



First evidence of legacy chlorinated POPs bioaccumulation in Antarctic sponges from the Ross sea and the South Shetland Islands[☆]

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ABSTRACT

Antarctica is no longer pristine due to the confirmed presence of anthropogenic contaminants like Persistent Organic Pollutants (POPs). Benthic organisms are poorly represented in contamination studies in Antarctica although they are known to bioaccumulate contaminants. Sponges (Phylum Porifera) are dominant members in Antarctic benthos, both in terms of abundance and biomass, and are an important feeding source for other organisms, playing key functional roles in benthic communities. To the best of our knowledge, legacy chlorinated POPs such as polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), and dichlorodiphenyltrichloroethane (DDT) and their metabolites have never been investigated in this Phylum in Antarctica. The aim of this work was to evaluate the bioaccumulation of PCBs, HCB, *o,p'*- and *p,p'*-DDT and their DDE and DDD isomers in 35 sponge samples, belonging to 17 different species, collected along the coast of Terra Nova Bay (Adèlie Cove and Tethys Bay, Ross Sea), and at Whalers Bay (Deception Island, South Shetland Islands) in Antarctica. Lipid content showed a significant correlation with the three pollutant classes. The overall observed pattern in the three study sites was $\Sigma\text{PCBs} > \Sigma\text{DDTs} > \text{HCB}$ and it was found in almost every species. The ΣPCBs , ΣDDTs , and HCB ranged from 54.2 to 133.7 ng/g lipid weight (lw), from 17.5 to 38.6 ng/g lw and from 4.8 to 8.5 ng/g lw, respectively. Sponges showed contamination levels comparable to other Antarctic benthic organisms from previous studies. The comparison among sponges of the same species from different sites showed diverse patterns for PCBs only in one out of four cases. The concentration of POPs did not vary significantly among the three sites. The predominance of lower chlorinated organochlorines in the samples suggested that long-range atmospheric transportation (LRAT) could be the major driver of contamination as molecules with a high long range transport potential (e.g. low chlorinated PCBs, HCB) prevails on heavier ones.

1. Introduction

Due to its geographical isolation and the absence of human activities, except for research, industrial fishing, and tourism, Antarctica and the Southern Ocean are usually regarded as one of the most pristine regions on Earth (Kim et al., 2015; Vecchiato et al., 2015; Vergara et al., 2019). Nevertheless, anthropogenic contaminants can reach Antarctica through long-range transport mechanisms. In fact, semi-volatile compounds are subjected to the global distillation process consisting of repeated

evaporation and condensation events that can transport Persistent Organic Pollutants (POPs) far from their emission sources (Wania & Mackay, 1993). Once in the Polar Regions, amplification mechanisms such as cold condensation (Wania and Mackay, 1993) or snow scavenging (Casal et al., 2019) result in a preferential accumulation of POPs in both the Arctic and Antarctica. POPs fall out through dry or wet depositions but also enter marine ecosystems transported by global ocean currents (Casas et al., 2020; Casas et al., 2021) and from pack ice melting (Casal et al., 2019; Potapowicz et al., 2019).

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Among legacy POPs, polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), and dichlorodiphenyltrichloroethane (DDT) are the most studied worldwide (Stockholm Convention, 2004). These persistent and toxic compounds, even if banned or restricted decades ago, are still found in every region worldwide, including Antarctica (Bargagli, 2008; Corsolini, 2009; Mello et al., 2016; Morales et al., 2022). Legacy POPs that may have been stored in the deeper layers of glaciers, perennial pack ice, and ice shelves may further be released during accelerated glacier melt due to climate change, becoming available again for bioaccumulation in the food webs (Ma et al., 2011; Potapowicz et al., 2019). Legacy contamination is increasingly being studied, as polar regions are experiencing some of the most rapid impacts of warming, acidification, and sea ice loss, and impacting benthic communities (Meredith et al., 2019; Brasier et al., 2021; Di Giglio et al., 2021; Figuerola et al., 2021, 2022). Bearing that in mind, it is valuable to keep studying the environmental fate of legacy POPs, their transfer through the marine food webs and their potential effects in Arctic and Antarctic ecosystems.

Antarctic food webs have peculiar characteristics: they are based on very few key species, such as the Antarctic krill *Euphausia superba* Dana 1950, and the Antarctic silverfish *Pleuragramma antarctica* Boulenger 1902, and thus they are likely fragile and vulnerable, with a very low resilience (Corsolini, 2009; Corsolini et al., 2017). Antarctic biota contamination studies have often focused on the most central species (*E. superba*, *P. antarctica* and penguins) of the pelagic food webs (Corsolini et al., 2002; Corsolini et al., 2017). Nevertheless, Southern Ocean benthic organisms are highly abundant, diverse, and able to bioaccumulate contaminants they are yet poorly represented in contamination studies (Di Giglio et al., 2021; Brasier et al., 2021; De Castro-Fernández et al., 2021). Consequently, knowledge about pollutants accumulation among them is still scarce. This could be due to the complex logistic sampling in remote areas (e.g. scuba diving, trawling) and the concentrations of POPs being usually lower than those in other regions (Krasnobaev et al., 2020). Bates et al. (2017) found that HCB could be remobilised from benthic biota with increasing temperatures, therefore, especially under global climate change, benthic communities deserve more attention as they can represent potential secondary sources of legacy pollutants. In this context, there is an urgent need to identify suitable benthic bioindicator species for environmental pollution monitoring in polar regions.

Among benthic organisms, the sponges (Phylum Porifera) represent a predominant component in the Antarctic benthos both in terms of abundance and biomass (Kersken et al., 2016), and are an important feeding source for many species such as sea stars, sea urchins, and nudibranch molluscs, thus playing a key role in the dynamics of the community (Dayton et al., 1974; García et al., 1993; Iken et al., 2002; McClintock, 1987; McClintock et al., 2005; Cardona et al., 2021). They are suspension-feeders, able to filter thousands of litres of water per day (Vogel, 1977; Negri et al., 2006), with an excellent retention capacity allowing them to capture particles in a range of 0.2–50 µm, with a lower limit far less than most of the other filter-feeders (Perez et al., 2004; Batista et al., 2013). Therefore, they may potentially accumulate large amounts of organic pollutants both in dissolved and suspended phases (Perez et al., 2004).

