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Occurrence and diffusive air-seawater exchanges of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in Fildes Bay, King George Island, Antarctica

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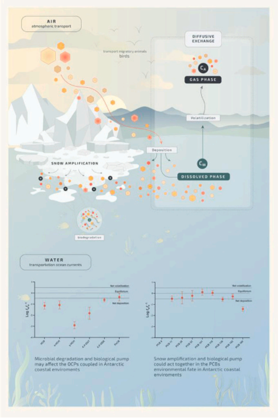
HIGHLIGHTS

- Organochlorine pesticides and polychlorinated biphenyls were analyzed in air and water in Fildes Bay, Antarctica.
- Air-water exchange direction was estimated in the studied area.
- Organochlorine pesticides presented air-to-water exchange direction during the sampling
- Polychlorinated biphenyls showed volatilization for PCB-9 and deposition for PCB-180.
- Biogeochemical processes involved in the POPs fate are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the levels of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in seawater and air, and the air-sea dynamics through diffusive exchange analysis in Fildes Bay, King George Island, Antarctica, between November 2019 and January 30, 2020. Hexachlorobenzene (HCB) was the most abundant compound in both air and seawater with concentrations around 39 ± 2.1 pg m^{-3} and 3.2 ± 2.4 pg L^{-1} respectively. The most abundant PCB congener was PCB 11, with a mean of 3.16 ± 3.7 pg m^{-3} in air and 2.0 ± 1.1 pg L^{-1} in seawater. The fugacity gradient estimated for the OCP compounds indicate a predominance of net atmospheric deposition for HCB, α-HCH, γ-HCH, 4,4′-DDT, 4,4′-DDE and close to equilibrium for the PeCB compound. The observed deposition of some OCs may be driven by high biodegradation rates and/or settling fluxes decreasing the concentration of these compounds in surface waters, which is supported by the capacity of microbial consortium to degrade some of these compounds. The estimated fugacity gradients for PCBs showed differences between congeners, with net volatilization predominating for PCB-9, a trend close to equilibrium for PCB congeners 11, 28, 52, 101, 118, 138, and 153, and deposition for PCB 180. Snow amplification may play an important role for less hydrophobic PCBs, with volatilization predominating after snow/glacier melting. As hydrophobicity increases, the biological pump decreases the concentration of PCBs in seawater, reversing the fugacity gradient to atmospheric deposition. This study highlights the potential impacts of climate change, through glacier retreat, on the biogeochemistry of POPs, remobilizing those compounds previously trapped within the cryosphere which in turn will transform the Antarctic cryosphere into a secondary source of the more volatile POPs in coastal areas, influenced by snow and ice melting.

1. Introduction

Persistent organic pollutants (POPs) are anthropogenic compounds, characterized by their low environmental degradation (Pennington, 2001) and their capacity to bioaccumulate in organisms and biomagnify through food webs (Fisk et al., 2001a, 2001b; Hop et al., 2002; Borgå and Di Guardo, 2005). Due to their semi-volatile nature, they are subject to long-range atmospheric transport (LRAT) through atmospheric transport and oceanic currents (Blais et al., 2007; Brown and Wania, 2008; Nash, 2011). In addition, due to their toxicity, they are harmful to wildlife and human health (Bourgeon et al., 2012; Brown et al., 2014). Some POPs are currently regulated internationally by the Stockholm Convention that aims to reduce and eliminate emissions to the atmosphere (UNECE, 1998; UNEP, 2006; Denison, 2013).

Studies on POPs reveal that these compounds reach the Antarctic continent mainly through LRAT (Blais et al., 2007; Brown and Wania, 2008; Nash, 2011; Jurado and Dachs, 2008). However, other vectors are able to transport these substances to Antarctica, such as ocean currents despite the Antarctic Circumpolar Current that acts as a barrier limiting their transport (Nash et al., 2010), and to a lesser extent migratory biota (Braune et al., 2005; Wild et al., 2022). In addition, local sources of POPs (e.g., PCBs and HCB) have also been reported nearby research stations and tourist access points (Risebrough et al., 1990; Larsson et al., 1992; Hale et al., 2008; Corsolini et al., 2021), although these levels tend to have a limited impact, mainly during summer season, contributing to an increase in ambient levels of POPs.

Low ambient temperatures in Antarctica play an essential role in the biogeochemical cycles of POPs, generating an increased partitioning of POPs from the atmosphere to seawater, soils, and snow, a process known as “cold trapping” (Wania and Mackay, 1996; Casal et al., 2019). In this context, polar regions act as a net sink for most of the studied compounds, where an imbalance of diffusive air-seawater exchanges has been registered with net deposition dominating over volatilization (Mackay and Wania, 1995; Kallenborn et al., 1998; Dickhut et al., 2005; Cincinelli et al., 2009; Baek et al., 2011; Cabrerizo et al., 2017; Galbán-Malagón et al., 2012, 2013a, 2013c; Montone et al., 2013). The direction of the air-seawater exchange depends mainly on sea-water temperature (Mackay and Wania, 1995) and dissolved-phase POP concentration (Achman et al., 1993; Swackhamer and Armstrong, 1987; Stange and Swackhamer, 1994; Dachs et al., 1999). Sea-water concentration of POPs is strongly influenced by biogeochemical processes, which affect POPs cycles and thus their occurrence in aquatic systems (Dachs et al., 1999; Nizzetto et al., 2010; Galbán-Malagón et al., 2012; Lammel et al., 2016; Tao et al., 2018). In this sense, Galbán-Malagón et al. (2013c) showed that organic matter sedimentation fluxes, a.k.a. the biological pump, decrease the concentrations of more hydrophobic POPs (i.e., Log $K_{OW} > 6.5$) from surface waters with higher primary productivity. Whereas, for those compounds with lower hydrophobicity (i.e., lower Log $K_{OW} < 6.5$), microbial degradation may play an essential role in the depletion of POPs in aquatic environments while the biological pump may also contribute but to a lesser extent (Berrojalbiz et al., 2011; Luarte et al., 2022). However, recorded patterns will most likely be affected due to rising temperatures caused by climate change and the remobilization of compounds, as recently observed in the Arctic (Hung et al., 2022). In this scenario, POPs that were trapped for decades in water, ice, and soil will start to volatilize, generating a secondary source of these compounds (Nizzetto et al., 2010; Ma et al., 2011; Cabrerizo et al., 2013; Hung et al., 2022). In Antarctica these secondary sources may lead to a re-exposure of local biota to POPs, especially in organisms with lipid-rich diets and higher trophic positions since both features imply a higher risk of accumulating toxic concentrations of POPs (Nash, 2011; Zhang et al., 2013; Vergara et al., 2019; Garcia-Cegarra et al., 2021). Some studies have addressed the potential negative consequences of POP accumulation, such as decrease and changes in the diversity of phytoplankton species (Echeveste et al., 2016), and negative effects during the developmental stages of krill species (Poulsen et al., 2011). In consequence, POP accumulation might affect eggshell thickness and therefore the reproductive potential of seabirds (Fossi and Panti, 2017), disruption of hemoglobin metabolism and therefore the diving capacity of penguins (Rudolph et al., 2016). These effects highlight the importance of studying the behaviour of legacy POPs in polar areas to better project their future dynamics and inform management strategies to limit the detrimental consequences to polar ecosystems.

Among legacy POPs, polychlorinated biphenyls (PCBs) and organochlorine compounds, such as hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB), have often been studied as model compounds to understand the environmental fate, as well as the biogeochemical cycling of POPs in polar regions (Nash, 2011; Galbán-Malagón et al., 2013b, 2013c, 2013d; Bigot et al., 2016; Wagner et al., 2019; Casal et al., 2019). Thus, the main objectives of the present study were i) determine the levels of POPs present in seawater and air, ii) elucidate the air-seawater exchanges using the fugacity ratio between the air and water iii) evaluate the different biogeochemical processes that may influence the dynamics of the studied compounds.

