RESEARCH ARTICLE

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Latitudinal distribution of OCPs in the open ocean atmosphere between the Argentinian coast and Antarctic Peninsula

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Abstract
Long-range atmospheric transport is one of the most important ways in which persistent organic pollutants can be transported from their source to remote and pristine regions. Here, we report the results of the first Argentinian measurements of organochlorine pesticides in the Antarctic region. During a 9665-km track onboard OV *ARA Puerto Deseado*, within the framework of Argentinian Antarctic Expeditions, air samples were taken using high-volume samplers and analyzed using GC-μECD. HCB, HCHs, and endosulfans were the major organic pollutants found, and a north-south gradient in their concentrations was evident by comparing data from the Argentinian offshore zone to the South Scotia Sea.

Keywords Antarctica · OCPs · Endosulfan · HCHs · HCB · Atmosphere

Introduction

Over the last decades, many organochlorine pesticides (OCPs) such as hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), and other compound have been continuously analyzed in almost all regions of the planet due to their negative health and environmental impacts (Tago et al. 2014; Yadav et al. 2015). Low concentrations in remote areas like the polar regions were found, despite the fact that these contaminants have never been used in those places. In the case of the south polar region, due to its geographical isolation (belted by the Southern Ocean), it is agreed that pollutants have reached that pristine area mainly by the so-called long-range atmospheric transport (LRAT) process. In this way, persistent substances can be transported by air masses flows, from distant latitudes where they have been released into the environment (Oehme 1991; Weber et al. 2010).

Because of their persistence, toxicity to human or wildlife, and their capability for LRAT, several OCPs have been internationally banned or restricted by the Stockholm Convention on Persistent Organic Pollutants under the United Nations Environmental Programme (United Nations Environment Programme 2002, 2010; United Nations Environmental Programme 2002). The worldwide restriction of OCPs has led to a notable reduction of their concentrations in the usage areas, while a progressive decline in the values encountered at remote sites was also observed (Szopińska et al. 2016). However, the high, and not often controlled, use of OCPs before ban still shows important residue levels in several environmental compartments (Cai et al. 2008; Cincinelli et al. 2009; Corsolini 2009; Ali et al. 2014). It is assumed that regions like South America, where OCPs have been extensively used for decades in agriculture, will remain as a source of OCP contamination for remote areas such as the Antarctic region for many years to come, as a consequence of LRAT and the Global Distillation Process. (Wania and Mackay 1993; Bargagli 2008).

In the last few decades, numerous works investigated levels of OCPs in polar regions, detecting and measuring them at different environmental compartments, demonstrating the long-range distribution of these pollutants (Oehme 1991; Li and Macdonald 2005; Xiao et al. 2008; Weber et al. 2010).

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Nevertheless, studies on the Antarctic region are still limited, covering only small subregions of West (Tanabe et al. 1983; Gambaro et al. 2005; Cincinelli et al. 2009; Xie et al. 2011; Pozo et al. 2017) or East Antarctica (Montone et al. 2005; Dickhut et al. 2005; Baek et al. 2011; Kallenborn et al. 2013; Galbán-Malagón et al. 2013; Khairy et al. 2016; Choi et al. 2008; Bigot et al. 2016a).

To determine the distribution and trends of OCPs from lower latitudes to the Antarctic region, atmospheric measurements along transects from north to south have been conducted either during cruises onboard of scientific research vessels (Tanabe et al. 1983; Iwata et al. 1993; Montone et al. 2005) or by a land-based measurements (Pozo et al. 2009; Baek et al. 2011; Kallenborn et al. 2013). Concentration gradients from the lower to the higher latitudes have been generally observed. However, to adequately estimate the amount of contaminants reaching the Antarctic region by LRAT, data about OCP levels in the southern hemisphere are still scarce.

The aim of this study was to determine the distribution of OCPs from the South-West Atlantic to the Southern Ocean. Air samples were taken along a north-south track onboard an oceanographic vessel during the annual Argentinian Antarctic Expedition. As a result of this process, we present the first Argentinian measurements of persistent pollutants in the so-called White Continent, covering an almost 10^4-km track from Mar del Plata (Argentina, 38.00° S; 57.33° W) to Ushuaia (Argentina, 54.48° S; 68.18° W) and the Antarctic region delimited by Ushuaia, Palmer Archipelago (64.15° S; 62.50° W), and Islas Orcadas del Sur (60.44° S; 44.44° W).

These data come to complement previous international efforts in the characterization and monitoring of OCPs worldwide. Further, these data may be helpful to evaluate the OCP input from the South American continent to the Antarctic region.