While sponges possess many traits of good bioindicators such as abundance, long lifespan (from years to millennia, Dayton, 1989; Gatti, 2002), large size (up to meters, Moran & Woods, 2012; van Soest et al., 2012), and efficient filtration capability (Rainbow, 1995), these organisms are less used than other filter-feeders as sentinels in biomonitoring programs (Genta-Jouve et al., 2012). This is probably due to their complex taxonomic identification compared to other common indicator species (Hooper & van Soest, 2002). However, some authors have already pointed out their potential and usefulness as indicators for trace elements and heavy metals (Perez et al., 2003; Negri et al., 2006; Batista et al., 2014; Gentric et al., 2016), POPs (Perez et al., 2004; Negri et al., 2006; Gentric et al., 2016), and polycyclic aromatic hydrocarbons

(Negri et al., 2006; Batista et al., 2013; Gentric et al., 2016). However, among the few studies currently available on POPs in Antarctic benthic organisms (e.g., Corsolini et al., 2003; Borghesi et al., 2011; Goutte et al., 2013; Grotti et al., 2016; Krasnobaev et al., 2020), none includes sponges.

The main objective of this study was therefore to assess the bioaccumulation of nineteen congeners of PCBs (including twelve dioxin-like congeners), the *p,p'*- and *o,p'*- isomers of DDT, and its main metabolites, DDD and DDE, as well as HCB (one of the POPs with the greatest atmospheric long-range transport potential), in several species of Antarctic sponges collected in the Ross Sea between 2001 and 2005 (Adèlie Cove; Tethys Bay) and in the Bransfield Strait in 2017 (Whalers Bay, Deception Island). Secondary objectives were: 1) to evaluate interspecific differences in the accumulation patterns and to compare individuals belonging to the same species collected in three distinct sites; 2) to compare pollutant levels in three differently impacted areas. We expected: i) low levels of POPs in such organisms due to their low lipid content together with their trophic level, even with their filtration capability; ii) to find differences in the species-specific pattern due to the biological variability; iii) Whalers Bay to show higher concentrations than Ross Sea sites due to its closer geographical position to South America and the number of local sources (increasing tourism and cruise ships in Deception Island, scientific stations, and its industrial past) that may affect POPs release.

2. Materials and methods

2.1. Study area and sponge species

Sponge samples were collected at Whalers Bay (Lat. 62°59'0" S, Long. 60°34'0" W, Port Foster, Deception Island) in the South Shetland Islands archipelago (Bransfield Strait), and at Adèlie Cove (Lat. 74°45'51" S, Long. 164°0'34" E, Terra Nova Bay) and Tethys Bay (Lat. 74°40'60" S, Long. 164°4'0" E, Terra Nova Bay) in the Ross Sea. Sampling areas are showed in Fig. 1. Whalers Bay is a sandy beach located on Deception Island, an active volcano with a safe natural harbour, that was used by sealers as the first centre of their hunting activities during the 19th century (Mão de Ferro et al., 2013). Nearly a century later, it was the most extensive docking station for whale processing factories ships and housed the Hektor whaling station; the only land based commercial activity in Antarctic history (Dibbern, 2010). Nowadays, Whalers Bay is one of the most frequently visited locations in Antarctica by tourists (Dibbern, 2010; Mão de Ferro et al., 2013) with >15,000 visitors per year (IAATO, International Association of Antarctica Tour Operators, 2018). Whalers Bay also hosts a well-developed rocky area in the southernmost part, where a rich filter-feeder community is found (Angulo-Preckler et al., 2018). Moreover, the South Shetland Islands archipelago presents one of the highest concentrations of scientific stations in the world (Barnes et al., 2008) and Deception Island hosts two summer scientific stations, one from Argentina and one from Spain (Roura, 2012; Mão de Ferro et al., 2013). The Western Antarctic Peninsula, where Whalers Bay is located, also represents one of the most impacted areas by industrial fishing (Aronson et al., 2011) that is also increasing in the Southern Ocean (Chown et al., 2015).

Tethys Bay is a small inlet nearby the Italian Mario Zucchelli Station (MZS); here the sea bottom is covered by littoral sediments that consists of coarse sands, pebbles, and gravel (Cerrano et al., 2009). Adèlie Cove is a 70-m depth V-shaped bay along the coast of Terra Nova Bay (Povero et al., 2001), with a bottom characterised by fine sediments rich in organic matter due to the presence of a breeding colony of Adèlie penguins (Cattaneo-Vietti et al., 2000). The bay is separated from the open sea by a 12–15 m depth sill that represent a natural barrier to the in- and out-flows (Cattaneo-Vietti et al., 2000). Outside of that sill the bottom becomes coarser and consists of large pebbles (Povero et al., 2001), where benthic communities dominate and sponges show high diversity and biomass (Cattaneo-Vietti et al., 2000). Adèlie Cove is located South

