Journal Pre-proof

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PII: S0269-7491(23)00663-2

DOI: https://doi.org/10.1016/j.envpol.2023.121661

Reference: ENPO 121661

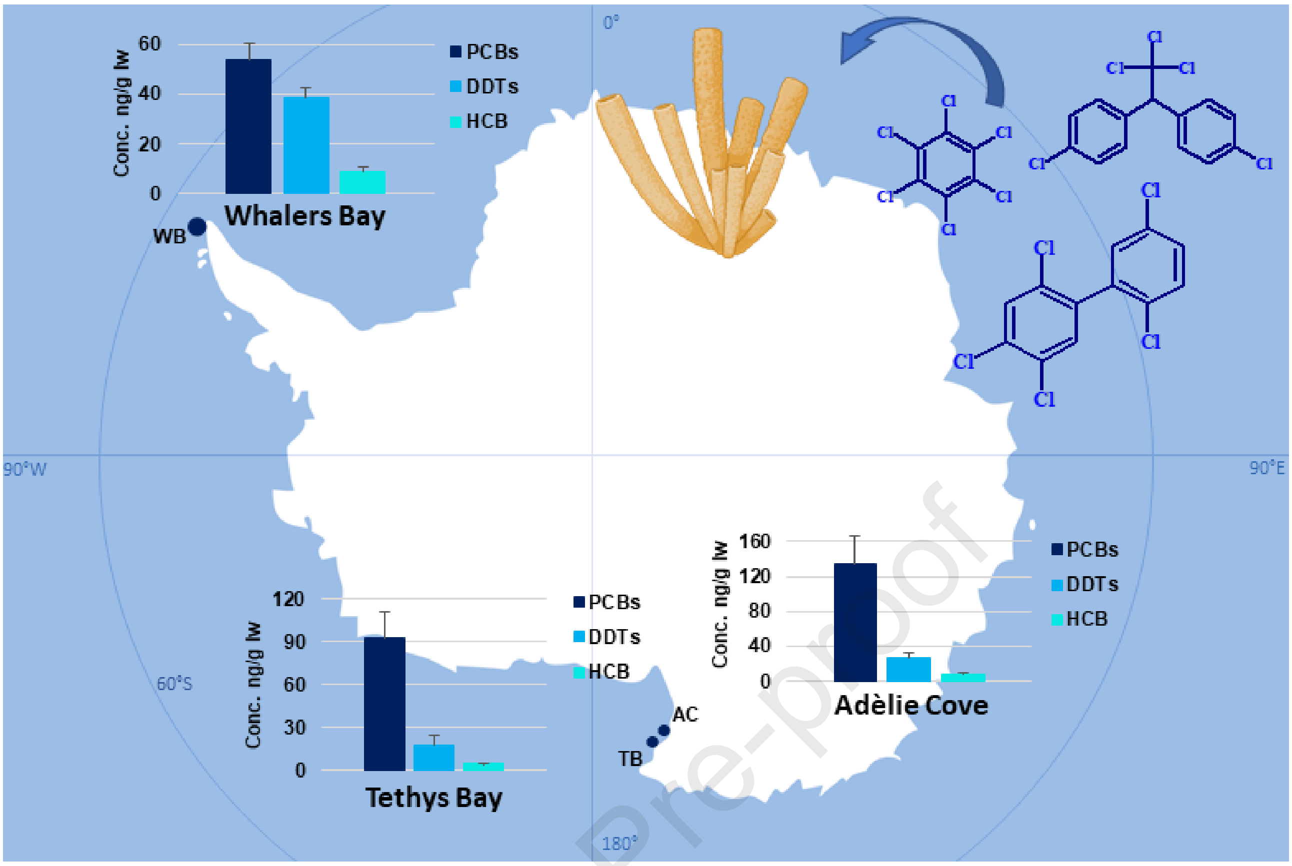
To appear in: *Environmental Pollution*

Received Date: 25 November 2022

Revised Date: 31 March 2023

Accepted Date: 16 April 2023

Please cite this article as: Pala, N., Jiménez, Begoñ., Roscales, J.L., Bertolino, M., Baroni, D., Figuerola, B., Avila, C., Corsolini, S., First evidence of legacy chlorinated POPs bioaccumulation in Antarctic sponges from the Ross sea and the South Shetland Islands, *Environmental Pollution* (2023), doi: https://doi.org/10.1016/j.envpol.2023.121661.



Whalers Bay
Conc. ng/g lw
60
40
20
0
PCBs
DDTs
HCB
WB
0°
90°W
90°E
60°S
180°
Tethys Bay
120
90
60
30
0
TB
AC
Adèlie Cove
160
120
80
40
Cl

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 ΣPCBs>ΣDDTs>HCB and it was found in almost every species. The ΣPCBs, ΣDDTs, and HCB ranged from 54.2 to133.7 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.

Keywords

PCBs

Chlorinated pesticides

Porifera

Southern Ocean

Bioaccumulation

Benthic organisms

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. 2022) and from pack ice melting (Casal et al. 2019; Potapowicz et al. 2019).

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. 2020; 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. 2020; Brasier et al. 2021; De Castro 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; Garcia et al. 1993; Iken et al. 2002; McClintock 1987, 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 inter-specific 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.

Materials and methods

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 Figure 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 (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; 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; 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 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°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).

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-analyzed® 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-analyzed® 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 °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 $^{13}C_{12}$-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 °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 °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 × 0.5 mm i.d. × 0.25 µm film thickness). Oven temperature program started at 120°C, held for 2 min, increased to 250°C at 35°C/min and held for 30 min, and finally ramped to 310 °C at 15°C/min and held for 30 min. The transfer line was set at a temperature of 280°C, the source at 230°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/µL) using the isotopic dilution technique.

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 ≤ 10 % of the mean values obtained for the calibration standards. Recoveries of labelled compounds were satisfactory in all cases (mean ± standard deviation): 93 ± 3 % for HCB, 89 ± 13 % for the PCB congeners nos. 28, 52, 101, 153, 138, 180, 209 (Σ_7PCBs) and 101 ± 13 % for the *o,p'*-DDT, *p,p'*-DDT and *p,p'*-DDE (Σ_3DDTs) (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 – 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 (Table S10, S11).

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 ½LOD. 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.

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: ∑PCB > ∑DDT > HCB in the three study sites (Table 1). Moreover, the pattern is confirmed in every individual (including the only Hexactinellid specimen) except for *Neopetrosia similis* (HCB > ∑PCB > ∑DDT) and one sample of *Dendrilla antarctica* (∑DDT > ∑PCB > HCB) (Figure 2). In fact, it is interesting to note that the species *N. similis* collected at Adèlie 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, ∑DDT percentage in the genus *Dendrilla* ranged from 30 to 50% while in the other genus it was between 4 and 30% (Figure 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.