Materials and methods

Sampling

A high-volume air sampler (TE-1000-PUF Ambient Air (Tisch Environmental Inc.)) was deployed on the upper deck of the vessel *ARA Puerto Deseado* facing the wind from February 6 to March 28, 2011, during the annual Argentinian Antarctic Expedition. Sampling was performed at open ocean between 37° and 65° S latitude of the Southwest Atlantic and Southern Ocean (Fig. 1). A total of 12 air samples (named as S1 to S12) were taken during the survey cruise, with collected air volumes ranging from 720 to 2000 m³ (36 to 72 h of continuous sampling). The details of sampling locations, date, air temperature, and total air volume sampled are shown in Table SI-2 in the Electronic

Supplementary Information section. Samples were obtained by pumping air (flow rate 0.25–0.27 m³/min) through the sampler, equipped with a quartz fiber filter (QFF; 102 mm, Tisch Environmental Inc.) and a polyurethane foam plug (PUF; height 78 mm, diameter 55 mm, Tisch Environmental Inc.). Prior to exposure, QFF filters were oven-baked at 400 °C for a period of 12 h in order to remove any possible organic compounds adsorbed, while PUF plugs were precleaned by washing with water and then Soxhlet-extracted with a hexane/diethyl eter (Hex/DEE) (9:1, *v/v*) mixture for 12 h, dried in a desiccator. Both were stored in glass jars, wrapped in hexane-cleaned aluminum foil for further use. Before each sampling, calibrations were performed to assess the sampler flow rate.

Sample preparation

The extraction process and chromatographic analyses were carried out in a preconditioned room on board the scientific vessel. For this purpose, the installation of the GC-µECD and the conditioning were made well before cruise starting, in order to evaluate work capacities and avoid unwanted interferences during the whole campaign.

For the determination of the extraction performance, precleaned PUF and QFF were spiked with OCP standards and were treated like a sample. External recoveries were in the range between 85 and 111% which were assumed acceptable (Table SI-3).

After removal from the high-volume air sampler, samples were either immediately extracted or well packed and frozen to − 18 °C on board for further extraction. No differentiation between particle and gas phase was made, and therefore, PUF plug and QFF were Soxhlet-extracted together for 24 h with 250 mL of a Hex/DEE (9:1, *v/v*) mixture. The extract was concentrated to 1 mL by using a Kuderna-Danish concentrator and by passing a gentle stream of ultra-pure nitrogen. Sample cleanup was performed on a silica column, consisting of silica gel and anhydrous Na_2SO_4 on top of it. The silica column was rinsed twice with 2 mL Hex, followed by 2 mL DCM and 2 mL methanol before use. Subsequently, the sample (1 mL extract) was eluted with 3 mL Hex, followed by 3 mL DCM. Finally, the sample volume was reduced under a gentle nitrogen stream, the internal standard (pentachloronitrobenzene) was added, and the solvent was changed to Hex to a final volume of 1 mL for further gas chromatography (GC) analyses.

Three field blanks (taken at Mar del Plata, Islas Orcadas del Sur, and Ushuaia, corresponding to the beginning, mid and end of sampling track) were performed during the cruise survey. Analytical method details (including QA/QC) are summarized in the Electronic Supplementary Information section.
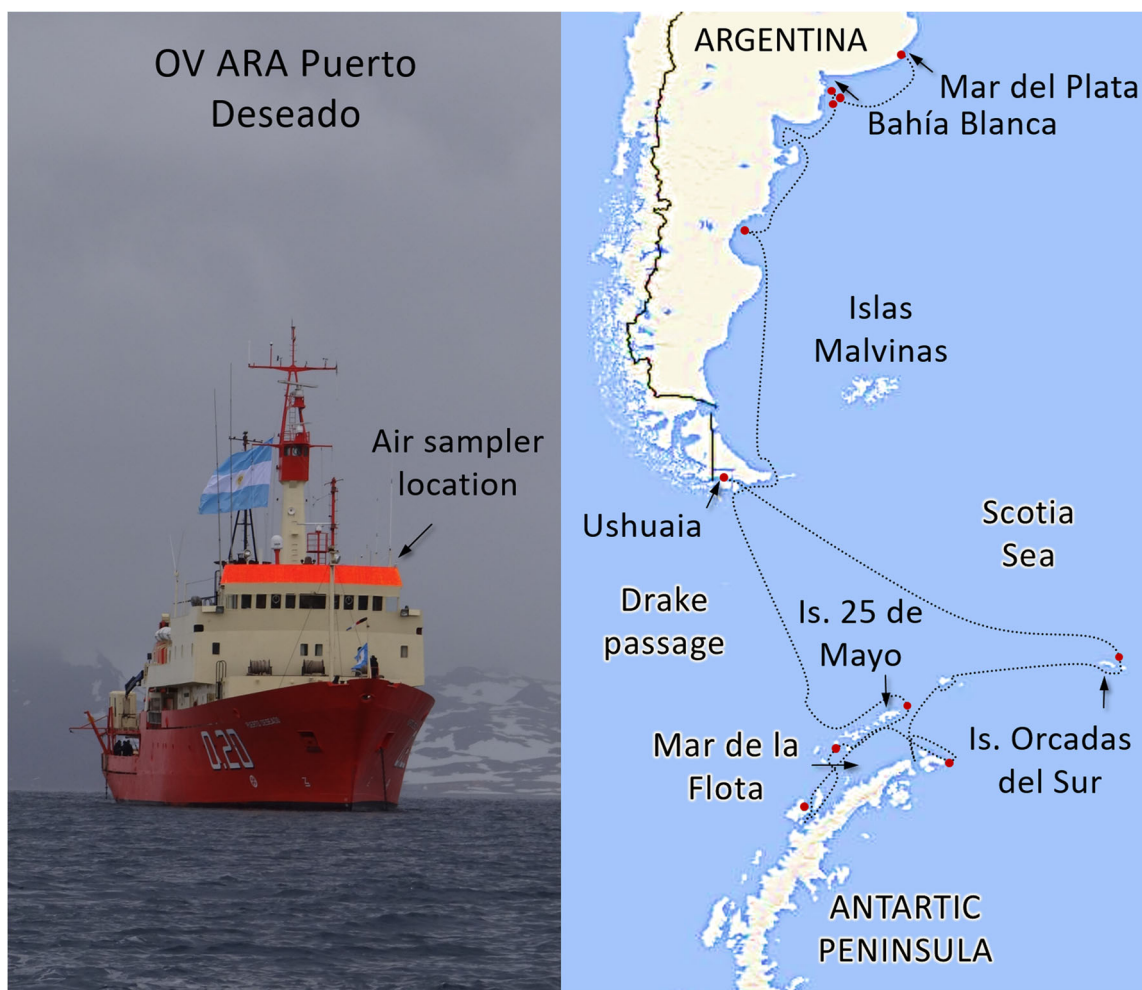
Fig. 1 High-volume air sampler location onboard OV ARA Puerto Deseado (left) and oceanic route described during Argentinian Summer Antarctic Campaign 2011 (right)