2. Materials and methods

2.1. Air and seawater sampling

We collected 25 air samples and 12 seawater samples periodically from November 30th (2019) to January 30th (2020) at Fildes Bay ("Base Escudero" 62°20′S, 58°23′W), in King George Island, South Shetlands Archipelago, Antarctica (Fig. 1, Table S1). Atmospheric samples were collected using a high-volume air sampler (device model: MCV: CAV-A/HF, Collbató, Spain), with an approximate volume of 1000 m^3 per sample. The high-volume sampler separates aerosols by filtering the air through a quartz microfiber filter (QMA 203 × 254 mm, 1-μm nominal pore size, Whatman International Ltd., Maidstone, England), while gas-phase POPs are retained on a polyurethane foam plug (PUF, 100 mm diameter×120 mm, Klaus Ziemer GmbH, Germany). Samples were

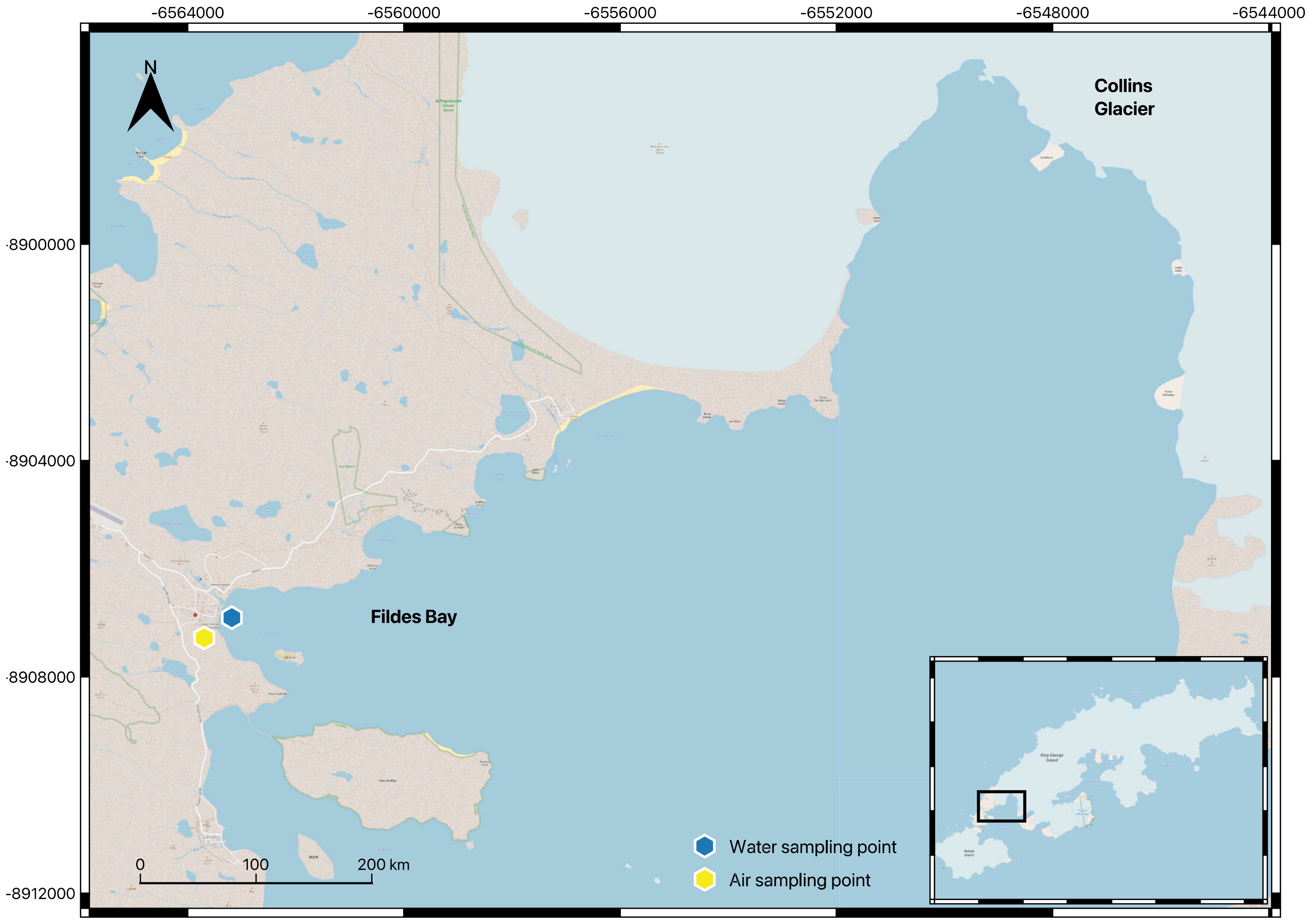

Fig. 1. Map of the air-water sampling points used in this study in Fildes Bay, King George Island, Antarctica.

collected at a flow rate of 40 m^3 h^{-1}. This sampling methodology has been previously described and widely used in remote and pristine environments (Nizzetto et al., 2012; Galbán-Malagón et al., 2012; Cabrerizo et al., 2014; Tucca et al., 2020; Luarte et al., 2022), presenting adequate performance. In parallel, seawater samples were obtained directly from the bay at 5 m depth using a water pumping system. For each sample, a volume of ~200 L (see Table S2 for details) passed through a filter holder equipped with a GF/F filter (142 mm diameter, 0.7 μm pore size, Whatman), and then into a stainless-steel column containing XAD-2 resin (SUPELCO). This procedure was carried out at a speed of 0.4 L min^{-1}, which has been shown to prevent the breakthrough of POPs in the dissolved phase (Berrojalbiz et al., 2011; Galbán-Malagón et al., 2013b; Luarte et al., 2022). After sampling, the air and seawater samples collected were kept at 4 °C and − 20 °C, respectively, until their subsequent extraction and instrumental analysis. Only the PUFs and the XAD samples were analysed for the present study.

2.2. Sample preparation and instrumental analysis

Before chemical analysis, samples were spiked with PCBs and OCPs isotope labelled standards (13C6: γ-HCH, PeCB, HCB, 13C12: p,p′-DDT, p,p′-DDD, p,p′-DDE, PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180, Cambridge Isotope Laboratories, MA, USA). Subsequently, air gas phase samples were extracted using a Soxhlet system (Büchi System B-811 automatic extractor) PUF samples for 24 h with hexane:acetone (1:1, v/v). XAD-2 samples were air-dried first, then extracted 3 × 15 min with 3 × 120 mL of DCM. All extracts were preconcentrated to 10 mL under gentle stream of nitrogen, using a LabEva concentrator and then divided into fractions (10 % and 90 %) by weighing on KERN weighing scales. A total of 90 % fractions of extracts for PCBs and OCPs analysis were cleaned using destructive acidic-silica gel glass column, containing 1 g of activated silica gel, 8 g of 44 % H_2SO_4 silica gel, 1 g of deactivated silica gel and 1 cm of anhydrous Na_2SO_4, eluted with 40 mL of hexane/dichloromethane 1:1. A volume of 50 μL of nonane was added to eluates as a keeper solvent and samples were concentrated in LabEva to final volume of 50 μL. Instrumental analysis samples were spiked with $^{13}C_{12}$-PCB95 syringe standard for determination of % recovery of surrogate (internal) standards.

PCBs and OCPs were analysed on 8890 GC (Agilent Technologies, USA) equipped with a 60 m × 0.25 mm × 0.25 μm Rxi-5Sil-MS column (Restek, FR) coupled to a 7000D tandem mass spectrometry (MS/MS; Agilent, USA) operated in electron ionization mode at 70 eV. The GC temperature program was 80 °C (1.5 min hold), then 40 °C min^{-1} to 200 °C (18 min hold), and finally 5 °C min^{-1} to 305 °C. Inlet temperature was 280 °C. Injection volume was 3 μL in splitless mode. Carrier gas was helium with flow rate of 1.5 mL min^{-1}. Temperature of the transfer line was 310 °C and 250 °C of the ion source. Mass spectrometer was operating in multiple reaction monitoring (MRM) mode with nitrogen as collision gas with flow rate of 1.5 mL min^{-1}.