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) (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 (Corsolini 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 Adélie 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; Corsolini 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 (Figure 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 (Figure 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 (Figure S1), also confirming a contribution by the LRAT. Corsolini 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 (Figure S1). It is interesting to note that PCB-101 is the most abundant congener in the 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 steineni* 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 (Figure 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* (Perez et al. 2003).

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. 2003; Montone et al. 2005). 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 (Figure 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.

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* 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 Adèlie 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 Adèlie 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; Kallenborn 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

(ΣPCBs>ΣDDTs>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.

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 intraspecific 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.

Acknowledgements

The Ross Sea samples were collected during expeditions in the framework of the Italian National Antarctic Research Programme (PNRA) (PdR2013 C1_04). The authors thank Prof. Gaetano Odierna, Dr. Luigi Michaud and Dr. Nicoletta Borghesi for the collection of samples in the Ross Sea. The Deception Island samples were collected during the DISTANTCOM-2 cruise by the authors. This work was also supported by the Spanish Ministry of Economy and Competitiveness (MINECO) through the SENTINEL (CTM2015-70535-P to B. Jiménez) and the DISTANTCOM and BLUEBIO projects (CTM2013- 42667/ANT and CTM2016-78901/ANT to C. Avila). This research is part of POLARCSIC activities. This research is part of the collaboration between S. Corsolini, B. Jiménez and J.L. Roscales within the Action Group of the Scientific Committee on Antarctic Research (SCAR) on Input Pathways of Persistent Organic Pollutants to Antarctica (ImPACT Action Group). This research is also part of Ant-ICON research program (SCAR). J.L.R. acknowledges CSIC and MITERD for his contract under Projects 15CAES004 and 17CAES004. B.F. received funding from the post-doctoral fellowships programme Beatriu de Pinós funded by the Secretary of Universities and Research (Government of Catalonia) and by the Horizon 2020 Programme of Research and Innovation of the European Union under the Marie Skłodowska-Curie grant agreement No. 801370 (Incorporation grant 2019 BP 00183) and the Juan de la Cierva Programme funded by the Ministry of Science and Innovation (Incorporation grant IJCI-2017-31478). Special thanks go to the personnel of the Spanish Antarctic Station Gabriel de Castilla for their help and support during the fieldwork.

References

Angulo-Preckler, C., Figuerola, B., Núñez-Pons, L., Moles, J., Martín-Martín, R., Rull-Lluch, J., Gómez-Garreta, A., Avila, C. 2018. Macrobenthic patterns at the shallow marine waters in the caldera of the active volcano of Deception Island, Antarctica. Continent. Shelf Res. 157, 20-31.

Aronson, R. B., Thatje, S., McClintock, J. B., & Hughes, K. A. 2011. Anthropogenic impacts on marine ecosystems in Antarctica. Annals of the New York Academy of Sciences, 1223(1), 82–107. https://doi.org/10.1111/j.1749-6632.2010.05926.x

Bailey, R.E., 2001. Global hexachlorobenzene emissions. Chemosphere 43, 167–182. https://doi.org/10.1016/S0045-6535(00)00186-7

Ballschmiter, K., Klingler, D., Ellinger, S., Hackenberg, R., 2005. High-resolution gas chromatography retention data as a basis for estimation of the octanol-water distribution coefficients (K_{ow}) of PCB: The effect of experimental conditions. Anal. Bioanal. Chem. 382, 1859–1870. https://doi.org/10.1007/s00216-005-3307-0

Bargagli, R., 2008. Environmental contamination in Antarctic ecosystems. Sci. Total Environ. 400, 212–226. https://doi.org/10.1016/j.scitotenv.2008.06.062

Barnes, D.K.A., Linse, K., Enderlein, P., Smale, D., Fraser, K.P.P., Brown, M., 2008. Marine richness and gradients at Deception Island, Antarctica. Antarct. Sci. 20, 271–279. https://doi.org/10.1017/S0954102008001090

Bates, M. L., Bengtson Nash, S. M., Hawker, D. W., Shaw, E. C. & Cropp, R. A., 2017. The distribution of persistent organic pollutants in a trophically complex Antarctic ecosystem model. J. Mar. Syst. 170, 103–114. http://dx.doi.org/10.1016/j.jmarsys.2017.02.005

Batista, D., Muricy, G., Rocha, R.C., Miekeley, N.F., 2014. Marine sponges with contrasting life histories can be complementary biomonitors of heavy metal pollution in coastal ecosystems. Environ. Sci. Pollut. Res. 21, 5785–5794. https://doi.org/10.1007/s11356-014-2530-7

Batista, D., Tellini, K., Nudi, A.H., Massone, T.P., Scofield, A. de L., Wagener, A. de L.R., 2013. Marine sponges as bioindicators of oil and combustion derived PAH in coastal waters. Mar. Environ. Res. 92, 234–243. https://doi.org/10.1016/j.marenvres.2013.09.022

Bengtson Nash, S.M., Wild, S.J., Hawker, D.W., Cropp, R.A., Hung, H., Wania, F., Xiao, H., Bohlin-Nizzetto, P., Bignert, A., Broomhall, S., 2017. Persistent organic pollutants in the east Antarctic atmosphere: Inter-annual observations from 2010 to 2015 using high-flow-through passive sampling. Environ. Sci. Technol. 51, 13929–13937. https://doi.org/10.1021/acs.est.7b04224

Borghesi, N., Corsolini, S., Focardi, S., 2011. Pop levels in two species of Antarctic invertebrates: the sea star (*Odontaster validus*) and the sea urchin (*Sterechinus neumayeri*). Organohalogen Compd. 73, 1087–1090.