Air mass trajectory calculations

Frequency maps (averaged by 1°) of the intermediate positions of the 48-h back-trajectories (one every 3 h) were calculated for the duration of samplings S10 and S11. The calculations have been performed using Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Stein et al. 2015) using the National Center for Environmental Prediction Global Data Assimilation System (NCEP GDAS) meteorological fields with a resolution of 0.5 × 0.5°. Endpoints of each air mass trajectory have been located at the midpoint between start and end ship position (a valid assumption as the total ship displacement was less than 120 km in both cases), with a height of 12 m above sea level.

Results and discussion

Air samples were taken in the area of South Atlantic Ocean close to the Argentinian coast, Drake Passage and Scotia Sea and Mar de la Flota (Bransfield Strait) as Fig. 1 shows, together with the sampler location onboard OV *ARA Puerto Deseado*. The sampler was deployed as far away as possible from the exhaust pipes to avoid vessel interferences. Start and finish coordinates as well as climatological parameters of each sampling site are given in Table SI-2 in the ESI section. After sample collection, conditioning, preparation, and extraction, GC-µECD was used as analytical method. The choice of this particular technique was made due to the high specificity towards halogenated (and null towards fully hydrogenated) compounds, as well as the sturdiness of the chromatographic system, which was installed on-board and enabled real-time analyses.

The present study covered a large region, involving from subtropical to polar climates. Despite the works presented by Montone et al. in which they showed a transect from the proximity of Rio de Janeiro, Brazil, to the South Shetland Islands in Antarctica (Montone et al. 2005) and that of Pegoraro et al. who have measurements that coincide with our starting point (Pegoraro et al. 2016), no wide range measurements since

1995 were made. Galbán-Magalón presented in 2013 the results of both 2008 and 2009 Antarctic survey cruises sailing from the Beagle Channel to the South Shetland Islands and South Scotia Sea, respectively (Galbán-Malagón et al. 2013). Figure 2 shows the schematic representations of survey cruises and land sampling sites of most relevant OCPs measurements at the Antarctic continent. This demonstrates the importance of our work, covering the 10^4-km track as shown Fig. 1.

During our cruise survey, a total of 11 organochlorinated compounds have been found frequently in the air samples above the quantification limit. HCB, HCH, and endosulfan family were the most abundant and they were present in almost all samples. As it is said, the exhaust gases of the vessel could introduce some uncertainties to some OCP concentrations. Nevertheless, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and some aliphatic compounds were not considered in this study. That is why we will focus specifically on the chlorinated persistent pesticides in this work.

OCP levels measured during the cruise survey ranged from 11.2 to 27.3 pg/m^3 for HCB, 2.14–2.90 pg/m^3 for ΣHCHs (α + γ-HCH), and 4.1–624 pg/m^3 for ΣEndo (Endo1 + Endo1 + Endo sulfate). As will be discussed later, Endo sulfate was found in high concentrations at the polar region, while the values encountered at higher latitudes were mostly below the detection limit; nevertheless, data collected in this work was sufficient to show a spatial tendency.

HCB

HCB is a fungicide employed for seed treatment, and it was widely used before its ban by the Stockholm Convention at the early 2000. HCB was found and quantified at all sampling sites, corroborating a latitudinal decrease trend as shown (Fig. 3 and Table 1). The highest HCB levels were found at the port of Ushuaia, Argentina (27.3 pg/m^3), and close to the port of Mar del Plata, Argentina (26.3 and 23.7 pg/m^3, respectively), while the lowest level was found close to the Anvers Island in the Palmer Archipelago (11.2 pg/m^3). Overall, the HCB concentration in the Antarctic region is half the average value at the Argentinian offshore (average 22.0 pg/m^3).