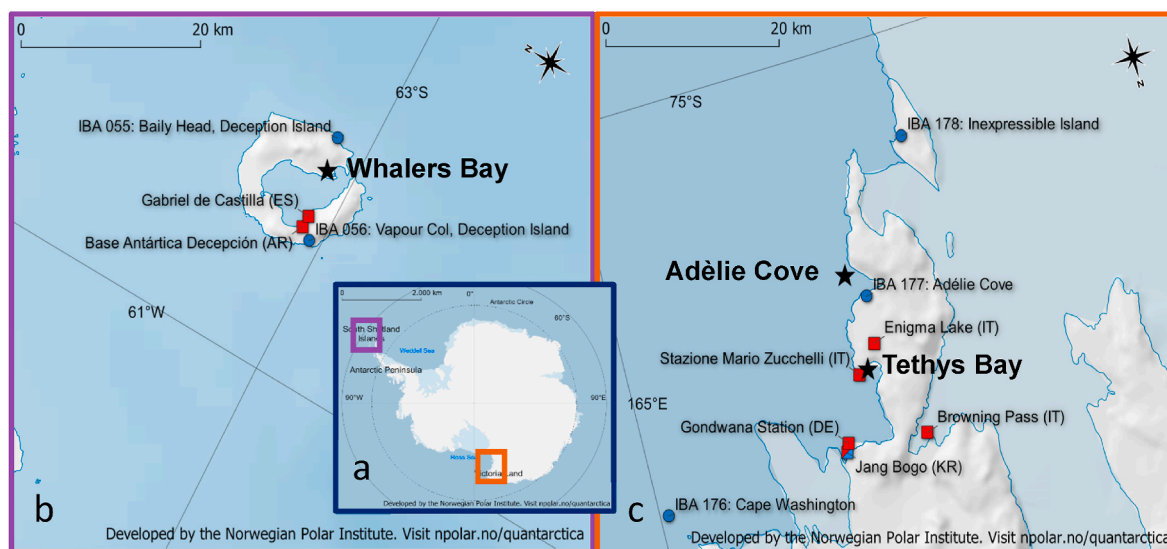


Fig. 1. a) Antarctic continent with the indication of the two areas where the sampling sites are located; b) Deception Island area in the South Shetland Archipelago ($n = 10$, year of sampling 2017); c) coastal area of Victoria Land in the Ross Sea (Tethys Bay: $n = 7$, year of sampling 2001–2002; Adèlie Cove: $n = 18$, year of sampling 2004–2005). Black stars show the sampling site. Red symbols indicate summer-only stations or facilities (e.g., Enigma Lake and Browning Pass airstrips) and blue-red symbols year-round stations. Blue dots indicate important bird areas. The map was created using Quantarctica 3.2 (Matsuoka et al., 2021). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of the Italian base and far from any other anthropogenic contamination source.

A total of 35 sponge specimens were collected in the Ross Sea ($n = 25$) and at Deception Island ($n = 10$) (Table S1). The Ross Sea samples were collected during the austral summers 2001/2002 at Tethys Bay and 2004/2005 at Adèlie Cove, in the framework of the XVII and the XX Italian Expedition of National Research Program in Antarctica (PNRA), respectively. The sampling was conducted along longitudinal transects (at Adèlie Cove it was conducted outside of the described sill) at a depth of 60–120 m by bottom trawls; samples were then stored in polyethylene bags. The Deception Island samples were collected by scuba diving at 15–20 m depth during the DISTANTCOM-2 Antarctic cruise in February 2017, wrapped individually in aluminium foils and stored in polypropylene bags. All the samples were stored at $-20\text{ }^{\circ}\text{C}$ until laboratory analyses.

All samples were identified at species-level (Table S1). The sponge species belong to two main classes: Hexactinellida and Demospongiae, most of them belonging to the second group (Table S1). Four species were found in both the Ross Sea sites (Table S1). Sponge samples were processed by standard methods (Rützler, 1978). Skeletal architecture was examined by light microscope. Hand-cut sections of the ectosome and choanosome were made following Hooper (2000). Taxonomic identifications were made using the Systema Porifera (Hooper & van Soest, 2002), the revision of Porifera classification of Morrow & Cárdenas (2015), and the World Porifera Database (WPD) (de Voogd et al., 2022).

2.2. Chemicals and residue analysis

Samples were analysed for 19 PCB congeners including the IUPAC numbers 28, 52, 101, 138, 153, 180, 194, and the dioxin-like IUPAC numbers 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189; HCB; the *o,p'* and *p,p'* isomers of DDT, DDE, and DDD.

Acetone, hexane (Scharlau, Sentmenat Spain), and dichloromethane (Honeywell Riedel-de-Haën™) purity grade >99.9% were used for glassware washing. During the sample preparation Acetone Pestinorm® supplied by VWR Chemicals (Leuven, Belgium) and *n*-hexane ultra resi-analysed® supplied by J.T.Baker® (Gliwice, Poland) were used. Labelled compounds solutions were prepared with *n*-nonane Picograde®

LGC Standards (Wesel, Germany). Sodium sulfate anhydrous (mesh 12–60) Ultra resi-analysed® and silica gel (mesh 70–230) for column chromatography were supplied respectively by J.T.Baker® (Center Valley, PA, U.S.A) and Merck (Darmstadt, Germany). Labelled standard solutions were purchased by Cambridge Isotope Laboratories Inc. (Andover, USA).

Firstly, samples were lyophilised at $-80\text{ }^{\circ}\text{C}$ and 0.2 mbar for 48 h with a Cryodos, Telstar Industrial, S.L. (Terrassa, Spain) and weighed to calculate the water content. Then, they were manually grounded with a ceramic mortar and pools of organisms were prepared when the amount was too low (number of pooled individuals is shown in Table S1); therefore, the total number of samples analysed was 23. Sample weight was about 5 g (3.50–5.03 g) (Table S1). Before extraction, procedural blanks and samples were spiked with a known amount of a solution containing the following ^{13}C -labelled compounds: PCB-28, -52, -101, -138, -153, -180, -209, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, and HCB. The extraction of the analytes was carried out by matrix solid-phase dispersion and the clean-up using multi-layer silica gel columns as previously described in Roscales et al. (2016b). Samples were transferred into vials and concentrated under a gentle nitrogen stream, then reconstituted with 20 μL of injection standard containing $^{13}\text{C}_{12}$ -PCB-111, -170, -178. The lipid content was determined gravimetrically using 0.5 g of each sample and following the same procedure used for the analytes extraction. The extract was rotary evaporated to nearly dryness and then dried at $80\text{ }^{\circ}\text{C}$ until steady weight.