Brasier, M. J., Barnes, D., Bax, N., Brandt, A., Christianson, A. B., Constable, A. J., Downey, R., Figuerola, B., Griffiths, H., Gutt, J., Lockhart, S., Morley, S. A., Post, A. L., & Renaud, P. E., 2021. Responses of Southern Ocean Seafloor Habitats and Communities to Global and Local Drivers of Change. Front. Mar. Sci. 8, 622721. doi: 10.3389/fmars.2021.622721Cai, C., Stewart, D.J., Reid, J.P., Zhang, Y.H., Ohm, P., Dutcher, C.S., Clegg, S.L., 2015. Organic component vapor pressures and hygroscopicities of aqueous aerosol measured by optical tweezers. J. Phys. Chem. A 119, 704–718. https://doi.org/10.1021/jp510525r

Cabrerizo, A., Dachs, J., Barceló, D., Jones, K.C., 2012. Influence of organic matter content and human activities on the occurrence of organic pollutants in Antarctic soils, lichens, grass, and mosses. Environ. Sci. Technol. 46, 1396–1405. https://doi.org/10.1021/es203425b

Cardona, L., Lloret-Lloret, E., Moles, J., Avila, C. 2021. Latitudinal changes in the trophic structure of benthic coastal food webs in the Antarctic Peninsula. Mar. Environ. Res. 167, 105290. https://doi.org/10.1016/j.marenvres.2021.105290

Casal, P., Casas, G., Vila-Costa, M., Cabrerizo, A., Pizarro, M., Jiménez, B., & Dachs, J.,2019. Snow amplification of persistent organic pollutants at coastal Antarctica. Environ. Sci. Technol. 53(15), 8872–8882. https://doi.org/10.1021/acs.est.9b03006

Casas, G., Martínez-Varela, A., Roscales, J. L., Vila-Costa, M., Dachs, J., & Jiménez, B.,2020. Enrichment of perfluoroalkyl substances in the sea-surface microlayer and sea-spray aerosols in the Southern Ocean. Environ. Pollut. 267, 115512. https://doi.org/10.1016/j.envpol.2020.115512

Casas, G., Martínez-Varela, A., Vila-Costa, M., Jiménez, B. & Dachs, J., 2021. Rain Amplification of Persistent Organic Pollutants. Environ. Sci. Technol. 55 (19), 12961–12972. https://doi.org/10.1021/acs.est.1c03295

Cattaneo-Vietti, R., Chiantore, M., Gambi, M.C., Albertelli, G., Cormaci, M., Di Geronimo, I., 2000. Spatial and Vertical Distribution of Benthic Littoral Communities in Terra Nova Bay. Ross Sea Ecol. 503–514. https://doi.org/10.1007/978-3-642-59607-0_36

Cerrano, C., Bertolino, M., Valisano, L., Bavestrello, G., Calcinai, B., 2009. Epibiotic demosponges on the Antarctic scallop *Adamussium colbecki* (Smith, 1902) and the cidaroid urchins *Ctenocidaris perrieri* Koehler, 1912 in the nearshore habitats of the Victoria Land, Ross Sea, Antarctica. Polar Biol. 32, 1067–1076. https://doi.org/10.1007/s00300-009-0606-5

Chen, D., Hale, R.C., La Guardia, M.J., Luellen, D., Kim, S., Geisz, H.N., 2015. Hexabromocyclododecane flame retardant in Antarctica: Research stations as sources. Environ. Pollut. 206, 611–618. https://doi.org/10.1016/j.envpol.2015.08.024

Chown, S. L., Clarke, A., Fraser, C. I., Cary, S. C., Moon, K. L., & McGeoch, M. A. (2015). The changing form of Antarctic biodiversity. Nature, 522(7557), 431–438. https://doi.org/10.1038/nature14505

Cincinelli, A., Martellini, T., Del Bubba, M., Lepri, L., Corsolini, S., Borghesi, N., King, M.D., Dickhut, R.M., 2009. Organochlorine pesticide air-water exchange and bioconcentration in krill in the Ross Sea. Environ. Pollut. 157, 2153–2158. https://doi.org/10.1016/j.envpol.2009.02.010

Cipro, C.V.Z., Bustamante, P., Taniguchi, S., Silva, J., Petry, M. V., Montone, R.C., 2019. Seabird colonies as relevant sources of pollutants in Antarctic ecosystems: Part 2 - Persistent Organic Pollutants. Chemosphere 214, 866–876. https://doi.org/10.1016/j.chemosphere.2018.09.030

Corsolini, S., 2009. Industrial contaminants in Antarctic biota. J. Chromatogr. A 1216, 598–612. https://doi.org/10.1016/j.chroma.2008.08.012

Corsolini, S., Ademollo, N., Focardi, S., 2003a. Persistent organic pollutants in selected organisms of an Antarctic benthic community. Organohalogen Compd. 61, 329-332.

Corsolini, S., Ademollo, N., Romeo, T., Olmastroni, S., Focardi, S., 2003b. Persistent organic pollutants in some species of a Ross Sea pelagic trophic web. Antarct. Sci. 15, 95–104. https://doi.org/10.1017/s0954102003001093

Corsolini, S., Ademollo, N., Martellini, T., Randazzo, D., Vacchi, M., & Cincinelli, A., 2017. Legacy persistent organic pollutants including PBDEs in the trophic web of the Ross Sea (Antarctica). Chemosphere, 185, 699–708. https://doi.org/10.1016/j.chemosphere.2017.07.054

Corsolini, S., Baroni, D., Martellini, T., Pala, N., Cincinelli, A., 2019. PBDEs and PCBs in terrestrial ecosystems of the Victoria Land, Antarctica. Chemosphere 231, 233–239. https://doi.org/10.1016/j.chemosphere.2019.05.126

Corsolini, S., Borghesi, N., Schiavone, A., Focardi, S., 2007. Polybrominated diphenyl ethers, polychlorinated dibenzo-dioxins, -furans, and -biphenyls in three species of Antarctic penguins. Environ. Sci. Pollut. Res. 14, 421–429. https://doi.org/10.1065/espr2006.01.017

Corsolini, S., Romeo, T., Ademollo, N., Greco, S., Focardi, S., 2002. POPs in key species of marine Antarctic ecosystem. Microchem. J. 73, 187–193. https://doi.org/10.1016/S0026-265X(02)00063-2

Corsolini, S., Sarà, G., 2017. The trophic transfer of persistent pollutants (HCB, DDTs, PCBs) within polar marine food webs. Chemosphere 177, 189–199. https://doi.org/10.1016/j.chemosphere.2017.02.116

Dayton, P.K., Robilliard, G.A., Paine, R.T., Dayton, L.B., 1974. Biological Accommodation in the Benthic Community at McMurdo Sound, Antarctica. Ecol. Monogr. 44, 105–128.

Dayton, P.K., 1989. Interdecadal variation in an Antarctic sponge and its predators from oceanographic climate shifts. Sci., 245, 1484-1486.