The values determined along the Argentinian coast were slightly higher, though within the same order of magnitude, than those reported in literature. Montone et al. measured in year 1995 HCB between 23° and 62° S and reported atmospheric levels ranging from < 0.6 to 10.9 pg/m^3 with an average of 5.9 pg/m^3 for the range 23 to 55 °C (Montone et al. 2005) for similar sampling sites as our work. At other different sites, but at same latitudes, Jaward et al. during a cruise from The Netherlands to Cape Town, South Africa (January and February 2001), determined OCP levels in the Atlantic Ocean and observed a concentration increase of atmospheric

HCB levels from 10 pg/m^3 (~ 10° S) to around 20 pg/m^3 in the vicinity of Cape Town (~ 34° S) (Jaward et al. 2004). Thus, the values at the same latitudes can be compared quite well with those here presented, being 22.7 pg/m^3 the average value found at an average latitude of 39.5° S, in concordance with our results.

The HCB levels determined in the Antarctic region were also in the same range of the values reported by Montone et al., Dickhut et al., and Galbán-Malagón et al. Montone and coworkers measured atmospheric HCB concentrations ranging from 17.4 to 25.3 pg/m^3 with an average of 22.3 pg/m^3 (55–62 °C) during a survey cruise in open ocean in November 1995. Dickhut et al. measured HCB in air 6 years after Montone et al. at the Palmer Archipelago and Southwest of Adelaide Island (Dickhut et al. 2005). During their winter sampling (September–October 2001), they reported atmospheric HCB values ranging from < 5 to 32.1 pg/m^3, with an average of 19.4 pg/m^3. In the proximity of the last mentioned sampling locations, Galbán-Malagón et al. measured an average level of HCB of 5.6 pg/m^3 during a cruise through South Scotia Sea in 2008, while in 2009, the average values determined at Weddell, Bransfield, and Bellingshausen Seas were 14.9, 15.8, and 13.6 pg/m^3, respectively (Galbán-Malagón et al. 2013). In comparison, Bidleman et al. measured atmospheric HCB concentrations during the summer of 1990 along a shipborne transect between New Zealand and the Ross Sea (Bidleman et al. 1993) with values of 70.0, 40.0, and 18.0 pg/m^3 taken at D'Urville, Somov, and Ross Seas in West Antarctica. Thus, a clear concentration decrease of HCB levels in the Antarctic air could be assumed, when considering the values reported by Bidleman et al. (campaign 1990; average 62.7 pg/m^3), Montone et al. (campaign 1995; average 22.3 pg/m^3), Dickhut et al. (campaign 2001; average 19.4 pg/m^3), Galbán-Malagón et al. (campaign 2008; average 5.6 pg/m^3 and 2009; average 14.7), and our data (campaign 2011; average 14.8 pg/m^3).

HCHs

Before the Rotterdam Convention, signed in 1998, lindane (γ-HCH) and technical HCHs (mixture of a total of eight HCH isomers, mainly α- and γ-HCH) were widely produced and consumed as insecticides. As for HCB, the HCH concentration measured showed a decreasing gradient from the offshore South American sampling sites to the Antarctic region from an average amount of 7 pg/m^3 at the Argentinian Patagonia to 2.5 pg/m^3 at the south Scotia Sea and Bransfield Strait. The highest levels of HCHs were found in the vicinity of Bahia Blanca, Argentina, in which α-HCH peaked to 15.2 pg/m^3 and γ-HCH to 10.4 pg/m^3 (Fig. 3).