The target compounds were PCBs (PCB9, PCB11, PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, and PCB180), HCHs (α-HCH, β-HCH, and γ-HCH), DDTs (p,p′-DDE, p,p′-DDD, p,p′-DDT, o,p′-DDE, o,p′-DDD, and o,p′-DDE), and hexachlorobenzene (HCB) and pentachlorobenzene (PeCB). PCBs and OCPs were quantified with an external calibration of eight points with concentration from 1 ng mL^{-1} to 1000 ng mL^{-1} and linearity was maintained in the whole range. Native PCBs and OCPs were quantified using surrogate (internal) standards (isotope-dilution method).

2.3. Quality assurance and quality control (QA/QC)

To avoid traces of POPs, prior to sampling, the PUFs were extracted with hexane:acetone (1:1) for 48 h, packed in aluminium foil and dried under vacuum in desiccators, and finally stored in double sealed plastic bags, until their subsequent use in the field. The QMA filters were packed in aluminium foil, burned at 450 °C for 4 h, and kept in sealed plastic bags. Nitrile gloves and tweezers previously cleaned with acetone were used to handle the PUFs and QMA filters. Meanwhile, the XAD inside the column was pre-cleaned with dichloromethane:hexane (3:1) and subsequently kept cold (−4 °C) with 200 mL of methanol. Recoveries of the studied compounds averaged 73.2 ± 18.7 % for PUFs while in the case of XAD recovery averaged 69.2 ± 18.9 %. All the compounds were corrected by recoveries average % obtained by multiplying each compound x 100 and dividing by the average recovery 73.2 and 69.2 respectively.

For blank collection, PUF was placed on the head of the high-volume sampler used for sampling for 1 min for every ten samples. Two XAD column was also used for water filtration placing the column during 20 min in the sampling device. Subsequently, one blank per 10 samples was extracted and analysed using the methodology described above. All blanks analysed yielded levels below the detection limit for all compounds. Limits of quantification (LOQ) were calculated from the lowest calibration point as a quantity yielding signal to noise S S/N = 10 (LOQ) (Table S8).

2.4. Diffusive air-seawater exchange

To calculate the air-seawater diffusive exchange, first we estimated the freely dissolved concentration (C_{TD}) in water following the methodology used in previous studies (Totten et al., 2001; Rowe et al., 2007; García-Flor et al., 2005; Nizzetto et al., 2011; Galbán-Malagón et al., 2013b; Luarte et al., 2022), with Eq. (1):

$$C_{TD} = \frac{C_W}{1 + 10^{-9} \bullet Kow\ DOC} \tag{1}$$

where C_W is the POP concentration measured in water (pg L^{-1}) and K_{OW} is the octanol-water partition constant, dissolved organic carbon (DOC) in mg L^{-1}, and the octanol-water partition coefficient (K_{OW}) corrected for temperature (see text S1; García-Flor et al., 2005). For DOC we used a concentration of 0.7 mg L^{-1}, following previous studies in the same area (e.g. Doval et al., 2002; Galbán-Malagón et al., 2013b). The 10^{-9} correction factor is for transforming units from mg to pg.

The net direction of air-seawater exchange was determined using the air-seawater fugacity ratio ($f_w\, f_a^{-1}$) as follows (Eq. (2)):

$$\frac{f_w}{fa} = \frac{C_{TD}\, H'}{C_G} \tag{2}$$

where C_{TD} is the concentration of freely dissolved POPs in seawater (pg m^{-3}, see below), C_G is the gas-phase POP concentration (pg m^{-3}), and H′ is Henry's law constant, dimensionless and corrected for salinity and temperature. For the latter, the enthalpy of phase change (ΔU_{AW}) was used for each POP. In contrast, for the salinity correction the constant 1.3 was used as a correction factor to account for the effect of salinity on the solubility of POPs in seawater (for more details, see text S2). In the case of C_G and C_{TD} concentrations lower than LOQ but higher than LOD, we used the LOQ divided by two to estimate fugacity gradient using a similar approach C_{TD}.

Due to uncertainties in air-seawater partition coefficients such as C_G, C_{TD} and H' (Bruhn et al., 2003), logarithm-transformed $f_w f_a^{-1}$ was used to indicate if the compounds are close to air-seawater equilibrium (Galbán-Malagón et al., 2013b). Values of fugacity ratios higher than 0.5 and lower than −0.5 indicate that the net direction of air-seawater exchange are net volatilization and net deposition, respectively. Values between −0.5 and 0.5 are within the range of uncertainty implying that the net exchange is negligible due to close equilibrium between air and seawater.

2.5. Microbial degradation

To evaluate the effect of microorganisms in the water column on the concentration of POPs, biodegradation losses (F_{DegM}, ng m^{-2} d^{-1}) were estimated following Eq. (3) used by Galbán-Malagón et al. (2013c) and Luarte et al. (2022):

$$F_{DegM} = h \times k_{DegM} \times C_{TD} \tag{3}$$

where, h is the depth within the water column (~5 m), k_{DegM} is the degradation constant rate in water (d^{-1}) derived from microbial degradation reported half-lives in surface waters (see Table S5), which was calculated from the microbial degradation half-life in seawater for each compound following the methodology used by Luarte et al. (2022; see also Table S5).

3. Results and discussion

3.1. Atmospheric levels of target OCPs and PCBs

The atmospheric levels for OCPs (HCB, α -HCH, γ-HCH, 4,4′-DDT, 4,4′-DDE and PeCB) in this study ranged from 0.07 to 42.3 pg m^{-3}. The mean concentrations (±SD) of the target OCP isomers decreased in the following order: HCB (39 ± 2.1 pg m^{-3}) > PeCB (7.2 ± 1 pg m^{-3}) > γ-HCH (0.6 ± 0.6 pg m^{-3}) > 4,4′-DDT (0.3 ± 0.6 pg m^{-3}) > 4,4′-DDE (0.2 ± 0.7 pg m^{-3}) > α-HCH (0.1 ± 0.03 pg m^{-3}) (Fig. 2A). The high atmospheric levels of HCB accounted for 82 % of total OCPs and 74 % of total target POPs in the present study. Similarly, HCB has been reported by other authors as the most abundant OCP, and even the most abundant POP. In Antarctic regions, HCB has been detected most frequently in the atmosphere (Kallenborn et al., 2013; Wang et al., 2018; Hao et al., 2019; Wu et al., 2020). The HCB levels detected in this study are lower than those reported by Bidleman et al. (1993) in East Antarctica and Hao et al. (2019) on King George Island. In turn, HCB levels are higher than the concentrations reported by Montone et al. (2005) on Ross Island, Gambaro et al. (2005) and Cincinelli et al. (2009) in Terra Nova Bay, Dickhut et al. (2005), in the Antarctic Plateau (Cabrerizo et al., 2017), and in Antarctica marginal seas (Wu et al., 2020) (Table 1). Moreover, some studies have also reported HCB levels within a similar range to the atmospheric levels reported by Kallenborn et al. (1998) in Signy Island (South Orkney Islands), Galbán-Malagón et al. (2013b) in Bellinghausen Sea, Kallenborn et al. (2013) in Troll Station and Queen Maud Land and Pozo et al. (2017) in the Ross Sea (Table 1).