De Castro-Fernández, P., Cardona, L. & Avila, C., 2021. Distribution of trace elements in benthic infralittoral organisms from the western Antarctic Peninsula reveals no latitudinal gradient of pollution. Sci. Rep. 11, 16266. https://doi.org/10.1038/s41598-021-95681-5

Dibbern, J.S., 2010. Fur seals, whales and tourists: A commercial history of Deception Island, Antarctica. Polar Rec. (Gr. Brit). 46, 210–221. https://doi.org/10.1017/S0032247409008651

Dickhut, R.M., Cincinelli, A., Cochran, M., Ducklow, H.W., 2005. Atmospheric concentrations and air-water flux of organochlorine pesticides along the Western Antarctic Peninsula. Environ. Sci. Technol. 39, 465–470. https://doi.org/10.1021/es048648p

Di Giglio, S., Agüera, A., Pernet, P., M'Zoudi, S., Angulo-Preckler, C., Avila, C., & Dubois, P., 2021. Effects of ocean acidification on acid-base physiology, skeleton properties, and metal contamination in two echinoderms from vent sites in Deception Island, Antarctica. Sci. Total Environ. 765, 142669. https://doi.org/10.1016/j.scitotenv.2020.142669

Evenset, A., Carroll, J., Christensen, G.N., Kallenborn, R., Gregor, D., Gabrielsen, G.W., 2007. Seabird guano is an efficient conveyer of persistent organic pollutants (POPs) to Arctic lake ecosystems. Environ. Sci. Technol. 41, 1173–1179. https://doi.org/10.1021/es0621142

Evenset, A., Hallanger, I.G., Tessmann, M., Warner, N., Ruus, A., Borgå, K., Gabrielsen, G.W., Christensen, G., Renaud, P.E., 2016. Seasonal variation in accumulation of persistent organic pollutants in an Arctic marine benthic food web. Sci. Total Environ. 542, 108–120. https://doi.org/10.1016/j.scitotenv.2015.10.092

Figuerola, B., Hancock, A. M., Bax, N., Cummings, V. J., Downey, R., Griffiths, H. J., Smith, J., & Stark, J. S., 2021. A Review and Meta-Analysis of Potential Impacts of Ocean Acidification on Marine Calcifiers From the Southern Ocean. Front. Mar. Sci. 8, 584445. https://doi.org/10.3389/fmars.2021.584445

Figuerola B, Griffiths H, Krzeminska M,Piwoni-Piorewicz A, Iglikowska A, Kuklinski P. 2022. Temperature as a likely driver shaping global patterns in mineralogical composition in bryozoans: Implications for marine calcifiers under Global Change. Ecography 10.1111/ecog.06381 doi: https://doi.org/10.1101/2022.09.30.510275

Focardi, S., Bargagli, R., Corsolini, S., 1993. Organochlorines in Antarctic Marine Food Chain at Terranova Bay (Ross Sea). Korean J. Polar Res. 4, 73–77.

García, F.J., Troncoso, J.S., Garcia-Gómez, J.C., Lucas, J., 1993. Anatomical and taxonomical studies of the Antarctic nudibranchs *Austrodoris kerguelenensis* (Bergh, 1884) and *A. georgiensis* n. sp. from the Scotia Sea. Polar Biol. 13, 417–421.

Gatti S., 2002. The role of sponges in high-Antarctic carbon and silicon cycling: a modelling approach. Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, 434, 1-134.

Geisz, H.N., Dickhut, R.M., Cochran, M. a, Fraser, W.R., Ducklow, H.W., 2008. Melting glaciers: A probably source of DDT to the Antarctic marine ecosystem. Environ. Sci. Technol. 42, 3958–3962. https://doi.org/10.1021/es702919n

Genta-Jouve, G., Cachet, N., Oberhänsli, F., Noyer, C., Teyssié, J.L., Thomas, O.P., Lacoue-Labarthe, T., 2012. Comparative bioaccumulation kinetics of trace elements in Mediterranean marine sponges. Chemosphere 89, 340–349. https://doi.org/10.1016/j.chemosphere.2012.04.052

Gentric, C., Rehel, K., Dufour, A., Sauleau, P., 2016. Bioaccumulation of metallic trace elements and organic pollutants in marine sponges from the South Brittany Coast, France. J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 51, 213–219. https://doi.org/10.1080/10934529.2015.1094327

Goutte, A., Chevreuil, M., Alliot, F., Chastel, O., Cherel, Y., Eléaume, M., Massé, G., 2013. Persistent organic pollutants in benthic and pelagic organisms off Adélie Land, Antarctica. Mar. Pollut. Bull. 77, 82–89. https://doi.org/10.1016/j.marpolbul.2013.10.027

Grotti, M., Pizzini, S., Abelmoschi, M.L., Cozzi, G., Piazza, R., Soggia, F., 2016. Retrospective biomonitoring of chemical contamination in the marine coastal environment of Terra Nova Bay (Ross Sea, Antarctica) by environmental specimen banking. Chemosphere 165, 418–426. https://doi.org/10.1016/j.chemosphere.2016.09.049

Hooper, John NA. Sponguide: guide to sponge collection and identification. Queensland museum, 2000.

Hooper, J.N. & van Soest, R.W., 2002. Systema Porifera. A guide to the classification of sponges. Springer, Boston, Massachusetts, 1707 + XCIV pp. https://doi.org/10.1007/978-1-4615-0747-5

Iken, K., Avila, C., Fontana, A., Gavagnin, M., 2002. Chemical ecology and origin of defensive compounds in the Antarctic nudibranch *Austrodoris kerguelenensis* (Opisthobranchia: Gastropoda). Mar. Biol. 141, 101–109. https://doi.org/10.1007/s00227-002-0816-7 K.

Kallenborn, R., Breivik, K., Eckhardt, S., Lunder, C.R., Manø, S., Schlabach, M., Stohl, A., 2013. Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. Atmos. Chem. Phys. 13, 6983–6992. https://doi.org/10.5194/acp-13-6983-2013

Kersken, D., Feldmeyer, B., Janussen, D., 2016. Sponge communities of the Antarctic Peninsula: influence of environmental variables on species composition and richness. Polar Biol. 39, 851–862. https://doi.org/10.1007/s00300-015-1875-9

Ko, F.C., Pan, W.L., Cheng, J.O., Chen, T.H., Kuo, F.W., Kao, S.J., Chang, C.W., Ho, H.C., Wang, W.H., Fang, L.S., 2018. Persistent organic pollutants in Antarctic notothenioid fish and invertebrates associated with trophic levels. PLoS One 13, 1–11. https://doi.org/10.1371/journal.pone.0194147

Krasnobaev, A., ten Dam, G., Boerrigter-Eenling, R., Peng, F., van Leeuwen, S.P.J., Morley, S.A., Peck, L.S., van den Brink, N.W., 2020. Erratum: Legacy and emerging persistent organic pollutants in Antarctic benthic invertebrates near Rothera point, western Antarctic Peninsula (Environ. Sci. Technol. 54(5), 2763-2771. DOI: 10.1021/acs.est.9b06622). Environ. Sci. Technol. 54, 7023. https://doi.org/10.1021/acs.est.0c01724