Montone in 1995 found average values of α- and γ-HCH of 11.8 and 12.5, 5.9 and 8.2, 4.0 and 4.6, and 4.5 and < 2.7 pg/m^3 for the Brazilian coast, Argentinian coast, South Atlantic Ocean, and surroundings of the Elephant Island,
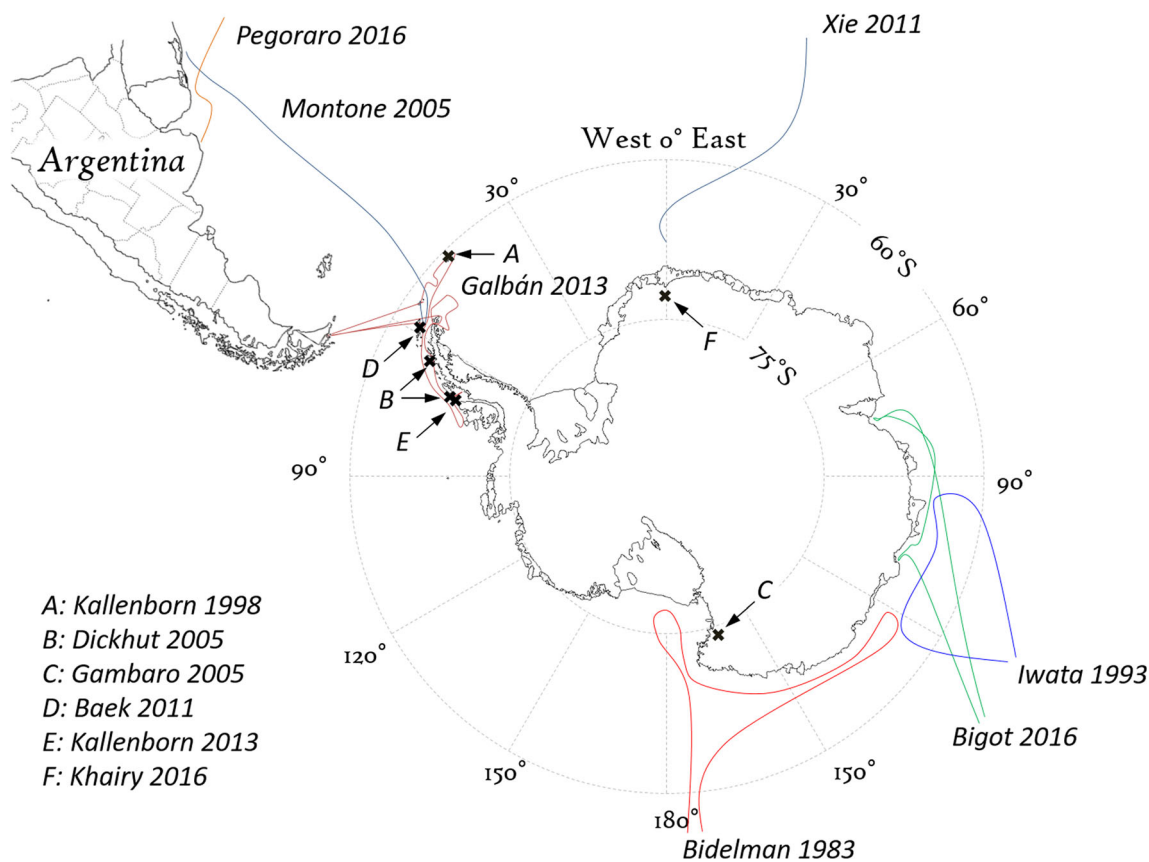
Fig. 2 Sampling sites and cruise survey tracks of reference works

respectively (Montone et al. 2005). Mean values of 0.3 and 0.5 were recorded by Dickhut and collaborators in the Adelaide Island for α- and γ-HCH, respectively, in 2001, while in 2002, corresponding values were 0.4 and 1.0 pg/m^3 encountered in the Palmer Archipelago (Dickhut et al. 2005).

Beak et al. reported measurements carried out at the King Sejong Antarctic Station in the 25 de Mayo/King George Island on 2006, being 2.3 pg/m^3 for α-HCH and 0.8 pg/m^3 for γ-HCH (Baek et al. 2011). Analogously, the average values encountered in 2008 at the South Scotia Sea were

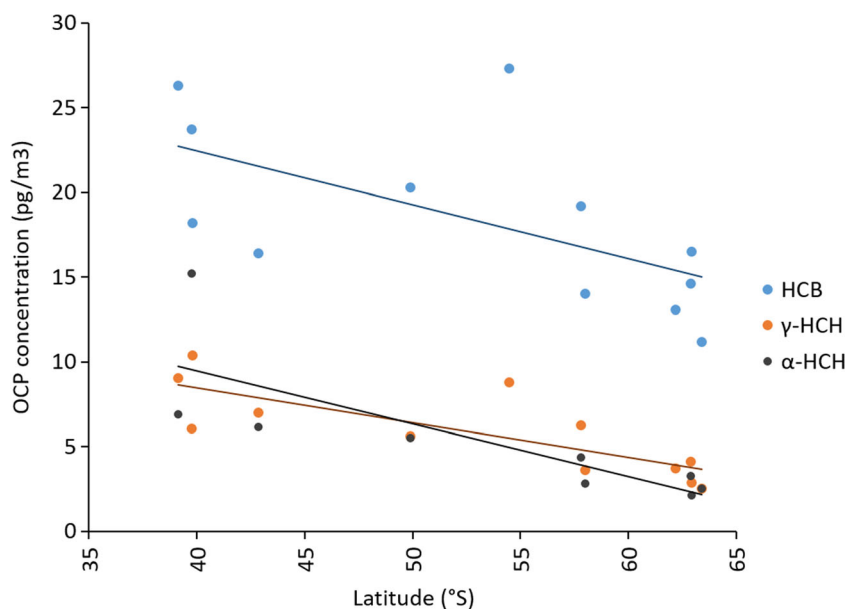**Fig. 3** Latitudinal trends found for HCB, α-HCH, and γ-HCH

Table 1 HCHs and HCB atmospheric concentrations reported for the Southern Ocean and related regions (pg/m³)