On the other hand, the levels of $\sum_2$HCHs are well below the levels previously reported by Tanabe et al. (1982) in the Southern Ocean and Kallenborn et al. (1998) in Newfoundland Bay (Table 1), and are within the range reported by more recent studies conducted in the Southern Ocean, Ross Sea, King George Island, and in the Antarctic marginal seas (Bigot et al., 2016; Pozo et al., 2017; Hao et al., 2019; Wu et al., 2020) (Table 1). This could be interpreted as a decreasing trend in the atmospheric levels of these compounds compared with previous decades (1980–2018; Tanabe et al., 1982, 1983; Bidleman et al., 1993; Kallenborn et al., 1998; Jantunen et al., 2004; Montone et al., 2005; Dickhut et al., 2005; Gambaro et al., 2005; Cincinelli et al., 2009; Baek et al., 2011; Galbán-Malagón et al., 2013b; Khairy et al., 2016; Kallenborn et al., 2013; Pozo et al., 2017; Cabrerizo et al., 2017; Bigot et al., 2016; Hao et al., 2019; Wu et al., 2020; Luarte et al., 2023). The recorded levels of the 4,4′-DDT and 4,4′-DDE isomers are in the same range of those reported by Bidleman et al. (1993), Kallenborn et al. (1998), Pozo et al. (2017), Wu et al. (2020) and Hao et al. (2019) (Table 1).

Air concentrations of $\sum_9$PCBs (PCBs 9, 11, 28, 52, 101, 118, 138, 153 and 180) ranged from 1.6 to 20.7 pg m^{-3}; mean concentrations

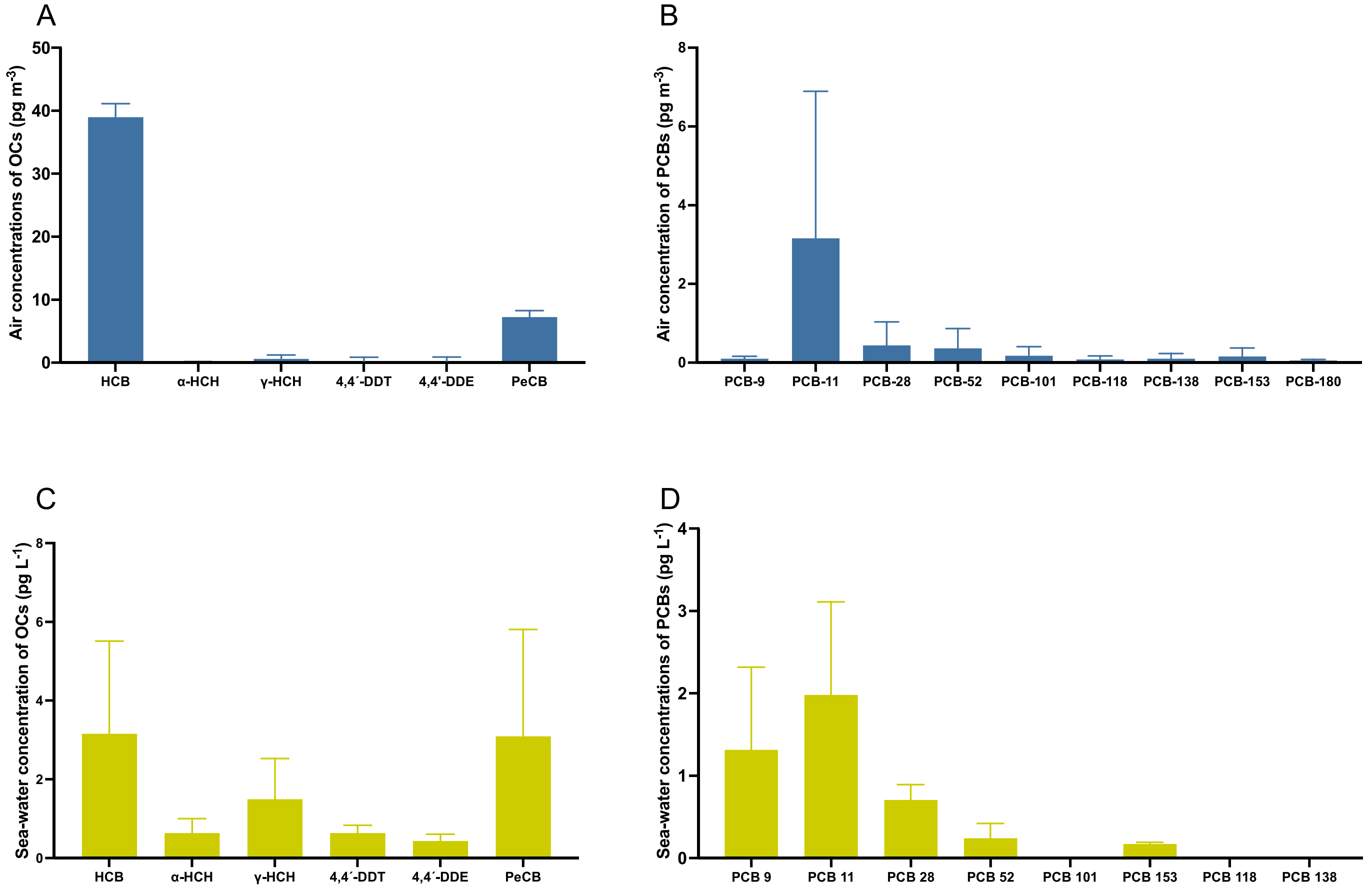

Fig. 2. Atmospheric (A & B) and water (C & D) concentrations of recorded POPs. An air concentration of OCs (pg m^{-3}), B air concentration of PCBs (pg m^{-3}), C seawater concentration of OCs (pg L^{-1}), and D seawater concentration of PCBs (pg L^{-1}).

Table 1
HCB and HCHs levels (pg m^{-3}) in Antarctic atmosphere. $\sum$n indicates the number of isomers included in the study.

Sampling area	Year	HCB	a-HCH	y-HCH	$\sum$HCHs	4,4-DDE	4,4 DDT	Reference
Queen Maud land	1980–1981				90–170			Tanabe et al., 1982
Queen Maud land	1981–1982				44–170			Tanabe et al., 1983
Cape town and Newmayer Station	1999		0.36	0.15				Lakaschus et al., 2002
Ross Island	1988–1999			25.8 (0.5–118)		1	2	Larsson et al., 1992
East Antarctica	1990	62.6 (40–78)	3.2 (2.8–3.6)	2.4 (1.1–5.6)	5.7			Bidleman et al., 1993
Signy Island	1994–1995		2.8	21.8	26.97	0.4	0.2	Kallenborn et al., 1998
East Antarctica	1997–1998		1.06 (0.81–1.4)					Jantunen et al., 2004
Terranova bay	1993	21 (nd–28)			13 (5–20.0)			Kallenborn et al., 1998
Ross Island	1995	(<0.6–25.3)			3.9–32.5	9.2	8.1	Montone et al., 2005
West of the Antarctic Peninsula and southwest of Adelaide Island	2001–2002	19.4 (<5–32.1)	0.3 (<0.05–0.52)	0.755 (<0.02–2.98)				Dickhut et al., 2005
Terra Nova Bay	2003–2004	11.4 (6.0–20)			0.8 (0.3–1.2)			Gambaro et al., 2005
Terra Nova Bay	2003–2004	11.4 (5.93–20.4)			0.22 (0.1–0.35)			Cincinelli et al., 2009
Ny-Ålesund, King George Island, and Chuuk	2005–2009							Baek et al., 2011
South Scotia Sea	2008	8.1 (2.18–15.82)	1.7(0.06–5.84)	4.6 (1.5–7.1)				Galbán-Malagón et al., 2013b
Wedell	2009	19.5 (2.4–30.1)	0.16 (0.05–2.09)	0.84 (0.1–1.87)				Galbán-Malagón et al., 2013b
Bransfield sea	2009	16.7 (3.3–34.24)	0.14 (0.04–0.46)	1.15 (0.2–3)				Galbán-Malagón et al., 2013b
Bellingshausen	2009	42.9 (27.31–49.71)	0.26 (0.22–0.16)	0.14 (0.07–0.19)				Galbán-Malagón et al., 2013b
Palmer station	2010	34 (26.2–37.7)	0.81–1.68	0.87–2.31				Khairy et al., 2016
Station troll/Queen Maud Land	2010	22.9						Kallenborn et al., 2013
Ross Sea	2010–2011	22.8 (0.8–50)	0.5 (nd–0.5)	nd	0.5 (nd–0.5)			Pozo et al., 2017
Antarctic Plateau	2011	(0.67–2.7)		BD-2.7				Cabrerizo et al., 2017
Antarctic marginal seas	2013–2014	2.6 (0.081–10)			(nd–6.8)	0.35	0.12	Wu et al., 2020
Southern Ocean between Australia and Antarctica	2014	(<22–35)	<0.13–1.1	<0.70–4.3	nd–3.65	<0.15–0.44	<7,8	Bigot et al., 2016
King George Island	2012–2018	163 (99.2–252)	1.4 (0.5–13.6)	0.1–7.9	0.7–22.3	0.6	0.24	Hao et al., 2019
Fildes Bay	2019–2020	39 (34.5–42.3)	0.12 (0.08–0.2)	0.6 (0.3–3.4)	0.7 (0.4–3.5)			This study