Target compounds were identified and quantified by gas chromatography coupled with low resolution mass spectrometry (GC-LRMS) following Roscales et al. (2016a). The analyses were performed using an Agilent 7890A gas chromatograph coupled with an Agilent 5975C mass spectrometer (Agilent, Palo Alto, CA, USA) in selected ion monitoring (SIM) mode with electron ionization (EI) at an electron voltage of 70 eV. The injector temperature was $250\text{ }^{\circ}\text{C}$ and the injected volume was 1 μL in splitless mode, the carrier gas was He (0.8 mL/min constant flux at a pressure of 17.9 psi). The GC was equipped with a BPX5 low bleed (SGE Analytical Science) capillary column (60 m \times 0.5 mm i.d. \times 0.25 μm film thickness). Oven temperature program started at $120\text{ }^{\circ}\text{C}$, held for 2 min, increased to $250\text{ }^{\circ}\text{C}$ at $35\text{ }^{\circ}\text{C}/\text{min}$ and held for 30 min, and finally ramped to $310\text{ }^{\circ}\text{C}$ at $15\text{ }^{\circ}\text{C}/\text{min}$ and held for 30 min. The transfer line was set at a temperature of $280\text{ }^{\circ}\text{C}$, the source at $230\text{ }^{\circ}\text{C}$, and the

quadrupole at 150 °C. The identification was based on the detection at the corresponding retention time of at least two m/z ions. The relative abundance of the monitored ions was respected. Native compounds quantification was based on the construction of a linear seven-point calibration curve (1–200 pg/ μ L) using the isotopic dilution technique.

2.2.1. Quality assurance/quality control (QA/QC)

Results were presented on lipid weight (lw) basis because a significant positive correlation (Spearman's correlation test, $p < 0.05$) was found between the lipid content and the dry weight-based analyte concentrations (PCB: $p = 0.0129$, $r = 0.5100$; HCB: $p = 0.0003$, $r = 0.6995$; DDT: $p = 0.0311$, $r = 0.4604$). Dry, lipid and wet-weight based concentrations are reported in SI (Tables S2–S7). Analytes were identified according to: i) retention times of the selected m/z ions within ± 0.1 min of those found in standard compounds; ii) variations in the relative abundances of the targeted ions $\leq 10\%$ of the mean values obtained for the calibration standards. Recoveries of labelled compounds were satisfactory in all cases (mean \pm standard deviation): $93 \pm 3\%$ for HCB, $89 \pm 13\%$ for the PCB congeners nos. 28, 52, 101, 153, 138, 180, 209 (Σ_7 PCBs) and $101 \pm 13\%$ for the o,p' -DDT, p,p' -DDT and p,p' -DDE (Σ_3 DDTs) (Table S8); correspondence between labelled and native compounds for identification and quantification is included in Table S9. One procedural blank was analysed with each batch, which consisted of 4 or 5 samples to check for laboratory interferences. Limit of detection (LOD) and limit of quantification (LOQ) were calculated with the signal to noise (s/n) ratio approach and defined as 3 and 10 times the s/n value, respectively. The average LOD values were in the range 0.8–6.0 ng/g lw for PCBs, between 3.3 and 4.6 ng/g lw for DDTs, and 0.8 ng/g lw for HCB. The LOQs averaged values ranged between 2.8 and 19.9 ng/g lw for PCBs, 11.1–15.2 ng/g lw for DDTs, and 2.5 ng/g lw for HCB. See the SI for detailed LOD and LOQ values and detection frequencies (Tables S10 and S11).

2.3. Data analysis

Statistical analyses were performed with Excel 2016 (Microsoft®), GraphPad Prism 5.01 (GraphPad Software), and XLStat 2016 (Addinsoft®). Values below LOD were substituted with $\frac{1}{2}$ LOD. Compounds below LOD in all samples were excluded from statistical comparisons and total concentration calculations. Concentrations of the analytes were corrected subtracting the corresponding procedural blank mean value. No corrections were applied according to recovery measures since the isotopic dilution technique was used for quantification. Data distribution was evaluated with Shapiro-Wilk test and was not normal even after a \log_n transformation. Thus, concentration variations among samples collected in different sites were evaluated through the non-parametric Kruskal-Wallis test (significance level: $p < 0.05$). The comparison of homologue patterns among sites and the evaluation of the contribution of PCB congeners or pollutants classes among species, were based on descriptive statistics.

3. Results and discussion

The lipid contents in the studied sample composites ranged from 0.7 to 8.5% (Table S1), in agreement with the values reported by McClintock (1987) and Batista et al. (2013) for different sponge species collected at McMurdo Sound (Antarctica) and along the Brazilian coast, respectively. The significant positive correlation described above, between the lipid contents and the contaminants, suggests that they are an important factor for the bioaccumulation. The water content of the samples ranged from 36 to 88% (Table S1). For both lipid and water content, the range observed may reflect a species-specific variability. All pollutant families showed detectable concentrations in all the samples with a common concentration pattern: Σ PCB $>$ Σ DDT $>$ HCB in the three study sites (Table 1). Moreover, the pattern is confirmed in every individual (including the only Hexactinellid specimen) except for

Table 1

Concentrations of HCB, PCB congeners and DDT isomers in the sponge samples from the three study sites (n = number of samples; ng/g lipid weight; mean \pm standard deviation, minimum and maximum values in brackets) and number of values $<$ LOD (%).