Year	Sample location	α-HCH	γ-HCH	HCB	Ref.
1990	New Zealand—offshore	(5.10 ± 1.39)	(6.50 ± 5.81)		Bidleman et al. (1993)
	Ross Sea	(2.80 ± 0.42)	(1.30 ± 0.35)	78.00	
	South Pacific Ocean	(4.50 ± 0.21)	(11.40 ± 7.71)		
	Somov Sea	3.30	1.40	40.00	
	D'Urville Sea	3.60	5.60	70.00	
1995	Brazil—offshore	(11.80 ± 4.73)	(12.50 ± 3.82)	(5.30 ± 4.02)	Montone et al. (2005)
	Argentina—offshore	(5.90 ± 3.00)	(8.20 ± 4.37)	(7.20 ± 4.21)	
	South Atlantic Ocean	(4.00 ± 1.10)	(4.60 ± 1.65)	(22.40 ± 4.37)	
	Elephant Is.	4.50	< 2.7	21.90	
2001	Adelaide Is.	(0.28 ± 0.11)	(0.47 ± 0.66)		Dickhut et al. (2005)
2002	Palmer Archipelago	(0.35 ± 0.11)	(1.04 ± 0.87)	(19.40 ± 7.60)	Dickhut et al. (2005)
2006	25 de Mayo/King George Is.	2.30	0.81		Baek et al. (2011)
2008	South Scotia Sea	(1.71 ± 2.16)	(4.56 ± 1.94)	(8.19 ± 5.63)	Galbán-Malagón et al. (2013)
2009	Weddell Sea	(0.17 ± 0.13)	(0.84 ± 0.92)	(19.49 ± 14.99)	Galbán-Malagón et al. (2013)
	Bransfield Strait	(0.24 ± 0.21)	(1.15 ± 1.60)	(16.72 ± 15.87)	
	Bellingshausen Sea	(0.16 ± 0.06)	(0.14 ± 0.06)	(42.95 ± 13.58)	
2010	Palmer Station	(1.28 ± 0.34)	(1.24 ± 0.51)	(33.60 ± 4.22)	Khairy et al. (2016)
2011	Argentina—offshore	(8.45 ± 4.53)	(7.82 ± 1.88)	(22.03 ± 4.43)	This study
	South Atlantic Ocean	4.39	6.25	19.20	
	Drake Passage	2.82	3.62	14.00	
	Mar de la Flota	(2.64 ± 0.58)	(3.33 ± 0.73)	(13.85 ± 2.25)	

1.7 pg/m³ for α-HCH and 4.6 pg/m³ for γ-HCH, while those values for the Weddell Sea, Bransfield Strait, and Bellingshausen Sea in 2009 were 0.2 and 0.8, 0.2 and 1.2, and 0.2 and 0.1 pg/m³, respectively, for α- and γ-HCH (Galbán-Malagón et al. 2013). Khairy and coworkers reported in 2010 α-HCH values ranging from 0.8 to 1.7 pg/m³ (average 1.3 pg/m³) and from 0.9 to 2.3 pg/m³ (average 1.2 pg/m³) for γ-HCH, sampling at Palmer U. S. Antarctic Station in the Anvers Island (Khairy et al. 2016). A recent report of Bigot et al. conveys the following mean values for α- and γ-HCH at the East of Southern Ocean and related areas in 2014: Mawson Sea, 1.10 and 1.93; Davis Sea, 0.30 and 1.98; and South Indian Ocean, 0.31 and 3.36 pg/m³ (Bigot et al. 2016b).

As can be noted, our data indicate a slight increase of α- and γ-HCH in the Antarctic zone probably due to unauthorized use beyond its banning date, as can be interpreted also from the high values measured in Bahía Blanca.

Table 1 summarizes all data published for HCB and HCHs. For more than one sample, an average value and standard deviation is informed.

Although standardized and validated EPA methods were used in the current study, as in many other works previously published, data here presented need to be consciously interpreted, regarding on possible losses of the more volatile OCPs during the collecting process. On the one hand, it is a fact that PUF plugs are the most well-known gas-phase sorbents used for active air samplers since their development in the early 1970s, and they are still widely used (Lewis et al. 1977). On the other hand, the more recent studies report on the "breakthrough" process, which means that the most volatile portion of OCPs, such as HCB, could be lost during the sampling procedure if only one PUF plug is used to retain the sample. In the case of having to sequential PUFs, the portion lost in the former one is retained in the second, and the amount, quantified.

It is well known that breakthrough increases proportionally to both, OCP vapor pressure, and sampling temperature. That is why an underestimation of concentrations of more volatile OCPs appears when sampling is done by a long term or in warm air temperatures (Melymuk et al. 2014, 2016, 2017). In this work, volumes were taken in the range from 700 to 2000 m³. Nevertheless, being these volumes sampled in the range of 2 to 7 °C, it could reasonable be thought that the loss of HCB can be disregarded. This assumption would eventually lead to an underestimation of its concentration, although authors that have used the two PUF system recognized that the amount found in the second PUF due to the breakthrough of the first one, occurred in a "modest degree" (Bidleman and Tysklind 2018).

Endosulfan

From all OCPs measured in the present study, endosulfans showed the highest levels quantified. Concentrations ranged from 1.6 to 523.0 pg/m³ for Endo I; 1.5 to 101.0 pg/m³ for Endo II, and 2.0 to 15.5 pg/m³ for Endo sulfate. A strong north-south gradient, with maximum and minimum values of 624.0 and 5.9 pg/m³ (Mar del Plata, Argentina and Elephant Island, respectively) was found for ΣEndo (Endo I + Endo II + Endo sulfate), as seen on Fig. 4. The average ΣEndo levels at the Argentinian offshore was more than 30 times the values determined in the Antarctic region (average 5.9 pg/m³).