decreased following the order: PCB 11 (3.16 ± 3.7 pg m^{-3}) > PCB 28 (0.44 ± 0.6 pg m^{-3}) > PCB 52 (0.37 ± 0.5 pg m^{-3}) > PCB 101 (0.18 ± 0.2 pg m^{-3}) > PCB 153 (0.16 ± 1.1 pg m^{-3}) > PCB 138 (0.1 ± 0.1 pg m^{-3}) > PCB 9 (0.1 ± 0.06 pg m^{-3}) > PCB 118 (0.08 ± 0.09 pg m^{-3}) > PCB 180 (0.05 ± 0.04 pg m^{-3}) (Fig. 2B). The most abundant congener in the air was PCB 11 representing 68 % of the total atmospheric PCBs in the study site. Our results agree with those reported on previous studies (Choi et al., 2008; Baek et al., 2011; Li et al., 2012a, 2012b; Wang et al., 2017), showing high levels of PCB-11 as the most abundant congener present in the atmosphere over King George Island. This compound's primary source is from pigments, especially diarylide yellow (Rodenburg et al., 2010; Shang et al., 2014). Considering the high values of the PCB 11 reported in this and other studies, further studies are required to report its source and toxicity. Nevertheless, the more volatile POPs are those showing higher snow-melt air fugacity rations (Casal et al., 2019), and thus the higher predominance of PCB 11 is consistent with remobilization of legacy reservoirs (see below). On the other hand, the concentrations of 7 indicator PCBs (PCB 28, 52, 101, 118, 138, 153, and 180) ranged from 0.4 to 9.9 pg m^{-3}, which concurs with previous reports in the Antarctic atmosphere by Kallenborn et al. (1998), Li et al. (2012a, 2012b), Pozo et al. (2017) and Wang et al. (2015, 2017), and lower for the levels reported by Larsson et al. (1992), Montone et al. (2001, 2003), Baek et al. (2011), Khairy et al. (2016), Galbán-Malagón et al. (2013c), Wang et al. (2017), and Hao et al. (2019) (Table 2).

3.2. *Concentrations of target OCPs and PCBs in seawater*

The levels recorded in surface waters of OCPs (HCB, α-HCH, γ-HCH, 4,4′-DDT, 4,4′-DDE and PeCB) ranged from 0.2 to 8.33 pg L^{-1}, where the HCB isomer showed the highest concentrations (3.2 ± 2.4 pg L^{-1}) followed by PeCB (3.1 ± 2.7 pg L^{-1}), and γ-HCH (1.5 ± 1.0 pg L^{-1}) (Fig. 2C), which represented 28 %, 27 % and, 13 % of the total OCPs in seawater, respectively. The seawater levels reported for the α -HCH, 4,4′-DDT and 4,4′-DDE isomers in this study did not exceed 0.6 pg L^{-1}(Fig. 2C). HCB concentrations are in the range reported in Antarctic seawater by other studies conducted in the Wedell Sea, Bransfield Strait, Bellinghausen Sea, South Scotia Sea (Galbán-Malagón et al., 2013b), and relatively lower than those reported near Ross Island (Cincinelli et al., 2009), and Dronning Maud land (Bigot et al., 2016) (Table 3). The levels of HCHs and DDTs isomers are in a similar range to those reported in different areas of Antarctica (see Table 3).

The $\sum_9$PCBs concentrations (PCBs 9, 11, 28, 52, 101, 118, 138, 153 and 180) ranged 0.09–1.6 pg L^{-1}. The highest mean concentration recorded in surface water was 2.0 ± 1.1 pg L^{-1} for PCB 11, followed by 1.3 ± 1.0 pg L^{-1} for PCB 9 and 0.7 ± 0.2 pg L^{-1} for PCB 28 (Fig. 2D), which represented, respectively, 45 %, 29 % and 15 % of the total PCBs present in surface seawater. PCB congeners 52 and 153 displayed lower mean concentrations of 0.06 ± 0.04 and, 0.04 ± 0.0004 pg L^{-1}, respectively (Fig. 2D). The other target PCB concentrations in this study

Table 2
PCBs levels (pg m^{-3}) in Antarctic atmosphere. ∑n indicates the number of congeners included in the study.

Sampling area	Year	∑PCBs	∑n	Reference
Ross Island	1988–1990	15.2	6	Larsson et al., 1992
King George Island	1993–1994	20.8 (12.09–42.8)	10	Montone et al., 2001
Signy Island	1994–1995	(0.01–17.2)	22	Kallenborn et al., 1998
Ross Island	1995	62.4	11	Montone et al., 2005
King George Island	1996–1996	37.4 (12.1–92.6)	10	Montone et al., 2003
Terra Nova Bay	2003–2004	1.06 (0.61–1.78)	61	Gambaro et al., 2005
Ny-Ålesund, King George Island, and Chuuk	2005–2009	60.3(22.8–87.1)	11	Baek et al., 2011
Ny-Ålesund, King George Island, and Chuuk	2005–2009	19.8 (11.1–31.9)	205	Baek et al., 2011
ICEPOS	2005	16.84 (7.12–25.65)	25	Galbán-Malagón et al., 2013c
South Scotia Sea	2008	45.13 (6.2–78.9)	25	Galbán-Malagón et al., 2013c
Antarctic peninsula	2009	12.13 (1.8–38.1)	25	Galbán-Malagón et al., 2013c
Polish beach	2009	(2.1–3.1)	25	Galbán-Malagón et al., 2013c
Livingston Island	2009	7.23 (3.5 12.9)	25	Galbán-Malagón et al., 2013c
King George Island	2009–2010	1.142	7	Li et al., 2012a
King George Island	2009–2010	36.837	19	Li et al., 2012b
King George Island, Antarctica.	2009–2010	4.34	7	Li et al., 2012b
Station troll/Queen Maud Land	2010	0.5	32	Kallenborn et al., 2013
Palmer station	2010	12	29	Khairy et al., 2016
Ross Sea	2010–2011	0.46 (0.14–1.13)	7	Pozo et al., 2017
Antarctic Plateau	2011	(0.8–27)	26	Cabrerizo et al., 2017
King George Island	2011–2014	5.39 (0.91–35.9)	7	Wang et al., 2017
King George Island	2011–2014	5.87–72.7 (26.1)	20	Wang et al., 2017
King George Island	2010–2018	10.4 (1.5–29.7)	19	Hao et al., 2019
Antarctic marginal seas	2013–2014	1.1 (nd–6.7)	14	Wu et al., 2020
King George Island and Ardley Island		0.078 (nd–0.137)	6	Wang et al., 2015
Fildes Bay	2019–2020	1.3 (0.4–9.6)	7	This study
Fildes Bay	2019–2020	4.6 (1.6–30.7)	9	This study

(PCBs 101, 118, 138 and 180) were below the quantification limit (Table S7). The values of $\sum_9$PCBs in surface seawater were similar to values reported in Wedell Sea, Bransfield Strait, Bellinghausen Sea, and South Scotia Sea (Galbán-Malagón et al., 2013c) and well below the levels reported in Terranova Bay (Fuoco et al., 2005), Ross Sea (Fuoco et al., 2009) and the Fildes Peninsula (Zhang et al., 2016, and Gao et al., 2018) (Table 3).