Ma, J., Hung, H., Tian, C., Kallenborn, R., 2011. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. Nat. Clim. Chang. 1, 255–260. https://doi.org/10.1038/nclimate1167

Mão de Ferro, A., Mota, A.M., Canário, J., 2013. Sources and transport of As, Cu, Cd and Pb in the environmental compartments of Deception Island, Antarctica. Mar. Pollut. Bull. 77, 341–348. https://doi.org/10.1016/j.marpolbul.2013.08.037

Matsuoka, K., Skoglund, A., Roth, G., de Pomereu, J., Griffiths, H., Headland, R., Herried, B., Katsumata, K., Le Brocq, A., Licht, K., Morgan, F., Neff, P. D., Ritz, C., Scheinert, M.,Tamura, T., Van de Putte, A., van den Broeke, M., von Deschwanden, A., Deschamps-Berger, C., Van Liefferinge, B.,Tronstad, S., Melvær, Y., 2021. Quantarctica, an integrated mapping environment for Antarctica, the Southern Ocean, and sub-Antarctic islands. Environ. Model. Softw. 140, 1-14. https://doi.org/10.1016/j.envsoft.2021.105015

McClintock, J.B., 1987. Investigation of the relationship between invertebrate predation and biochemical composition, energy content, spicule armament and toxicity of benthic sponges at McMurdo Sound, Antarctica. Mar. Biol. 94, 479–487. https://doi.org/10.1007/BF00428255

McClintock, J.B., Amsler, C.D., Baker, B.J., Soest, R.W.M. Van, Oceans, T.S., 2005. Ecology of Antarctic Marine Sponges: An Overview. Integr. Comp. Biol. 45, 359–368.

Mello, F. V., Roscales, J. L., Guida, Y. S., Menezes, J. F. S., Vicente, A., Costa, E. S., Jiménez, B., & Torres, J. P. M., 2016. Relationship between legacy and emerging organic pollutants in Antarctic seabirds and their foraging ecology as shown by δ13C and δ15N. Sci. Total Environ. 573, 1380–1389. https://doi.org/10.1016/j.scitotenv.2016.07.080

Meredith, M., Sommerkorn, M., Cassotta, S., Derksen, C., Ekaykin, A., and Hollowed, A., et al., (eds) 2019. IPCC Special Report on the Oceans and Cryosphere in a changing climate. Geneva: Intergovernmental Panel on Climate Change.

Montone, R.C., Taniguchi, S., Weber, R.R., 2003. PCBs in the atmosphere of King George Island, Antarctica. Sci. Total Environ. 308, 167–173. https://doi.org/10.1016/S0048-9697(02)00649-6

Morales, P., Roscales, J. L., Muñoz-Arnanz, J., Barbosa, A., & Jiménez, B., 2022. Evaluation of PCDD/Fs, PCBs and PBDEs in two penguin species from Antarctica. Chemosphere, 286 (3), 131871. https://doi.org/10.1016/j.chemosphere.2021.131871

Moran, A. L., & Woods, H. A. (2012). Why might they be giants? Towards an understanding of polar gigantism. J. Exp. Biol., 215(12), 1995–2002. https://doi.org/10.1242/jeb.067066

Morrow, C. & Cárdenas, P., 2015. Proposal for a revised classification of the Demospongiae (Porifera). Front. Zool. 12 (1), 7. https://doi.org/10.1186/s12983-015-0099-8

Negri, A., Burns, K., Boyle, S., Brinkman, D., Webster, N., 2006. Contamination in sediments, bivalves and sponges of McMurdo Sound, Antarctica. Environ. Pollut. 143, 456–467. https://doi.org/10.1016/j.envpol.2005.12.005

Perez, T., Vacelet, J., Rebouillon, P., 2004. In situ comparative study of several Mediterranean sponges as potential biomonitors for heavy metals. Boll. Mus. Ist. Biol. Univ. Genova 68, 517–525.

Perez, T., Wafo, E., Fourt, M., Vacelet, J., 2003. Marine sponges as biomonitor of polychlorobiphenyl contamination: Concentration and fate of 24 congeners. Environ. Sci. Technol. 37, 2152–2158. https://doi.org/10.1021/es026234v

Potapowicz, J., Szumińska, D., Szopińska, M., Polkowska, Ż., 2019. The influence of global climate change on the environmental fate of anthropogenic pollution released from the permafrost: Part I. Case study of Antarctica. Sci. Total Environ. 651, 1534–1548. https://doi.org/10.1016/j.scitotenv.2018.09.168

Povero, P., Chiantore, M., Misic, C., Budillon, G., Cattaneo-Vietti, R., 2001. Land forcing controls pelagic-benthic coupling in Adèlie Cove (Terra Nova Bay, Ross Sea). Polar Biol. 24, 875–882. https://doi.org/10.1007/s003000100286

Pozo, K., Sarkar, S. K., Estellano, V. H., Mitra, S., Audi, O., Kukucka, P., Přibylová, P., Klánová, J., & Corsolini, S. (2017). Passive air sampling of persistent organic pollutants (POPs) and emerging compounds in Kolkata megacity and rural mangrove wetland Sundarban in India: An approach to regional monitoring. Chemosphere, 168, 1430–1438. https://doi.org/10.1016/j.chemosphere.2016.09.055

Rainbow, P.S., 1995. Biomonitoring of heavy metal availability in the marine environment. Mar. Pollut. Bull. 31, 183–192. https://doi.org/10.1016/0025-326X(95)00116-5

Ricking, M., Schwarzbauer, J., 2012. DDT isomers and metabolites in the environment: An overview. Environ. Chem. Lett. 10, 317–323. https://doi.org/10.1007/s10311-012-0358-2

Romero-Romero, S., Herrero, L., Fernández, M., Gómara, B., Acuña, J.L., 2017. Biomagnification of persistent organic pollutants in a deep-sea, temperate food web. Sci. Total Environ. 605–606, 589–597. https://doi.org/10.1016/j.scitotenv.2017.06.148

Roosens, L., Van Den Brink, N., Riddle, M., Blust, R., Neels, H., Covaci, A., 2007. Penguin colonies as secondary sources of contamination with persistent organic pollutants. J. Environ. Monit. 9, 822–825. https://doi.org/10.1039/b708103k