	Tethys Bay (n = 7)	Adèle Cove (n = 13)	Whalers Bay (n = 3)	<LOD (%)
PCB-28	7.5 \pm 6.7 (<LOD – 21.2)	14.9 \pm 14.9 (<LOD – 52.4)	3.5 \pm 1.9 (1.9–5.6)	9
PCB-52	17.5 \pm 18.9 (<LOD – 43.5)	21.1 \pm 18.9 (4.4–68.6)	6.0 \pm 1.9 (4.9–8.2)	4
PCB-101	12.5 \pm 12.4 (<LOD – 36.1)	30.3 \pm 51.1 (0.3–196.2)	21.5 \pm 10.0 (10.5–30.1)	4
PCB-105	3.2 \pm 1.4 (<LOD – 5.1)	6.4 \pm 4.0 (<LOD – 16.5)	4.1 \pm 0.3 (<LOD – 4.4)	74
PCB-118	4.3 \pm 3.2 (0.7–9.8)	10.6 \pm 14.0 (0.8–52.1)	5.1 \pm 0.9 (4.1–5.8)	0
PCB-123	5.0 \pm 2.4 (<LOD – 8.5)	9.0 \pm 4.8 (<LOD – 17.0)	2.7 \pm 0.0 (<LOD – 2.7)	91
PCB-126	3.0 \pm 1.7 (<LOD – 5.4)	6.1 \pm 3.2 (<LOD – 10.9)	1.7 \pm 0.0 (<LOD – 1.7)	96
PCB-138	10.0 \pm 6.8 (2.6–21.6)	12.5 \pm 13.0 (1.5–46.3)	4.4 \pm 0.9 (3.6–5.5)	0
PCB-153	10.4 \pm 12.8 (1.5–38.5)	12.5 \pm 14.2 (1.5–41.9)	2.9 \pm 0.3 (2.7–3.2)	0
PCB-167	2.0 \pm 1.4 (<LOD – 4.9)	2.2 \pm 1.2 (<LOD – 4.2)	0.7 \pm 0.0 (<LOD – 0.7)	87
PCB-180	17.5 \pm 30.8 (<LOD – 86.2)	8.2 \pm 8.1 (0.5–26.0)	1.4 \pm 1.4 (0.4–3.0)	4
Σ PCB	92.8 \pm 47.6 (27.7–164.7)	133.7 \pm 119.3 (39.8–482.8)	54.2 \pm 10.8 (41.9–62.0)	
o,p' -DDT	2.5 \pm 2.8 (<LOD – 8.2)	2.9 \pm 1.4 (<LOD – 5.1)	3.4 \pm 2.8 (1.5–6.6)	78
p,p' -DDT	4.8 \pm 6.2 (<LOD – 17.3)	5.1 \pm 3.6 (<LOD – 14.7)	11.0 \pm 2.1 (9.6–13.4)	70
o,p' -DDE	1.5 \pm 0.6 (<LOD – 2.2)	2.7 \pm 1.4 (<LOD – 5.2)	3.9 \pm 1.8 (1.8–5.3)	78
p,p' -DDE	7.3 \pm 8.9 (<LOD – 24.5)	14.1 \pm 12.5 (<LOD – 38.3)	19.6 \pm 5.0 (13.9–23.6)	30
p,p' -DDD	1.3 \pm 0.6 (<LOD – 1.9)	2.4 \pm 1.2 (<LOD – 4.5)	0.7 \pm 0.0 (<LOD – 0.7)	91
Σ DDT	17.5 \pm 18.3 (5.6–53.7)	27.2 \pm 17.1 (9.3–59.2)	38.6 \pm 7.4 (31.3–46.1)	
HCB	4.8 \pm 1.8 (3.0–7.3)	8.1 \pm 5.0 (<LOD – 19.6)	8.5 \pm 4.0 (5.7–13.1)	4

^a mean calculated on 12 samples.

Neopetrosia similis (HCB $>$ Σ PCB $>$ Σ DDT) and one sample of *Dendrilla antarctica* (Σ DDT $>$ Σ PCB $>$ HCB) (Fig. 2). In fact, it is interesting to note that the species *N. similis* collected at Adèle Cove showed the highest HCB percentage, exceeding the 60%; this pattern might be due to individual variability. For this reason, this outlier value was not included in the statistical calculations. Noteworthy, Σ DDT percentage in the genus *Dendrilla* ranged from 30 to 50% while in the other genus it was between 4 and 30% (Fig. 2), regardless of the sampling site, perhaps suggesting a peculiar inability to degrade the pesticide. Thus, concerning the accumulation pattern, species-specific variability was relevant in less cases than expected. No other relevant differences can be observed about the pattern in individuals of the same species collected in different site.

3.1. PCBs

Among PCBs, 11 out of 19 were detected at least in one sample (Table 1) including the seven indicator PCBs –28, –52, –101, –118, –138, –153, –180 and, among the coplanar dioxin-like congeners (other than –118) three mono-ortho –105, –123, –167 and the non-ortho –126, one of the most toxic congeners together with the –169 and –77 that resulted $<$ LOD in all the samples. Detection frequencies of indicator PCBs were always above 90% and in 5 out of 7 cases (only excluding PCB-28 and PCB-180) reached the 100% confirming the ubiquity of these POPs in the environment (Montone et al., 2003)