The ΣEndo values determined at the Argentinian offshore sites were the highest observed during the whole sampling campaign. Nevertheless, these values are low, compared to the ΣEndo concentration determined in the same zone (Bahia Blanca, Argentina), during the 3-month air sampling carried out in 2005 as part of the Global Atmospheric Passive Sampling (GAPS) Network (Pozo et al. 2009). The ΣEndo value in summer period determined by Pozo et al. and Tombesi et al. revealed concentrations in the order of ng/m³ with a strong influence of agricultural usage (Pozo et al. 2006;

Tombesi et al. 2014). These high concentrations make ΣEndo the single most abundant OCP in this area. Until government prohibition in 2013 (SENASA - Servicio Nacional de Sanidad y Calidad Agroalimentaria 2011), this site, considered as one of the most important agricultural sector of South America, employed endosulfan as pest control agent, mainly in potatoes, garlic, and soybean crops. Having been measured in air, it would be expected to have some correspondence in the other environmental compartments. In this sense, other studies revealed the presence of endosulfan in soil (Miglioranza et al. 2003) and water (Jergentz et al. 2005; Gonzalez et al. 2012), but no correlations were made up to today.

The ΣEndo contamination was originated from the agricultural areas in Argentina, as demonstrated by air mass backward trajectory modeling. A study of frequency of the intermediate positions of 48-h air mass back-trajectories was made in order to corroborate the influence of land emissions, using samples S10 and S11, represented for this purpose by their mean (39.80° S, 61.22° W) and (39.74° S, 61.10° W) locations (Fig. 5). As can be noted, both air masses sampled have passed previously through the agricultural area in the center of the province of Buenos Aires, Argentina. These analyses of air mass trajectories confirm that the concentrations measured respond to freshly land-emitted and volatilized OCP from contaminated soil during the warm season.

Despite the previously discussed values, a clear north-south concentration gradient was observed. The mean concentrations for Endo I and Endo II encountered in this study were 10.70 and 2.47 pg/m³ for the South Atlantic Ocean, 4.62 and 2.07 pg/m³ for the Drake Passage, and 2.63 and 3.28 pg/m³ for the Mar de la Flota/Bransfield Strait, respectively, which are in concordance with bibliographic data published previously.

Baek et al. reported results from an entire-year passive sampling monitoring. They reported a mean concentration of Endo I of 13.0 and 88.5 pg/m³ at 25 de Mayo/King George Island during 2006 and 2007, respectively (Baek et al. 2011). On the other hand, measurements at Palmer Station in 2010 by Khairy et al. gave an average value of 1.72 pg/m³ of Endo I. Beyond the uncertainty of reported values, a time-decrease trend can be noted, as a direct consequence of the worldwide restriction in the use of endosulfan in the past years.

Endo sulfate was measured in seven sampling sites out of the total 12. Nevertheless, the obtained values (Patagonian offshore, Ushuaia, Drake Passage and vicinity of Islas Orcadas) showed the correspondent north-south gradient, from 15.5 to 2.6 pg/m³ in agreement with the levels encountered for Endo I.

It is well known that the major metabolite of the oxidation process of both Endo I and II produces Endo sulfate, which is a stable substance with an environmental half-life longer than the parent isomers, as was found in several environmental compartments (Weber et al. 2010). The global distribution of endosulfan shows a relative abundance on the order of Endo I

Fig. 4 Endo I, Endo II, and Endo sulfate concentrations and latitudinal variation of Endo sulfate/(ΣEndo) ratio
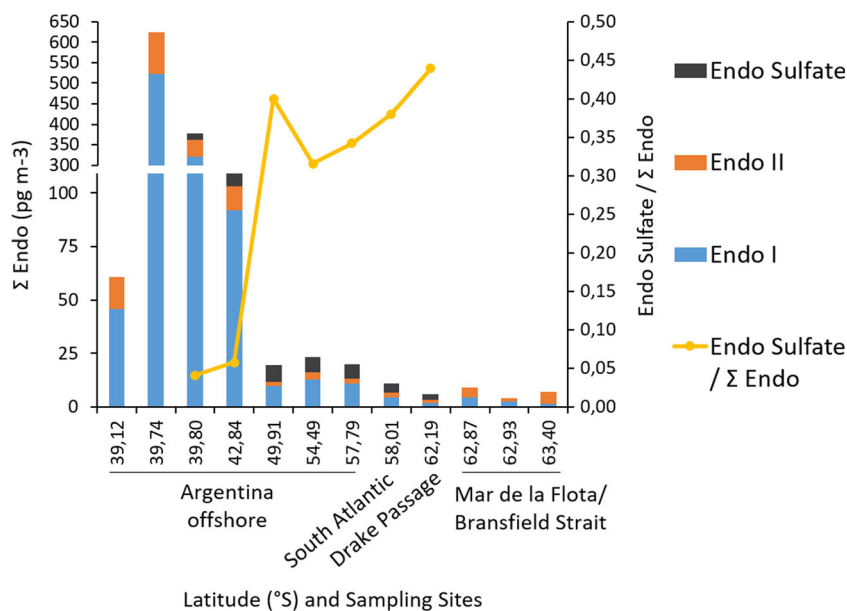
> Endo II > Endo sulfate. Hence, Endo sulfate/Σ Endo ratio gives a clear idea of the "age" of the encountered OCPs. In this way, when ΣEndo becomes the most important factor in the equation, small values of the mentioned ratio were encountered, indicating high abundance of fresh endosulfan (e.g., intense usage at the surrounding area), while an increasing ratio value is a consequence of degradation process over the long range transported molecules, being the Endo sulfate metabolite concentration higher than Endo I and II isomers. The obtained data showed values close to 0.45 in the proximity of the Islas Orcadas and Drake Passage, demonstrating remote emissions and confirming LRAT process of endosulfan and its related metabolites. On the other hand, values close to 0.05 at the offshore area of Bahia Blanca (Argentina)