Roscales, J.L., González-Solís, J., Zango, L., Ryan, P.G., Jiménez, B., 2016a. Latitudinal exposure to DDTs, HCB, PCBs, PBDEs and DP in giant petrels (*Macronectes* spp.) across the Southern Ocean. Environ. Res. 148, 285–294. https://doi.org/10.1016/j.envres.2016.04.005

Roscales, J.L., Vicente, A., Muñoz-Arnanz, J., Morales, L., Abad, E., Aguirre, J.I., Jiménez, B., 2016b. Influence of trophic ecology on the accumulation of dioxins and furans (PCDD/Fs), non-ortho polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) in Mediterranean gulls (*Larus michahellis and L. audouinii*): A three-isotope approach. Environ. Pollut. 212, 307–315. https://doi.org/10.1016/j.envpol.2016.01.078

Roura, R., 2012. Being there: examining the behaviour of Antarctic tourists through their blogs. Polar Res. 31, 10905. https://doi.org/10.3402/polar.v31i0.10905

Rützler, K., 1978. Sponges in coral reefs. In: Stoddart, D.R. & Johannes, R.E. (Eds.), Coral reefs: research methods. Monographs on oceanographic methodology. Vol. 5. Unesco, Paris, pp. 299–313.

Stockholm Convention, 2004. Stockholm Convention available at. http://chm.pops.int

Van Den Brink, N., Riddle, M., Van Den Heuvel-Greve, M., Allison, I., Snape, I., Van Franeker, J.A., 2009. Correspondence on Geisz et al. melting glaciers: A probable source of DDT to the Antarctic marine ecosystem. Environ. Sci. Technol. 43, 3976–3977. https://doi.org/10.1021/es8034494 van Soest, R. W. M., Boury-Esnault, N., Vacelet, J., Dohrmann, M., Erpenbeck, D., de Voogd, N. J., Santodomingo, N., Vanhoorne, B., Kelly, M., & Hooper, J. N. A., 2012. Global diversity of sponges (Porifera). PLoS ONE, 7(4), e35105. https://doi.org/10.1371/journal.pone.0035105

Vecchiato, M., Zambon, S., Argiriadis, E., Barbante, C., Gambaro, A., Piazza, R., 2015. Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Antarctic ice-free areas: Influence of local sources on lakes and soils. Microchem. J. 120, 26–33. https://doi.org/10.1016/j.microc.2014.12.008

Vogel, S., 1977. Current-induced flow through living sponges in nature. Proc. Natl. Acad. Sci. 74, 2069–2071. https://doi.org/10.1073/pnas.74.5.2069

de Voogd, N.J.; Alvarez, B.; Boury-Esnault, N.; Carballo, J.L.; Cárdenas, P.; Díaz, M.-C.; Dohrmann, M.; Downey, R.; Hajdu, E.; Hooper, J.N.A.; Kelly, M.; Klautau, M.; Manconi, R.; Morrow, C.C. Pisera, A.B.; Ríos, P.; Rützler, K.; Schönberg, C.; Vacelet, J.; van Soest, R.W.M. (2022). World Porifera Database. Accessed at https://www.marinespecies.org/porifera on 2022-01-31. doi:10.14284/359

Wang, G., Lu, Y., Han, J., Luo, W., Shi, Y., Wang, T., Sun, Y., 2010. Hexachlorobenzene sources, levels and human exposure in the environment of China. Environ. Int. 36, 122–130. https://doi.org/10.1016/j.envint.2009.08.005

Wania, F., Mackay, D., 1993. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio 22, 10–18. https://doi.org/10.2307/4314030

Zanardi-Lamardo, E., Mitra, S., Vieira-Campos, A. A., Cabral, C. B., Yogui, G. T., Sarkar, S. K., Biswas, J. K., & Godhantaraman, N., 2019. Distribution and sources of organic contaminants in surface sediments of Hooghly river estuary and Sundarban mangrove, eastern coast of India. Mar. Pollut. Bull., 146, 39–49. https://doi.org/10.1016/j.marpolbul.2019.05.043

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 ± standard deviation, minimum and maximum values in brackets) and values < LOD (LOD %).

	Tethys Bay (n=7)	**Adèlie Cove (n=13)**	**Whalers Bay (n=3)**	**<LOD %**
PCB-28	7.5 ± 6.7	14.9 ± 14.9	3.5 ± 1.9	9
	(<LOD – 21.2)	(<LOD – 52.4)	(1.9 – 5.6)	
PCB-52	17.5 ± 18.9	21.1 ± 18.9	6.0 ± 1.9	4
	(<LOD – 43.5)	(4.4 – 68.6)	(4.9 – 8.2)	
PCB-101	12.5 ± 12.4	30.3 ± 51.1	21.5 ± 10.0	4
	(<LOD – 36.1)	(0.3 – 196.2)	(10.5 – 30.1)	
PCB-105	3.2 ± 1.4	6.4 ± 4.0	4.1 ± 0.3	74
	(<LOD – 5.1)	(<LOD – 16.5)	(<LOD – 4.4)	
PCB-118	4.3 ± 3.2	10.6 ± 14.0	5.1 ± 0.9	0
	(0.7 – 9.8)	(0.8 – 52.1)	(4.1 – 5.8)	
PCB-123	5.0 ± 2.4	9.0 ± 4.8	2.7 ± 0.0	91
	(<LOD – 8.5)	(<LOD – 17.0)	(<LOD – 2.7)	
PCB-126	3.0 ± 1.7	6.1 ± 3.2	1.7 ± 0.0	96
	(<LOD – 5.4)	(<LOD – 10.9)	(<LOD – 1.7)	
PCB-138	10.0 ± 6.8	12.5 ± 13.0	4.4 ± 0.9	0
	(2.6 – 21.6)	(1.5 – 46.3)	(3.6 – 5.5)	
PCB-153	10.4 ± 12.8	12.5 ± 14.2	2.9 ± 0.3	0
	(1.5 – 38.5)	(1.5 – 41.9)	(2.7 – 3.2)	
PCB-167	2.0 ± 1.4	2.2 ± 1.2	0.7 ± 0.0	87
	(<LOD – 4.9)	(<LOD – 4.2)	(<LOD – 0.7)	
PCB-180	17.5 ± 30.8	8.2 ± 8.1	1.4 ± 1.4	4
	(<LOD – 86.2)	(0.5 – 26.0)	(0.4 – 3.0)	
∑PCB	**92.8 ± 47.6**	**133.7 ± 119.3**	**54.2 ± 10.8**	
	(27.7 – 164.7)	**(39.8 – 482.8)**	**(41.9 – 62.0)**	
***o,p'*-DDT**	2.5 ± 2.8	2.9 ± 1.4	3.4 ± 2.8	78
	(<LOD – 8.2)	(<LOD – 5.1)	(1.5 – 6.6)	
***p,p'*-DDT**	4.8 ± 6.2	5.1 ± 3.6	11.0 ± 2.1	70