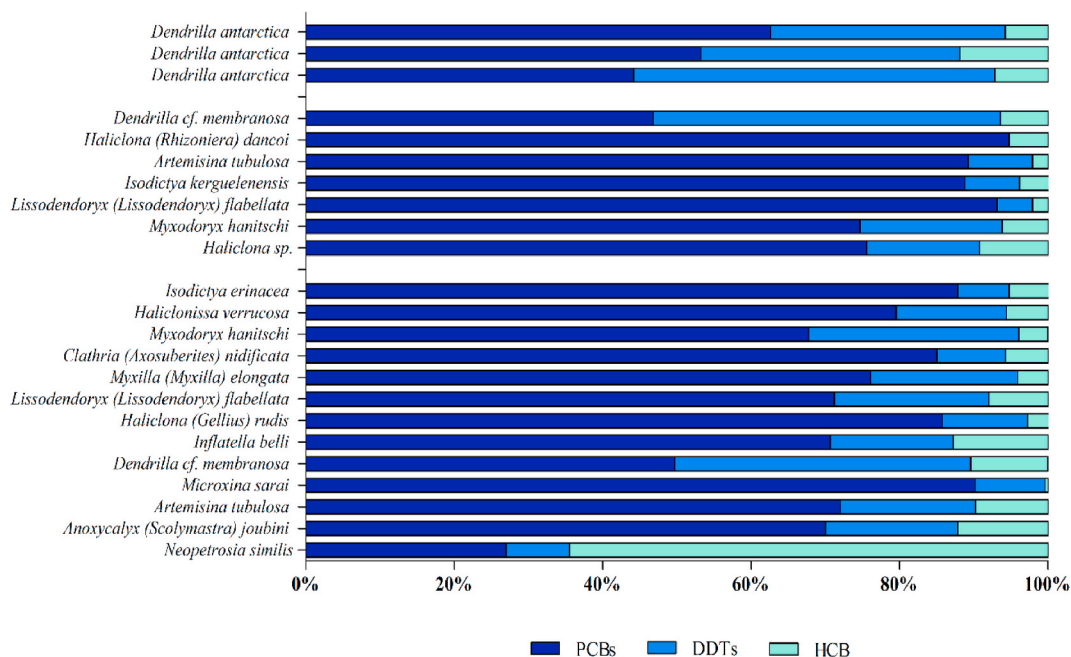


Fig. 2. Contribution (%) of PCBs, DDTs, and HCB in the 23 Antarctic sponge species from the three study sites (Whalers Bay, Tethys Bay, Adèlie Cove).

(Table 1).

Sponges had similar PCB concentrations to those reported (for most sampling years) by Grotti et al. (2016) in the mollusc *Adamussium colbecki* (E. A. Smith, 1902) (Table S12), collected near Mario Zucchelli station, likely due to its filter-feeding habits. In contrast, sponges showed lower levels of PCBs (one order of magnitude) than the sea star *Odontaster validus* Koehler, 1906 and the sea urchin *Sterechinus neumayeri* (Meissner, 1900), previously collected near Mario Zucchelli station (Borghesi et al., 2011) and near Durmont D’Urville French station (Goutte et al., 2013) (Table S12), as expected by their different dietary habits (Corsoini et al., 2003a), being relevant predators in Antarctic ecosystems (Dayton et al., 1974). Ko et al. (2018) reported concentrations two to three orders of magnitude higher than this study in the brittle star *Ophionotus victoriae* Bell, 1902 and *S. neumayeri* from Chinese (Chun-Shan) and Australian (Davis) stations (Table S12), this is probably due to their proximity to that permanent research stations. Our findings also confirm that Antarctica is one of the least contaminated regions on Earth as the PCB levels found here were three to four orders of magnitude lower compared to Mediterranean sponge specimens (Perez et al., 2003) (Table S12). In spite of the major role of anthropogenic activities in Whalers Bay and its closeness to the American continent compared to the rest of sites, spatial differences were not statistically significant ($p = 0.2829$). The Ross Sea sites showed the highest levels of PCBs (Table 1). In contrast, the only local input of PCBs at Adèlie Cove could be the presence of a large Adèlie penguin rookery in the cove. Wildlife may have a role in the POP redistribution and local amplification, as already reported in Polar Regions (Evenset et al., 2007; Roosens et al., 2007). In fact, penguins, being intermediate predators, could accumulate lipophilic pollutants through biomagnification and release them in the surrounding environment by excreta, abandoned or unhatched eggs, and carcasses (Roosens et al., 2007; Cipro et al., 2019; Corsoini et al., 2019; Morales et al., 2022). Concerning Tethys Bay samples, the observed values could be related to the presence of local inputs of PCBs from the near research station (Cabrerizo et al., 2012; Chen et al., 2015; Vecchiato et al., 2015). The absence of differences among the sites, nevertheless their different characteristics, could be due to a regional scale redistribution of the pollutants, due to both oceanic and atmospheric transport, making them more available than expected for the bioaccumulation in Ross Sea sponges. However, this result has to

be evaluated carefully taking into account that it could be affected by other factors, such as the different number of samples, species-specific differences and temporal differences in the sampling time.

The abundance of the PCB homologues was similar in the studied samples. The PCB homologue pattern was penta- > hexa- > tetra- > tri- > hepta-CBs in samples from Adèlie Cove and Whalers Bay, and penta- > hexa- > tetra- = hepta- > tri-CBs for those from Tethys Bay (Fig. 3). In the samples from the Tethys Bay, the presence of high-chlorinated and less volatile congeners like the hexa-CBs (-138, -153, -167) and hepta-CB (-180), accounting for more than 40% of the total residue (Fig. S1), might confirm a local contamination source from near scientific stations (Chen et al., 2015; Vecchiato et al., 2015). However, the lower chlorinated congeners nos. 28, 52 and 101 made up about 40% of the residue (Fig. S1), also confirming a contribution by the LRAT. Corsoini et al. (2002, 2003b) reported a similar pattern to that observed for *E. superba* and *P. antarcticum* collected in the same area and highlighted its similarity to the Kanechlor technical mixtures (KC-500 and -1000) profile, used in Asian countries, perhaps suggesting a long-range transportation from those areas.

The Adèlie Cove and Whalers Bay samples showed a high presence of low-chlorinated PCBs: -28, -52, -101, -105, -118, -123, -126, accounting for more than 70% and 80%, respectively (Fig. S1). It is interesting to note that PCB-101 is the most abundant congener in the

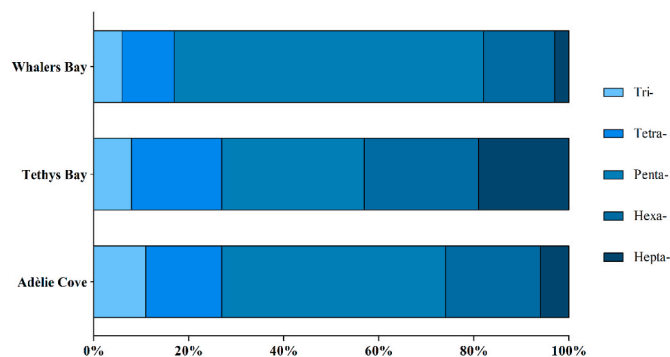


Fig. 3. Homologue pattern (%) in sponges from the three study sites (Adèlie Cove; Tethys Bay; Whalers Bay).

