on POPs concentration in air for this region and indicate that the concentrations of POPs (namely PCBs, OCPs, and PBDEs) remain elevated in the near-shore environment and then drops-off substantially beyond a distance of about 400 km. This suggests the influence of a continental or regional air mass that exists in the near-shore region that integrates advective inputs of POPs from regional land-based sources. This has been observed in previous studies in other parts of the world (Lammel et al., 2007; Zhang et al., 2007). This has implications for atmospheric deposition and uptake of contaminants in the aquatic near-shore environment.

Acknowledgments

This work was partially funded by ANPCyT-PRH N20 (PICT103), CONICET (PIP659) and SECyT-UNMdP (15/E516 -EXA568/12). The authors would like to thank to the scientific chief Alberto Piola and the crew of the research vessel A.R.A. Puerto Deseado for their support and Sebastian Grondona for drafting the map. We also acknowledge the help of the Hazardous Air Pollutants (HAPs) Laboratory (Environment and Climate Change Canada). CNP acknowledges a PhD fellowship from CONICET as well as a DFATD (Canada) fellowship from ELAP (Emerging Leaders in the Americas Program).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.07.149>.

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