It is important to note that PCB 11 was the congener with the highest concentrations in the atmosphere and seawater. However, to our knowledge, prior studies on this compound only analysed air samples (see above), and there are no records of PCB11 levels in aquatic systems, but as noted above, this is consistent with the amplification potential of snow reservoirs of POPs.

3.3. Diffusive air-sea exchange

Estimation of fugacity ratios (log $fwfa^{-1}$) performed for OCP isomers revealed a predominance of net atmospheric deposition for HCB, α-HCH, γ-HCH, 4,4′-DDT, 4,4′-DDE isomers (Fig. 3A). In contrast, PeCB was close to equilibrium between atmospheric and surface water levels (Fig. 3A). The air-seawater imbalance reported in this study for HCHs has been widely reported in other studies conducted in the Southern Ocean, which concurs with our study, showing atmospheric deposition of α-HCH and γ-HCH (Galbán-Malagón et al., 2013b; Dickhut et al., 2005; Xie et al., 2011; Cincinelli et al., 2009; Bigot et al., 2016; Casal et al., 2019). On the other hand, we found net deposition for HCB similarly to what was reported in previous studies (Galbán-Malagón et al., 2013b; Dickhut et al., 2005). However, it was also found that HCB was close to equilibrium in other areas like the Ross Sea (Cincinelli et al., 2009). To our knowledge, no air-seawater fugacity relationships have been reported for DDT and PeCB in the Southern Ocean. However, for DDT isomers, atmospheric deposition has been reported from Izmir Bay, Turkey (Odabasi et al., 2008), the Great Lakes, Canada and the United States (Khairy et al., 2014), concurring with our results.

The estimated log $f_W f_a^{-1}$ for PCBs showed differences between congeners, with a predominance of net volatilization from surface waters to the atmosphere for PCB 9 (Fig. 3B). Whereas a trend close to equilibrium was observed for PCB congeners 28, 52, 101, 118, 138, and 153 (Fig. 3B). Finally, PCB 180 showed a predominance of net deposition (Fig. 3B). Previous studies in Antarctica showed that atmospheric deposition dominates over PCB volatilization in open waters of the Southern Ocean (Galbán-Malagón et al., 2013c), while in coastal areas, volatilization is the dominant process (Casal et al., 2019). The air-seawater imbalances documented in this study can be related to biotic and abiotic factors interacting with snow-melt sources, as described below.

3.4. Factors associated with air-water disequilibrium

In the case of the organochlorine pesticides, imbalances between air and water has been described in different areas of Antarctica due to different biogeochemical processes affecting pesticide concentrations in seawater. In this sense, the two main responsible processes are degradation (biological or chemical) and the sequestration of pollutants to deep waters by the biological pump, including their incorporation into the trophic web, as evidenced by high levels of it recorded in phytoplankton, krill, marine birds, and marine mammals (Nash, 2011; Echeveste et al., 2016; Poulsen et al., 2011; Rudolph et al., 2016; Vergara et al., 2019). The degradation processes, in surface waters, include the basic hydrolysis and microbial degradation. In the case of Antarctic coastal waters, the pH ranged from 7.9 to 8.3, which could enhance the hydrolytic degradation pathway (Kapsenberg et al., 2015). However, this pathway has been proven to be a minor degradation pathway in Antarctic waters (Galbán-Malagón et al., 2013b, 2013d), as well as in other places, e.g., The Great Lakes (Bidleman et al., 2021). The microbial degradation pathway is carried out by microbial communities and could affect the levels of HCHs in water. Degradation by microbes may result in relatively low levels of OCs in seawater (Bigot et al., 2016). This has been suggested as an important pathway in the case of HCHs in Antarctic and Arctic surface waters (Galbán-Malagón et al., 2013b, 2013d; Hung et al., 2022) and the Great Lakes (Bidleman et al., 2021). Our estimations of biodegradation fluxes due to microbial activity in Fildes Bay ranged from 5.9 to 0.3 ng m^{-2} d^{-1} for the studied compounds (Table S9). Microbial degradation of HCHs in water would increase air to water exchange. We speculate that microbial biodegradation processes may play a key role in the net deposition recorded for the analysed HCHs,

Table 3

OCPs (organochlorine pesticides) and PCBs levels (pg L^{-1}) in Antarctic water. $\sum$n indicates the number of congeners included in the study.

Sampling area	Year	HCB	α-HCH	γ-HCH	ΣHCHs	4,4′-DDT	4,4DDE	$\sum_n$PCBs	Reference
Terranova Bay	1997–1998							(30–120)	Fuoco et al., 2005
Ross Sea	1997–2003							50	Fuoco et al., 2009
Ross Sea	2003–2004	11.4 (5.9–20.4)	0.2 (0.1–0.4)	0.56 (0.2–1.1)					Cincinelli et al., 2009
Wedell	2009	0.97 (0.4–1.6)	0.26 (0.2–0.3)	1.0 (0.4–1.7)	6.3 (1.3–11.5)			1.4 (1.3–1.5)	Galbán-Malagón et al., 2013b
Bransfiel	2009	0.4 (0.2–0.6)	0.2 (0.09–0.3)	0.4 (0.3–0.8)	1.5 (1.3–12.3)			1.2 (1.2–1.5)	Galbán-Malagón et al., 2013b
Bellinghausen	2009	0.3 (0.2–0.3)	0.2 (0.1–0.3)	0.8 (0.5–1.3)	1.3 (1.2–2.2)			2.2 (1.8–3.2)	Galbán-Malagón et al., 2013b
South Scotia	2009	0.4 (0.3–0.6)	0.2 (0.1–0.4)	0.8 (0.6–1.2)	1.4 (1.2–2.1)			1.4 (0.7–1.9)	Galbán-Malagón et al., 2013b
Fides peninsula	2013–2014							810–3160	Zhang et al., 2016
Southern Ocean, Australia and Antarctica	2014	(2.6–4.1)	(2–4.4)	(0.7–1.9)		(0.3–3.2)	(0.6–1.8)		Bigot et al., 2016
Fides peninsula	2015–2016							(390–1500)	Gao et al., 2018
Coast of Antarctica			0.06 (ND–0.28)	0.01 (ND–0.01)	0.25				Vudamala et al., 2023
Fildes Bay	2019–2020	3.1 (0.9–6.9)	0.6 (<LOQ–1.3)	1.5 (0.2–3.3)	2.1 (0.47–4.6)	0.6 (<LOQ–0.9)	0.4 (<LOQ–0.7)	3.7 (0.8–8.1)	This study

where degradation fluxes estimated for γ-HCH were on average 2.39 ng $m^{-2}d^{-1}$, and for α -HCH 5.91 ng $m^{-2}d^{-1}$.