Whalers Bay samples, far exceeding the 60% of the total residue. Consistent with our results, the PCB-101 shows a higher bioaccumulation potential (Log Kow 6.19; Ballschmiter et al., 2005) respect to other prevailing congeners like PCB-28 (Log Kow 5.58; Ballschmiter et al., 2005) and PCB-52 (Log Kow 5.91; Ballschmiter et al., 2005) and it has been already reported as one of the dominant congeners in Antarctic air (Montone et al., 2003) as well as in penguins (Corsolini et al., 2007). Moreover, the overall abundance of penta- and hexa-chlorinated congeners was already reported in some lower trophic level organisms, such as molluscs *A. colbecki* (Grotti et al., 2016), sea cucumbers (*Heterocucumis steineri* Ludwig, 1898), ascidians (*Cnemidocarpa verrucosa* Lesson, 1830), sea stars (*O. validus*), limpets (*Nacella concinna* Strebel, 1908) and sea urchins (*S. neumayeri*) (Krasnobaev et al., 2020). Our results also agree well with a previous study by Goutte et al. (2013), reporting the predominance of penta- over hexa-CBs in Antarctic benthic species such as the starfish *Saliasterias brachiata* Koehler, 1920 and the sea urchin *S. neumayeri*.

Comparing the individuals belonging to the four species collected at both the Ross Sea sites (Fig. 4), the general observed pattern was mostly confirmed; samples from Tethys Bay showed higher percentage of the heaviest congeners compared to Adèlie Cove specimens in three out of four cases. However it is interesting to note that *Artemisina tubulosa* showed a slightly inverted pattern with the percentages for Tethys Bay moved towards lighter congeners than Adèlie Cove; this could be due to a species-specific ability to transform and excrete selected congeners by the sponge itself or its associated microorganisms, like hypothesized for some PCBs in *Spongia officinalis* Linnaeus, 1759 (Perez et al., 2003).

3.2. DDTs

Five DDT isomers were > LOD in 30% of samples; the *o,p'*-DDD isomer was < LOD in all samples (Table 1). DDTs were mostly undetectable in the samples from the Ross Sea, showing 73% and 77% of the values < LOD in Tethys Bay and Adèlie Cove samples (excluding the *o, p'*-DDD isomer), respectively (Table 1). The DDT isomer concentrations were not reported in one sample from Tethys Bay due to a co-eluting unknown compound that made the quantification uncertain. Instead, samples from Deception Island showed values < LOD in 20% of the cases (Table 1).

Samples collected at Whalers Bay and Tethys Bay showed concentration values lower than those of *O. validus* and higher than those of *S. neumayeri* reported previously by Borghesi et al. (2011) (Table S12). However, samples from Adèlie Cove showed values on the same order of magnitude than those detected in the sea urchin from the same study (Table S12). Focusing on the *p,p'*-DDE isomer, sponges from Whalers

and Tethys Bays showed similar values to *O. validus* and higher than *A. colbecki* and *S. neumayeri* as reported by Corsolini et al. (2003a) (Table S12). Adèlie Cove samples showed concentrations lower than the sea stars and similar to molluscs and sea urchins from the same study (Table S12).

As discussed for PCBs, dietary differences may explain these results when comparing them to those from the literature (e.g. lower concentrations in sponges than in predators like *O. validus*) (Corsolini et al., 2003a). However, more studies are needed to interpret differences among species.

Differences in DDT concentrations among sites were not statistically significant ($p = 0.1575$), although they were higher in sponges from Whalers Bay (Table 1). On one hand, concentrations found in Whalers Bay could be influenced by its proximity to South America, where this pesticide has been used along history (Montone et al., 2003; Dickhut et al., 2005; Corsolini et al., 2007) and from which it could be transported via LRAT to Antarctica (Dickhut et al., 2005; Montone et al., 2003). On the other hand, local inputs, such as the penguin rookery near Adèlie Cove, could contribute to increasing concentrations in this site. Inputs from these sources at each site may have flattened the expected differences among the two areas. Moreover, the frequency of values < LOD in the two areas seems to be in line with the expected results being higher in the Ross Sea than at Whalers Bay (70% and 20% respectively). An explanation for these apparently contrasting results could be found in the species-specific characteristics; noteworthy, in fact, the only Ross Sea samples in which DDTs were found were of the same genus of the Whalers Bay samples (Dendrilla). However, again, other factors such as the different number of samples analysed, and the year of sampling have to be taken into account.

The *p,p'*-DDE showed the highest values in all samples from each site, followed by its precursor *p,p'*-DDT; thus the ratio *p,p'*-DDT/*p,p'*-DDE was <1 (Fig. S2), indicating an old contamination event (Ricking & Schwarzbauer, 2012). Nonetheless, the detection of *p,p'*-DDT in all samples from Deception Island and in four samples from the Ross Sea could be related to the current use of this pesticide against the mosquitoes *Anopheles* (Stockholm Convention, 2004; Pozo et al., 2017; Zanardi-Lamardo et al., 2019), vector of the malaria disease, as well as other current applications like antifouling paints (Pozo et al., 2017; Zanardi-Lamardo et al., 2019) and the following LRAT from those countries where it is applied notwithstanding the Stockholm Convention. Geisz et al. (2008) also suggested the melting glaciers as a possible secondary mechanism for DDTs to enter the marine Antarctic ecosystem. Since the Antarctic Peninsula is suffering the highest warming events due to climate change (Turner et al., 2005), this mechanism could also support Whalers Bay sponges presenting higher frequencies of detection of DDTs than the Ross Sea samples. An uncompleted degradation of DDTs by sponges or by their symbiotic bacteria associations may be another reason of its detection. For example, Krasnobaev et al. (2020) reported concentrations < LOD for *p,p'*-DDT in some benthic invertebrates (sea cucumbers, ascidians, sea stars, limpets, and sea urchins) collected in 2017 (the same year we collected our Whalers Bay samples), near Rothera Point (Western Antarctic Peninsula), suggesting a complete transformation of DDTs into *p,p'*-DDE instead of a lack of the still debated recent input (Van den Brink et al., 2009). Further studies are needed to clarify if our results were determined mostly by the scarce degradation capability of sponges following an old contamination event or by a new LRT event due to its continued use in countries where DDT is still crucial to control malaria.

3.3. HCB

HCB values were <LOD only in one sample collected at Adèlie Cove (Table 1), confirming its global distribution, persistence, and wide past usage (Bailey, 2001; Wang et al., 2010).

The HCB concentrations were lower than those previously reported in the seastar *O. validus* and higher than in the sea urchin *S. neumayeri*

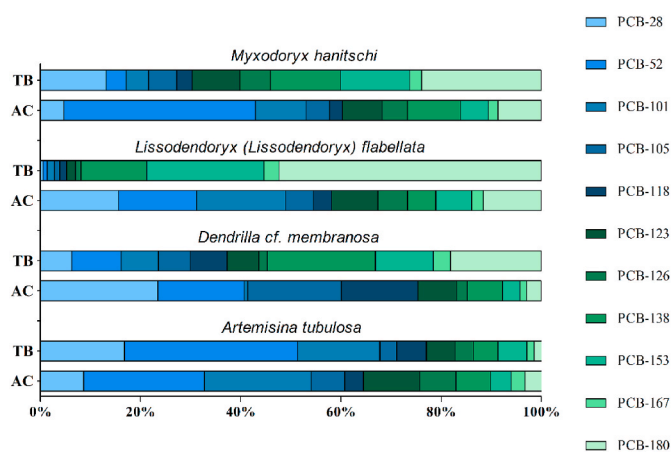


Fig. 4. Percentage contribution of PCB congeners to the total residue (%) in eight Antarctic sponges belonging to four different species and collected from Adèlie Cove (AC) and Tethys Bay (TB).

from Antarctica (Borghesi et al., 2011) (Table S12). However, our values were lower than in the sea star and sea urchin and of the same order of magnitude of those reported for the bivalve *A. colbecki* in a previous study (Corsolini et al., 2003a) (Table S12). Again, these contrasting results suggest that not only different dietary habits, but also metabolism, season of sampling, and environmental concentrations could play a key role in determining these interspecific variabilities. In addition, these comparison results, being not consistent in terms of prey-predator patterns, did not allow further considerations on biomagnification processes as expected for a benthic trophic web (Evenset et al., 2016; Romero-Romero et al., 2017).

HCB concentrations were of the same order of magnitude in all samples with no significant differences among sites ($p = 0.2719$) except for some samples from Adèle Cove and Whalers Bay, which showed concentrations one order of magnitude higher (Table 1). The lack of significant spatial variations could be related to the physical-chemical properties of the pesticide: its vapour pressure combined with water solubility and persistence, in fact, make it widespread globally (Bailey, 2001). Furthermore, other factors could contribute to the result; for example, in Whalers Bay, changes in the frequency of snowfalls may locally amplify the HCB concentration, as suggested by Krasnobaev et al. (2020), and the same may happen by biological transportation in Adèle Cove.

Several studies have found that among legacy POPs, HCB predominates in the Antarctic atmosphere, mainly due to the wide use, high volatility, and persistence of this chemical (Cincinelli et al., 2009; Kalenborn et al., 2013; Bengtson Nash et al., 2017). Some studies have shown that this pattern sometimes is also reflected in wildlife, being HCB the most abundant compound in various marine organisms, such as fish and krill (Corsolini, 2009; Corsolini & Sarà, 2017). Particularly, Corsolini et al. (2003a) and Krasnobaev et al. (2020) found HCB concentrations above those of DDTs in some marine invertebrate species collected in 1999/2000 in the Ross Sea and in 2017 in the Western Antarctic Peninsula. In our study, HCB was the less abundant pollutant in the three study sites ($\Sigma\text{PCBs} > \Sigma\text{DDTs} > \text{HCB}$). The peculiarity of sponges in terms of feeding habits, biodegradation capability, and longevity may be responsible of these diverse POP bioaccumulation profiles and deserves further efforts to better understand trophodynamic, transportation, and fate of these pollutants.

4. Conclusions

To the best of our knowledge, no published data are available on the presence of HCB, DDTs and PCBs in Antarctic Porifera. Sponges showed legacy POP levels comparable to other benthic organisms from the same habitat and, as expected, much lower than sponge from northern temperate latitudes, confirming the Southern Ocean as one of the less contaminated ecosystems on Earth. The samples from the Ross Sea showed, in general, lower concentrations respect to the South Shetland Island samples, although differences were not statistically significant. In general, long-range atmospheric transport was confirmed as the major driver for contamination in the Antarctic areas where the study was performed. However, human presence and activities connected with research stations, as well as wildlife amplification and ice melting could also affect the bioaccumulation pattern found in these sponges. Future studies should also focus on increasing threats like tourism activities and fishing to better understand how and to which extent they could act synergically with other impacts in affecting the Antarctic ecosystems. While evaluation of species-specific patterns showed a few interesting results (peculiar patterns observed in the genus *Dendrilla* and in the *N. similis* individuals), further research is needed to clarify which mechanisms are involved in determining the observed inter- and intra-specific differences. Our results indicate that sponges may be suitable bioindicators for the benthic marine habitat. Moreover, they provide baseline data for future monitoring and contamination trend studies that, in the light of climate change, may well represent valid tools to

understand and make predictions on the threats Antarctica has to cope with.

Author statement

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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 availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.121661>.

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