	(<LOD – 17.3)	(<LOD – 14.7)	(9.6 – 13.4)	
***o,p'*-DDE**	1.5 ± 0.6	2.7 ± 1.4	3.9 ± 1.8	78
	(<LOD – 2.2)	(<LOD – 5.2)	(1.8 – 5.3)	
***p,p'*-DDE**	7.3 ± 8.9	14.1 ± 12.5	19.6 ± 5.0	30
	(<LOD – 24.5)	(<LOD – 38.3)	(13.9 – 23.6)	
***p,p'*-DDD**	1.3 ± 0.6	2.4 ± 1.2	0.7 ± 0.0	91
	(<LOD – 1.9)	(<LOD – 4.5)	(<LOD – 0.7)	
∑DDT	**17.5 ± 18.3**	**27.2 ± 17.1**	**38.6 ± 7.4**	
	(5.6 – 53.7)	**(9.3 – 59.2)**	**(31.3 – 46.1)**	
HCB	**4.8 ± 1.8**	***8.1 ± 5.0**	**8.5 ± 4.0**	4
	(3.0 – 7.3)	**(<LOD – 19.6)**	**(5.7 – 13.1)**	

*mean calculated on 12 samples

Figure legends

Figure 1: a) Antarctic continent with the indication of the two areas where the sampling site 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.

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

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

Figure 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).

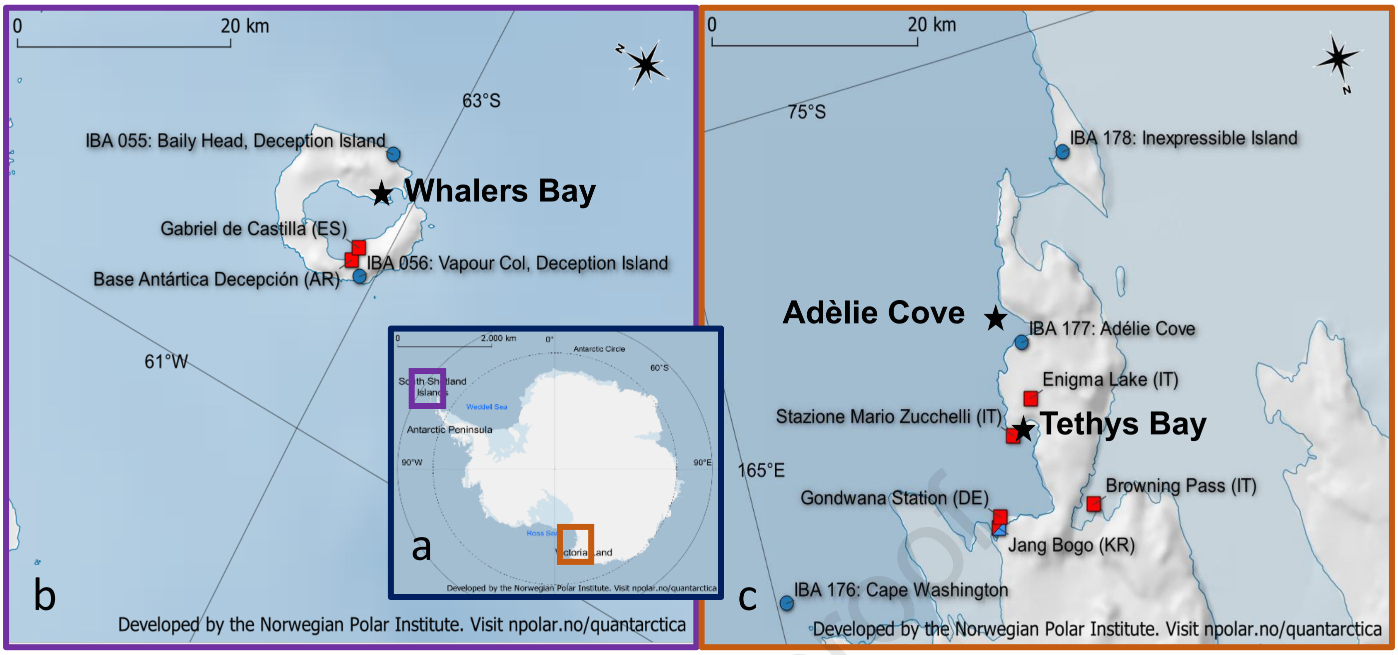

0
20 km
63°S
IBA 055: Baily Head, Deception Island
Whalers Bay
Gabriel de Castilla (ES)
IBA 056: Vapour Col, Deception Island
Base Antártica Decepción (AR)
61°W
b
Developed by the Norwegian Polar Institute. Visit npolar.no/quantarctica
2.000 km
Antarctic Circle
60°S
Weddell Sea
Antarctic Peninsula
90°W
90°E
a
Developed by the Norwegian Polar Institute. Visit npolar.no/quantarctica
0
20 km
75°S
IBA 178: Inexpressible Island
Adèlie Cove
IBA 177: Adélie Cove
Enigma Lake (IT)
Stazione Mario Zucchelli (IT)
Tethys Bay
165°E
Gondwana Station (DE)
Browning Pass (IT)
Jang Bogo (KR)
IBA 176: Cape Washington
c
Developed by the Norwegian Polar Institute. Visit npolar.no/quantarctica