Should Antarctic microbial communities from water be able to degrade HCHs, microbial genomes should bear specific genes involved in degradation pathways. The enzymatic breakdown of HCHs involves four genes *linA*, *linB*, *linC*, and *linD*, where each of them encode for each successive step of the microbial degradation pathway of HCHs (Nagata et al., 1999; Tabata et al., 2011; Shrivastava et al., 2015). While this process has been shown in the laboratory to be relevant for all HCHs, it has been shown to be more efficient for α and γ, than for β and others (Álvarez et al., 2022; Geueke et al., 2013). We focused on the *linA* and *linB* genes which are involved in the two initial and key steps of the degradation pathway. Additionally, the protein encoded by *linA* catalyzes a stereoselective dehydrochlorination of hexachlorocyclohexanes, stereoisomers with higher capacity to metabolize α and γ compared to the other isomers (Geueke et al., 2013). The gene *linA* encodes a hexachlorocyclohexane dehydrochlorinase that dechlorinates the HCH molecule into 1,3,4,6-tetrachloro-1,4-cyclohexadiene, while *linB* encodes for a haloalkane dehalogenase that metabolizes the 1,3,4,6-tetrachloro-1,4-cyclohexadiene into 2,5-dichloro-2,5-cyclohexadiene-1,4-diol (Geueke et al., 2013; Álvarez et al., 2022; Nagata et al., 1999; Tabata et al., 2011; Shrivastava et al., 2015). To determine whether these genes were actively expressed by local microbial communities, we used metatranscriptomes obtained from seawater in Fildes Bay during summer 2020–2021. The results from the examined metatranscriptomes showed that both genes, *linA* and *linB* were been actively expressed in the studied area (Fig. 4). Transcripts found for *linA* were an order of magnitude more abundant than those of *linB*. The narrow substrate specificity of *linA* suggests that the microbial degradation of the reported HCH isomers could be active during the summer in the studied area, and may play a role in the environmental fate of HCHs (Nagata et al., 1993, 2001). This result agrees with previous works suggesting the role of bacterial communities in the fate of HCHs in the water column in polar areas (Galbán-Malagón et al., 2013a, 2013d; Bigot et al., 2016). However, this metabolic pathway could be different depending on the racemic mixture of HCHs as suggested for α-HCH (Harner et al., 1999, 2000; Law et al., 2004).

In the case of studied polychlorinated biphenyls we see that PCB 9 net exchange direction was dominated by volatilization, whereas in the case of PCB 180 we registered net deposition. The other polychlorinated biphenyls compounds were close to equilibrium between air and water, The estimated imbalance for PCBs 9 and 180 can be due to various processes. The net deposition of PCB 180 could be due to the transfer through the food web, or by the direct removal through the biological carbon pump that might be actively sequestering pollutants from surface waters and transporting them to the seafloor, lowering their concentrations in surface waters, due to the relatively high hydrophobicity of these pollutants (log $K_{OW} > 6.5$; Table S5) (Cincinelli et al., 2009; Dachs et al., 2002; and Galbán-Malagón et al., 2012, 2013a, 2013b, 2013c, 2013d). However, the role of the biological pump could also prevent the trophic transfer of this compounds trough the food web, as suggested in previous studies conducted in Antarctic waters, where the rate of the settling fluxes could significantly exceed the transfer from primary producers to consumers (Galbán-Malagón et al., 2018) for dioxin-like PCBs and dioxins. Further, the influence of the biological pump can be evidenced by plotting Log $f_w\ f_a^{-1}$ versus the temperature-corrected octanol-water partition constant (log K_{OW}) (Galbán-Malagón et al., 2013c). The more hydrophobic compounds are prone to be uptaken by primary producers that settle through the water column because of the low solubility of these compounds, which is lower in Antarctic cold waters (increasing logK_{OW} by a factor of two on average). As shown above there is an imbalance between the concentrations in the gas and the dissolved phase for some compounds and this also was illustrated in previous works for OC and PCBs (Galbán-Malagón et al., 2013c). Thus, we performed a piecewise linear regression analysis between the two variables that showed a slight negative but not significant ($p > 0.05$) relationship for compounds with a log$K_{OW} < 6.5$, whereas for compounds with a log$K_{OW} > 6.5$ (more hydrophobic congeners) the decrease in Log $f_w f_a^{-1}$ was steeper (Fig. 4). However, we report a lower number of compounds compared to other studies (Galbán-Malagón et al., 2013c), so the statistical power of the regression is low but consistent with previous studies showing that, in the case of compounds with log$K_{OW} >$ 6.5, there is a significative settling flux of these compounds (Galbán-Malagón et al., 2013c). This suggest that the biological pump may efficiently remove PCBs with high hydrophobicity values from surface waters, then exporting them to the seafloor, which in turn increases the air-seawater fugacity gradient for PCB 180, the congener with the highest atmospheric net deposition flux recorded in this study. The net volatilization of the highly volatile PCB 9 may be related to remobilization processes specially in the coastal environment. Climate change and rising temperatures are enhancing glacier retreat and snow melting during summer periods in West Antarctica (Turner et al., 2005; Chapman and Walsh, 2007; Rückamp et al., 2011; Lee et al., 2017; Dryak and Enderlin, 2020). There is previous evidence on the influence

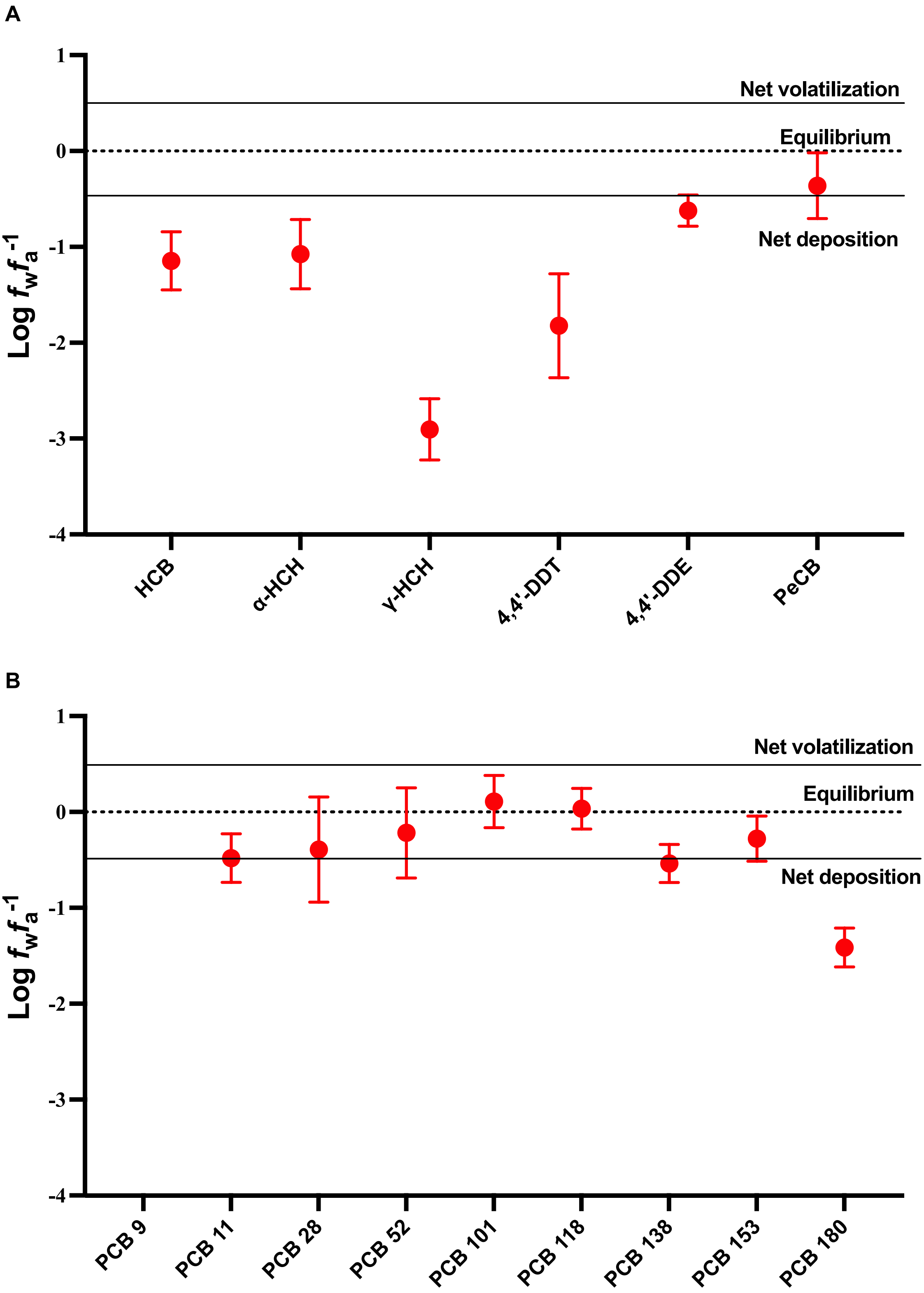

Fig. 3. Estimated air-to-water fugacity ratios (Log $f_w f_a^{-1}$) for OCs (A) and PCBs (B).

of ice/snow melting on coastal surface waters concentrations of these compounds (Casal et al., 2019). Compounds with higher snow–air partition coefficient and the dimension-less Henry's Law constant ($K_{SA}H'$) are prone to increase the fugacity amplification in surface waters due to ice/snow melting (Casal et al., 2019). This suggests that the influence of this process could even reverse the air-water fugacity gradient, as previously described in Arctic coastal environments (Cabrerizo et al., 2019). This situation may exert a significant influence on PCBs concentrations in coastal waters due to snow/ice acting as legacy reservoirs of POPs that are released into the environment after ice/snow melting (Burniston et al., 2007; Geisz et al., 2008; Casal et al., 2019). In this context, Fildes Bay receives significant snow-ice melt inputs from Collins Glacier (see Fig. 1), which affects the concentration of trace elements in its surface waters (Krause et al., 2021) and most likely

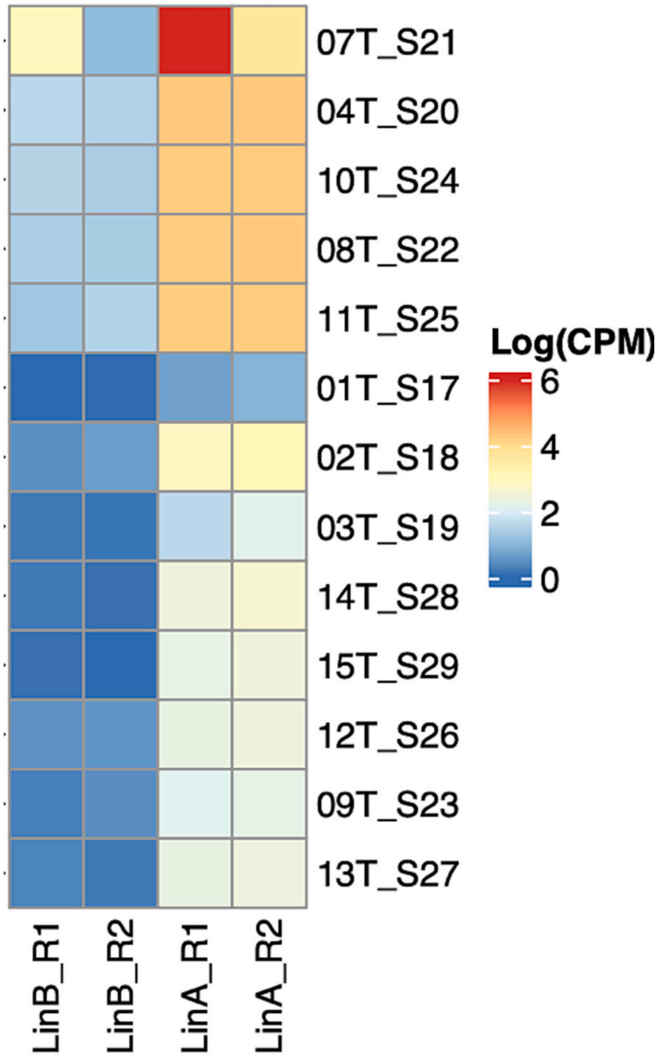

Fig. 4. The heatmap shows the relative abundance of transcripts for the *linA* and *linB* genes in the different samples. The samples are arranged in rows and the genes are arranged in columns. The colour of each cell represents the logarithmic transformation of the gene relative abundance in Counts Per Million (CPM) in logarithm scale. The dendrograms show the hierarchical clustering of the samples or gene replicates according to their distance based on the relative abundance of gene transcripts.

also increase the seawater concentrations of PCB 9, promoting its air-seawater fugacity, with a predominance of net volatilization.

4. Conclusions

The studied area is highly influenced by seasonal meltwater inputs from local cryosphere sources carrying micro-nutrients (e.g., iron) (Höfer et al., 2019; Hopwood et al., 2019) that are released into Fildes Bay surface waters (Krause et al., 2021). Nutrient inputs and water column stratification due to glacial melting may trigger massive algal blooms in Antarctic coastal waters (Mitchell and Holm-Hansen, 1991; Jones et al., 2017; Wang et al., 2020; Rozema et al., 2017; Brown et al., 2019) including King George Island and Fildes Bay (Höfer et al., 2019; Wasiłowska et al., 2022; Schloss et al., 2014). This enhances primary productivity of Antarctic coastal waters during spring and summer (e.g., Kim et al., 2018) and thus increases the role of the biological carbon pump that removes POPs, with Log$K_{OW} > 6.5$, from surface waters and move them to the seafloor through sinking particles, consistent with previous works (Galbán-Malagón et al., 2013a, 2013b, 2013c, 2013d), which in turn decreases the concentration of POPs across the water column. Also, the nutrient inputs from ice/snow melting, can also modify the microbial communities, and the extend of microbial degradation, as shown recently for PAHs (Polycyclic Aromatic Hydrocarbons) by stimulating microbial community metabolism (Iriarte et al., 2023). Thus, the action of the biodegradation coupled to the biological pump and snow amplification may play a significant role in the air seawater exchange for OCs, and the PCBs in Antarctic surface waters. Therefore, continuous monitoring is needed to assess the environmental fate of these compounds focusing on studying the effects of meltwater inputs on POPs biogeochemistry.

CRediT authorship contribution statement

Thais Luarte: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Andrea Hirmas-Olivares:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Juan Höfer:** Writing – review & editing, Writing – original draft, Investigation. **Ricardo Giesecke:** Writing – review & editing, Writing – original draft, Methodology, Data curation. **Mireia Mestre:** Writing – review & editing, Methodology, Data curation. **Sergio Guajardo-Leiva:** Writing – review & editing, Writing – original draft, Software, Methodology, Data curation. **Eduardo Castro-Nallar:** Writing – review & editing, Software, Methodology, Data curation. **Andrés Pérez-Parada:** Writing – review & editing, Investigation. **Gustavo Chiang:** Writing – review & editing, Methodology, Investigation. **Rainer Lohmann:** Writing – review & editing. **Jordi Dachs:** Writing – review & editing. **José Pulgar:** Writing – review & editing, Resources, Investigation, Data curation. **Karla Pozo:** Writing – review & editing, Writing – original draft, Resources, Investigation, Funding acquisition, Data curation. **Petra P. Přibylová:** Writing – review & editing, Writing – original draft, Resources, Methodology, Data curation. **Jakub Martiník:** Writing – review & editing, Writing – original draft, Resources, Methodology, Data curation. **Cristóbal Galbán-Malagón:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data accessibility

The data for this study have been deposited in the National Center for Biotechnology Information (NCBI) under accession number PRJNA 986281 (https://submit.ncbi.nlm.nih.gov/subs/sra/SUB13559226/overview).

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Appendix A. Supplementary data

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