demonstrating proximity to areas where direct and fresh applications were made.

An additional calculation can be made to presume the age of the endosulfan in the environment. Since Endo I is converted to the oxidized metabolite more readily than Endo II, in sites where fresh emissions were done, the Endo I/Endo II ratio will be higher than in sites where degradation process, due to a long-term presence, affected to the original mixture (Bussian et al. 2015). The following values were encountered at our sampling sites: 5.8 for the Argentina offshore sites, 4.3 for South Atlantic Ocean, 2.2 for the Drake Passage, and 0.8 for sites located at Mar de la Flota/Bransfield Strait. As was analyzed before, the presence of endosulfan at southern regions is due mainly to LRAT processes.
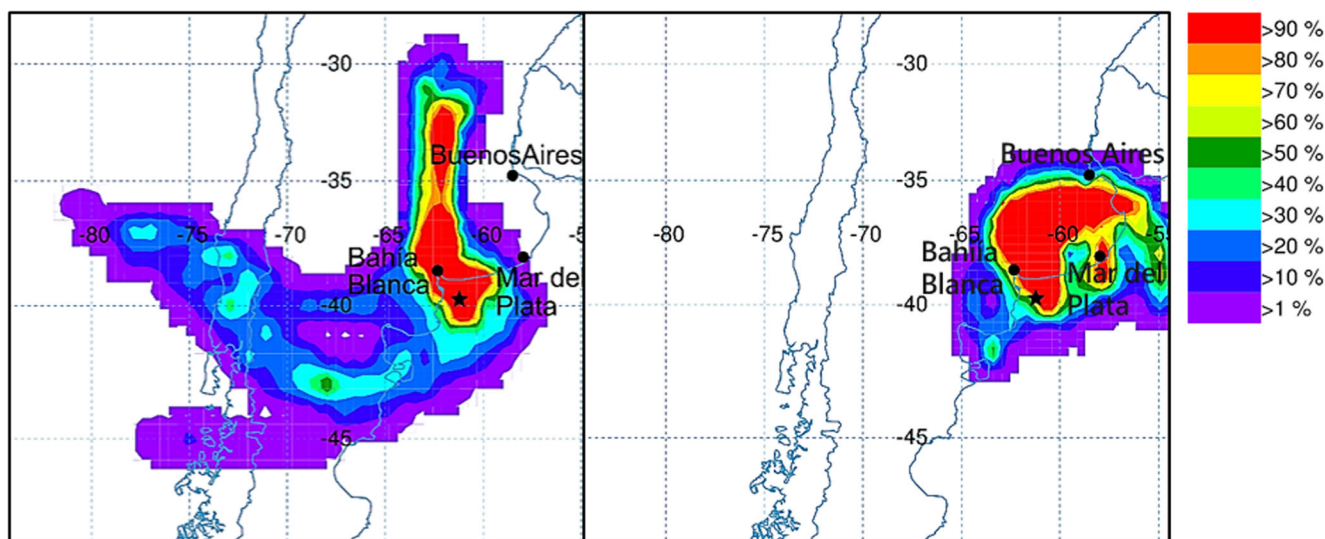

Fig. 5 Relative frequency of intermediate positions of air masses for 48-h back-trajectories before reaching measurement site close to Bahia Blanca. The star marks the average ship position

Conclusions

HCB, HCHs, and endosulfans were detected and quantified during a north-south transect from Mar del Plata (Argentina) and Palmer Archipelago, passing though South Orcadas Islands and Southern Ocean. LRAT seems to be the main input of those contaminants to the pristine environment of Antarctic region. Nevertheless, measured values show a decreasing trend over the past years as a consequence of the banning. However, further research is needed, as well as seasonal monitoring to assess the role of global distillation process and the impact of direct application of pest agents in the continental areas of South America, Africa, and Australia. This study also confirms that OCPs (in addition to others POPs) pollution refers to a global problem well beyond the local and regional problems in places which suffer high pollution episodes due to noncontrolled or illegal applications.

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