Figure 1

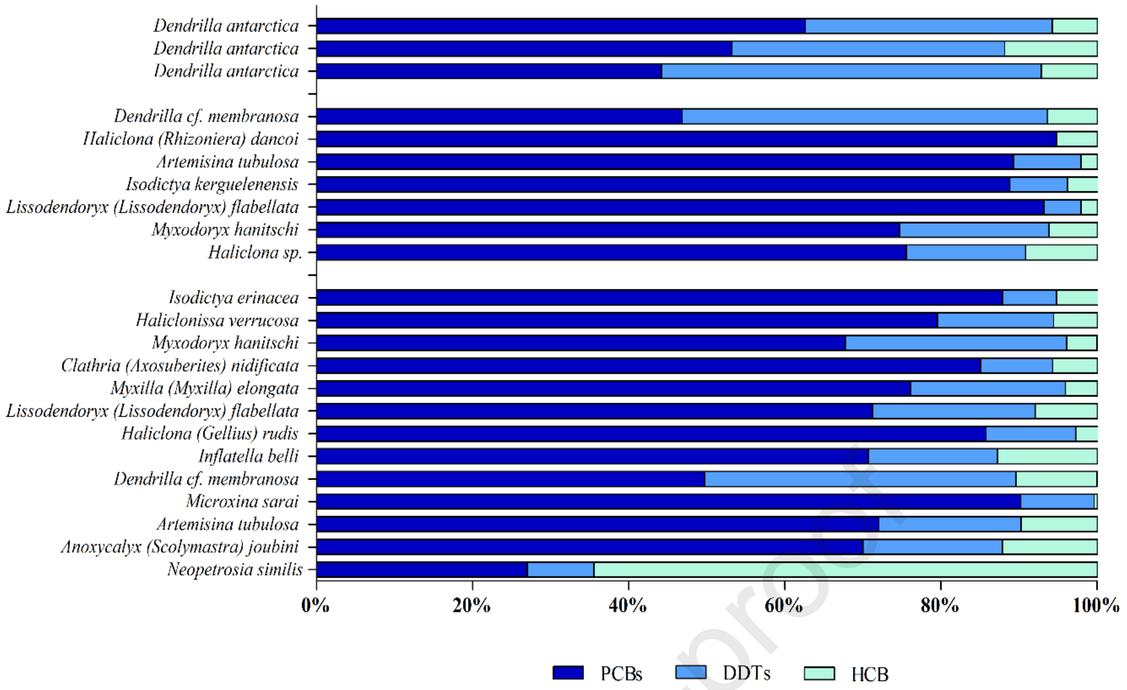

Dendrilla antarctica
Dendrilla antarctica
Dendrilla antarctica
Dendrilla cf. membranosa
Haliclona (Rhizoniera) dancoi
Artemisina tubulosa
Isodictya kerguelenensis
Lissodendoryx (Lissodendoryx) flabellata
Myxodoryx hanitschi
Haliclona sp.
Isodictya erinacea
Haliclonissa verrucosa
Myxodoryx hanitschi
Clathria (Axosuberites) nidificata
Myxilla (Myxilla) elongata
Lissodendoryx (Lissodendoryx) flabellata
Haliclona (Gellius) rudis
Inflatella belli
Dendrilla cf. membranosa
Microxina sarai
Artemisina tubulosa
Anoxycalyx (Scolymastra) joubini
Neopetrosia similis
0%
20%
40%
60%
80%
100%
PCBs
DDTs
HCB

Figure 2

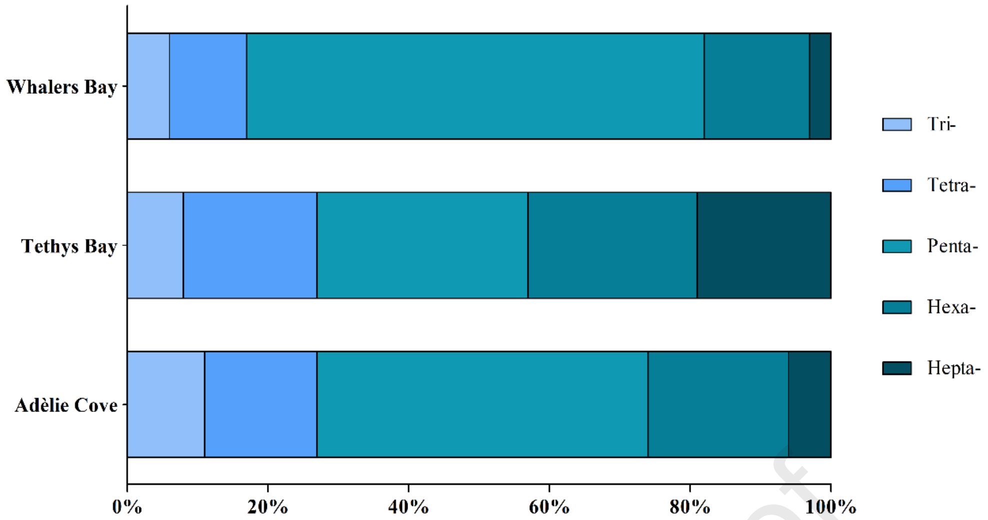
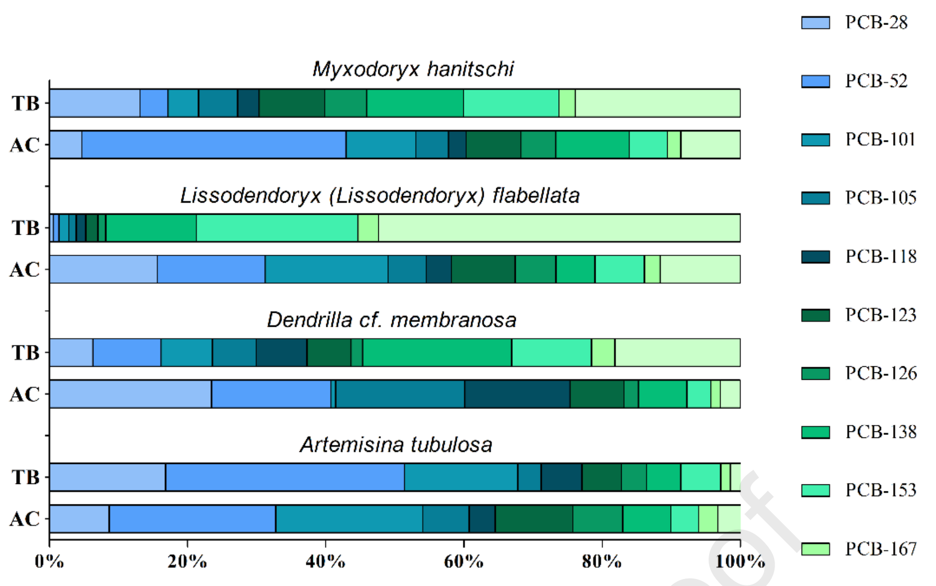

Whalers Bay
Tethys Bay
Adèlie Cove
0%
20%
40%
60%
80%
100%
Tri-
Tetra-
Penta-
Hexa-
Hepta-

Figure 3



843

844 Figure 4

Highlights

- First data about legacy chlorinated POPs in Antarctic sponges are reported
- Antarctic sponges are suitable organisms for legacy POPs contamination studies
- Sponges showed levels of contamination comparable to other benthic organisms
- DDTs and HCB concentrations in sponges: South Shetland Island > Ross Sea

Author statement

Nicolas Pala: Conceptualization, Formal analysis, Investigation, Data curation, Methodology, Writing - original draft.

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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: