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Organochlorine Pollutants in Western Antarctic Peninsula Sediments and Benthic Deposit Feeders.

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Abstract

Sediments and benthic deposit feeding holothurians were collected near the Palmer Long Term Ecological Research grid during the austral winter of 2008. Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were measured in Western Antarctic Peninsula continental shelf sediments, porewater, and benthic biota. Concentrations and fluxes in sediments decreased sharply away from the tip of the peninsula towards its interior. Sedimentary PCB fluxes were order of magnitudes lower than reported elsewhere, supporting the notion of a pristiner Antarctic environment. Hexa-chlorinated biphenyls dominated (40-100%) the PCB profiles in the sediments, while tri-chlorinated biphenyl 28 was the most abundant PCB congener in the porewater. PCB and OCP concentrations in holothurians were comparable to concentrations in other low trophic level biota in the Antarctic food web (i.e., krill). The partitioning of PCBs and OCPs between the sediments and porewater can be explained by a dual-mode model which included both organic carbon and black carbon as partitioning media. Alternatively, a simpler one-parameter prediction assuming coal tar-like organic carbon performed equally well in explaining porewater concentrations. The majorities of PCBs (63-94%) in the Western Antarctic Peninsula sediments were bound to black carbon or recalcitrant tar-like organic carbon, thereby lowering porewater concentrations. PCBs and OCPs in the holothurians were in equilibrium with those in the porewater.

Introduction

The Southern Ocean plays a pivotal role in the global carbon cycle and climate change ⁽¹⁾, leading to an increasing amount of scientific activities and the establishment of numerous research stations in the Antarctic ⁽²⁾. Increased anthropogenic activity will very likely place extra stress on Antarctic ecosystems, which includes the contamination by anthropogenic organic pollutants ⁽³⁾. Several baseline studies around deserted and current scientific research stations have been conducted to investigate local levels of contaminants ^(2, 4, 5). They have found patchy distribution of persistent organic pollutants (POPs) and higher concentrations of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) adjacent to scientific station ^(5, 6), indicating contamination from human activities. Atmospheric and oceanic long range transport may also contribute to the presence of POPs in the Antarctic ⁽⁷⁾. Fuoco et al. showed that PCBs were supplied by surrounding seas to the Ross Sea region ⁽⁸⁾. However, the 'westerlies' and Antarctic Circumpolar Current act as physical/dynamical barriers that may significantly impede the atmospheric and oceanic transport of POPs from the north ^(3, 9). The inter-hemispheric exchange in the atmosphere is slow as reflected by the strong hemispheric gradients in gas phase concentrations of POPs ⁽¹⁰⁾ and the north-south atmospheric delivery is less efficient than west-east within the Southern Hemisphere ⁽³⁾. It would take several hundred years for seawater formed in the Arctic to travel to the Southern Ocean according to the ¹⁴C data ^(11, 12) and modeling studies found the transport time for

North Atlantic Deep Water from 47°N to 30°S is about 150 years (25 ~ 300 years) and another 95 years (25 ~ 422 years) from 30°S to the Southern Ocean ^(13, 14)

Since the first detection of PCBs and organochlorine pesticides (OCPs) in the Antarctic five decades ago ^(15, 16), there have been dozens of investigations on the occurrence, distribution of POPs in Antarctic air ⁽¹⁷⁻²⁰⁾, water ^(8, 21), soil ^(2, 4), sediments ^(22, 23), and biota ⁽²⁴⁻³³⁾. Most of the studies were conducted at the tip of the Western Antarctic Peninsula (WAP) and Ross Sea area ^(2, 6). The physico-chemical properties of POPs plus the seasonal change in the sea ice result in POPs entering the Antarctic coastal waters. POPs deposit on the sea ice and migrate into it. Following sea ice melting, the POPs are released back into the water, where they can enter the sea ice microbial community, and surface phytoplankton and then be transferred within the food web. POPs in the pelagic food web in the Antarctic were found to biomagnify with trophic level ^(30, 33). Due to their lipophilic nature, POPs can be carried by sinking particulate organic matter (POC) downward to the sediments. When the POC is remineralized by microbes, POPs are released back to the water column or porewater, rendering them available for uptake by the benthos and microbes. To the best of our knowledge, no studies have been conducted on the fate of POPs in sediments and benthic biota in Antarctica. Previous studies suggested benthic-pelagic coupling during winter could occur ⁽³⁴⁾ when the pelagic food sources are limited. Partitioning of POPs from benthic media to benthos may represent another bioaccumulation pathway along the WAP food web.

POPs in the benthic media may be less available for uptake by biota due to the presence of black carbon. Previous studies have shown that adsorption onto black carbon present in the sediments can greatly reduce the availability of POPs in the porewater ⁽³⁵⁻³⁹⁾. Yet these studies have focused on areas strongly affected by human activities and have not investigated pristine locations such as Antarctic. Passive samplers have been proven to be a robust sampling device to determine truly dissolved porewater concentration of POPs ⁽³⁵⁻⁴⁰⁾. The importance of black carbon for reducing bioavailability in the porewater thus can be assessed using passive sampler ⁽³⁵⁻⁴⁰⁾.

The objectives of this study are to 1) provide the first data of POPs in the WAP benthic biota and porewater; 2) investigate the bioaccumulation of POPs by benthic deposit feeders and determine whether different feeding strategies affect body burdens; and 3) study the influence of sediment geochemistry (e.g., black carbon) on the porewater concentrations of POPs in the WAP sediments.

Materials and Methods

Sampling Locations

Sediments and benthic biota samples were collected from five different locations on the WAP shelf near the Palmer long term ecological research (LTER) grid in Jul 2008 (Fig1) ⁽⁴¹⁾. Sites 1 to 5 in this study are corresponding to site AA, B, E, F, and G in the FOODBANCS-2 project⁽⁴²⁾(http://www.soest.hawaii.edu/expeditions/blog_antarctica/foodbanacs2.html). The sampling locations covered a relatively large spatial range with site 1 close to

Livingstone Island (62.60°S, 60. 50°W) which is in the Southern Ocean away from the northern end of WAP, site 2 near Palmer Station (64.67°S, 64.05°W), and the rest further south towards the interior of the WAP (see Table 1 for details). The most northern site 1 is about 565 Km away from the most southern site 5. The top sediments (0-5 cm) were collected at approximately 600m depth using a Bowers and Connelly Megacorer (OSIL, Havant, Hampshire, UK, www.osil.co.uk). The benthic megafaunal samples were collected using a 5.5m semi-balloon otter trawl (2cm mesh). The sediments and biota samples were stored in clean amber glass jars with aluminum foil lined lids at -20° C until analysis.

Tumbling experiment

A non-depletive, polyethylene (PE) passive sampling technique was employed to measure the freely dissolved concentrations of PCBs and OCPs. Passive sampling has been shown by previous studies to be a reliable and robust approach to obtain porewater concentrations of POPs⁽³⁵⁻⁴⁰⁾. The detailed methods have been described elsewhere⁽³⁷⁾. Approximately 100 g wet weight (40 - 60 g, dry weight) of sediments was added to clean, 250 mL flat-bottom glass jars. A PE sampler (~ 2g) and sodium azide (final concentration = 0.43 µmol/mL) were also added to each jar which was then filled with Milli-Q water. Laboratory blanks were composed of a PE sheet, sodium azide, and Milli-Q water. The sodium azide acted as a biocide to avoid any biological interference with diffusion into the passive sampler. The sealed sediment-water slurries were placed on a shaker table and agitated until equilibrium was reached (~8 weeks).

During this time, the samples were kept in an environmental chamber at $20 \pm 1^\circ\text{C}$. Performance reference compounds (PRCs) were pre-impregnated in the PE and used to quantify the equilibrium between porewater-PE system following literature methods ^(43, 44, 44). See detailed information on PRCs in SI on page 6 and physical-chemical properties used in Table SI-7.

Laboratory Analysis

Details on organic carbon (OC), black carbon (BC), sample extraction, analysis, derived sedimentary fluxes, and QA/QC are given in the SI.

Partitioning models

The partitioning of hydrophobic POPs between the lipids in biota and porewater is governed by the partitioning coefficient (K_{lipid}) when equilibrium is reached.

$$K_{\text{lipid}} = \frac{C_{\text{lipid}}}{C_{\text{porewater}}} \quad \square$$

Where C_{lipid} is the concentrations of POPs in the lipids of biota (ng/g lipid) and $C_{\text{porewater}}$ is the concentrations of POPs in the porewater (pg/L). Traditionally, absorption into OC was considered as the dominant sorption process between sediments and porewater. This process can be modeled as:

$$K_D = f_{\text{TOC}} K_{\text{OC}} \quad \square$$

$$K_{\text{OC}} = \frac{C_{\text{sediments}}}{C_{\text{porewater}}} \quad \square$$

where K_D is the observed partitioning coefficients between the sediment and the pore water (mL/g), $C_{\text{sediments}}$ is the concentration of PCBs and OCPs in the sediments (ng/g dry weight), f_{TOC} is the OC fraction present in the sediment (%), g

OC/g sediment dry weight) and K_{OC} is the equilibrium partitioning coefficient between OC and water (mL/g).

Absorption of POPs from water into octanol has been used as a standard partitioning reference to describe the absorptive partitioning to general organic phases. A slope close to 1 of the linear regression between $\log K_{OC}$ and $\log K_{OW}$ indicated similar processes controlled partitioning into OC and n-octanol ⁽⁴⁵⁾.

$$\log K_{OC} = 0.97 \cdot \log K_{OW} - 0.12 \quad \square$$

The K_{OC} values were derived from the linear free energy relationship (LFER) with corresponding octanol-water partitioning coefficients (K_{OW}) (Equation $\square$) ⁽⁴⁵⁾. The K_{OC} LFER relationship was derived for only biogenic source OC and humic substances that were not produced by burning (pyrogenic source > 50 °C) and not altered by diagenetic effects ⁽⁴⁶⁾. In other words, the derived K_{OC} did not include any BC contribution which is suitable for this partitioning model (Equation $\square$). The OC is also defined as amorphous organic carbon (AOC) in other studies ⁽³⁶⁾.

The following bimodal partitioning model has been proposed to account for the partitioning into BC ⁽⁴⁷⁾:

$$K_D = f_{OC} K_{OC} + f_{BC} K_{BC} C_{porewater}^{n-1} \quad \square$$

where f_{BC} is the fraction of BC present in the sediment (g BC/ g sediment, dry weight), $C_{porewater}$ in this equation $\square$ has a unit of ng/mL, K_{BC} is the equilibrium partitioning coefficients of POPs between BC and porewater (mL/g), which is dominated by adsorptive partitioning. And n is the Freundlich exponent for

adsorption onto BC, which reflects non-linear partitioning and often is found to be between 0.3 and 1⁽⁴⁸⁾. See detailed information on K_{BC} and K_{OW} in Table SI-7. Previous studies also provided an alternative one-carbon model approach (total organic carbon) to interpret the partitioning of pollutants between sediments and porewater^(36, 49-52). The TOC include both AOC and BC. Hawthorne et al⁽³⁶⁾ compiled log K_{TOC} (L/kg_{TOC}) for 53 different sediments historically contaminated with PCBs and suggested to use a coal-tar poly parameter linear-free energy relationship (pp-LFER) for estimating log K_{TOC} (See detailed information on log K_{TOC} in Table SI-7). We also followed this approach to predict the partitioning behavior of PCBs between sediment and porewater by modifying equation 2 (replacing K_{OC} with K_{TOC}).

Results and Discussion

Sediment & Biota Characteristics

Phytoplankton derived organic matter can be stored in the WAP shelf on the time scales of months and years, acting as a “foodbank” for benthic detritivores^(34, 53, 54). Previous studies also suggested that there was no or little variability among the organic matter in the WAP sediments, though there were seasonal pulse inputs of bloom-generated organic matter from the overlying water column⁽⁵⁵⁾. This has been evidenced by previous stable isotope studies on sinking particulate organic matter (POM), sediments, and benthic biota⁽⁵⁵⁾. The isotope signatures of POM and sediments showed little seasonal and inter-annual variations⁽⁵⁵⁾. Thus, benthic deposit feeders were exposed to similar fresh detrital carbon year-round⁽⁴²⁾. It is also expected that benthic detritivores showed

relatively little temporal changes in stable isotope ratios ⁽⁵⁵⁾. Bulk $\delta^{15}\text{N}$ measurements showed these benthic deposit feeders were one trophic level above sediment detrital food sources ⁽⁵⁵⁾. The *Protelpidia murrayi*, *Peniagone vignoni*, and *Bathyplores natans* are mobile, surface-deposit feeding holothurians. The *Molpadia musculus* is a head-down subsurface deposit feeding holothurian (or conveyor-belt feeder). According to the excess ^{234}Th activities in gut sediments ⁽³⁴⁾, *Peniagone* is a more selective feeder than *Bathyplores*, which in turn is more selective than *Protelpidia*, and than *Molpadia*. The former feeds selectively on high-quality fresh material at the sediment-water interface during all seasons even though labile organic matter may be less abundant during the winter. The latter ingests sediment POM less discriminately, especially the subsurface deposit feeding *Molpadia* which ingest particles from below the sediment-water interface ⁽⁵⁵⁾. The differences in feeding strategies of different holothurians were reflected in their body $\delta^{13}\text{C}$ from this study, which retains the signatures of their food sources. *Peniagone* and *Protelpidia* had similar $\delta^{13}\text{C}$ (-24.45±0.20‰ and -23.54±0.32‰) whereas *Molpadia* had a much enriched $\delta^{13}\text{C}$ (-18.35±0.87‰) ⁽⁵⁵⁾, probably due to its less-selective feeding activity.

The total organic carbon percentages ($f_{\text{TOC}}\%$) in the bottom sediments were fairly low in the five locations (0.5-1%, Table 1), which were similar to f_{TOC} found in the marine tidal sediments (0.04-1.71%) on James Ross Island, Antarctica (63.8°S, 57.8°W), but lower compared to the f_{TOC} in other oceanic sediments (Baltic Sea 2.4-5.9%) ⁽⁴⁰⁾. The black carbon concentrations ($f_{\text{BC}}\%$) were independent of locations averaged around 0.1%. The BC was composed of a higher portion of

the TOC (BC/TOC 10-21%) compared to other open ocean environments such as the Baltic Sea (3-5%) ⁽⁴⁰⁾, but lower than sites in the tropical Atlantic Ocean ⁽⁵⁶⁾. The relative high BC/TOC ratios might be due to the lack of fresh organic matter input during the austral winter when the samples were collected. The BC fluxes to the sediments were highly variable among sampling locations (Table SI-1a). The lowest one ($4.4 \mu\text{g cm}^{-2} \text{ y}^{-1}$) at site 5 was comparable with other findings in offshore marine sediments (Table SI-1b). Derived BC fluxes at the other sites would require seasonal input from land-based emission sources via air and water, and could be affected by method artifacts.

The $\delta^{13}\text{C}$ of the TOC showed a decreasing trend from the North (site1, -24.9‰) towards the South (site 5, -21.9‰) with an average of $-23.4 \pm 1.1\text{‰}$, very similar to literature values (-24~-25‰) ⁽⁵⁵⁾. While the $\delta^{13}\text{C}$ of black carbon ($\delta^{13}\text{C}_{\text{BC}}$) at site 1 was more depleted (-18.2‰) which was similar to previously reported values in the Southern Ocean ($-18.6 \pm 1.4\text{‰}$) ⁽⁵⁷⁾, $\delta^{13}\text{C}_{\text{BC}}$ were higher and similar at other locations ($-14.2 \pm 0.5\text{‰}$) suggesting a different type of BC than site1 and a possible source of C₄ plants burning. The $\delta^{13}\text{C}$ labile organic carbon calculated from isotope mass balance equation was $-25.0 \pm 1.0\text{‰}$ similar to the value of phytodetritus collected at the WAP ($\sim -25\text{‰}$) ⁽⁵⁵⁾.

Concentrations of PCBs & OCPs in Sediments

The $\Sigma_{\text{ICES}}[\text{PCB}]_{\text{sediment}}$ ranged from 0.003 to 0.35 ng/g d.w. with the highest concentration found at site 2. Site 2 was very close to the Palmer Station (Fig 1) where Aroclor 1260 might have been used before and an Argentine ship *Bahia Paraiso* sank in 1989 ⁽⁵⁹⁻⁶¹⁾. Site 1 was very close to King George Island (South

Shetland Islands) which has the highest density of scientific stations on the Antarctic Peninsula (Fig 1b). The observed $\Sigma_{ICES}[PCB]_{\text{sediment}}$ distribution pattern was a result of the magnitude of surface pollution combined with differences in sedimentation rates. The sediment accumulation rates decreased more than ten times from the north (site 1) towards the south (site 5) on a 1000-year timescale according to ^{14}C data (Table SI-1a) ⁽⁴²⁾. Correspondingly, the PCB flux at site 5 were two orders of magnitude smaller than those at site 1-3 (Table SI-1a). The sedimentary fluxes of PCBs at site 5 was very close to those reported for Lake LV09 in Canadian Arctic (Table SI-1c). The fluxes at site 1-3 were comparable to those found in a remote lake in Rocky Mountains (US), but several orders of magnitudes smaller than others found in less remote locations (Table SI-1c). The most abundant PCBs were hexa-chlorinated (Cl) congeners ranging from 40-100% of $\Sigma_{ICES}[PCB]$, likely due to their high lipophilicity leading to their preferential binding with organic matter ($\log K_{ow} > 7.0$).

HCB was the most frequently detected OCP in the sediments ranging from 0.002 to 0.13 ng/g d.w. Chlordanes and p,p'-DDE were only found at sites 1 to 3.

Similar to PCBs, the highest OCP concentrations were found at site 2. These OCPs were also frequently detected in Antarctica vegetation and soils ⁽⁴⁾. The sedimentary fluxes of various OCPs were in line with the those found in a lake sediment core in Canadian Arctic (Table SI-1c)

Only few studies have determined the PCB and OCP concentrations in sediments in the Antarctic region. Comparison made with these studies can be found in SI on page 8 and in Table SI-4. These studies suggested anthropogenic

activity such as scientific activities and tourism in the Antarctic are another possible source of local pollution for POPs ^(2, 3, 5, 6, 24, 58) in addition to long-range transport. Higher levels of contamination were always found in the vicinity of scientific stations, and the concentration levels decreased dramatically (an order of magnitude) within a relatively short distance (i.e. hundreds of meters) from the 'hotspot' sources ^(5, 6). Most likely, this strong gradient is due to the low temperature in the Antarctic, reducing the mobility of the POPs away from point sources.

Concentrations of PCBs & OCPs in Porewater

The $\Sigma_{\text{ICES}}[\text{PCB}]_{\text{porewater}}$ ranged from 0.06 to 3.4 pg/L with an average percentage for PCB 28 (tri-Cl PCB) of 68%. In contrast to the sediment concentrations, low-chlorinated PCBs were the major components of PCBs in the porewater (Table SI-2). Di- and tri-Cl PCBs accounted for 71% and 21% of the total PCBs measured ($\Sigma_{10}[\text{PCB}]$). Slightly higher porewater PCB concentrations were reported in the remote Baltic marine sediments (4.5 ± 3.1 pg/L) with a corresponding higher average sediment concentration (4.5 ± 5.4 ng/g) ⁽⁴⁰⁾. A similar PCB congener pattern was found in the Baltic Sea study with PCB 28 accounting for $68 \pm 7\%$ of the $\Sigma_{\text{ICES}}[\text{PCB}]_{\text{porewater}}$. These findings suggest that lower chlorinated congeners PCB congeners dominate the PCBs in porewater and passive samplers are only retrieving the truly dissolved phase rather than the more hydrophobic ones that are sorbed to the sediment matrix. HCB was the most abundant OCPs detected in the porewater with concentrations ranging from

0.63 to 6.7 pg/L. p,p'-DDE was detected with a decreasing trend from site 1 (1.0 pg/L) through 3 (0.11 pg/L) with an average concentration of 0.49 pg/L.

Chlordanes were only detected at a couple sites with low average concentrations (CC, 0.60 pg/L, TC, 1.2 pg/L).

Benthic biota that live at the sediment-water interface are exposed to the contaminants in both porewater and overlying water column. Ideally, concentrations in both matrixes are needed to assess their body burdens. We are not aware of measurements for PCBs and OCPs in the water column near the Palmer LTER region as part of this or other studies. There have been measurements of PCBs and OCPs in the Ross Sea from Italian Antarctic expeditions. A depth profile of PCB concentrations was reported in the Ross Sea from the 2002-2003 expedition, with deep water (>170m) concentrations about two times higher than those in the shallow water (30 and 60 m, 45 pg/L)⁽⁸⁾. It was argued that modified circumpolar deep water carried higher levels of PCBs from the Pacific Ocean⁽⁸⁾. The XIX Italian Antarctic Oceanographic cruise (Dec 2003 – Jan 2004) reported a HCB concentration of 6.33 ± 4.38 (1.72-16.2) pg/L⁽⁸⁾.

However, the highest $\Sigma_{ICES}[\text{PCB}]$ reported in recent cruises in the South Pacific was 7.8 pg/L and [HCB] was 0.8 pg/L⁽¹⁰⁾. The higher concentration at depth could also result from the remineralization of sinking particulate organic matter (POC) at deeper water and release of bound POPs back to water column⁽⁶²⁾. A study conducted at the remote Baltic Sea measured sediment porewater and overlying water column concentrations simultaneously⁽⁴⁰⁾. It suggested that less hydrophobic PCBs (PCB 28 through 153) had a higher water column

concentration than porewater, whereas more hydrophobic ones (PCB 138 and 180) had similar concentrations in both water phases. Even though the porewater concentrations of POPs were low or below detection at our sampling sites 4 and 5 in the Palmer LTER grids, PCBs (up to congener no. 101) and OCPs (i.e. HCB, p,p'-DDE, and chlordanes) with $\log K_{OW} < 7$ could have a higher water column concentration than that in porewater based upon the Baltic Sea results.

Concentrations of PCBs & OCPs in Biota

The concentrations of PCBs and OCPs were normalized to lipid percentage (f_{lipid} %). Lipids are considered as the major accumulation compartments in biota for lipophilic PCBs and OCPs ⁽⁴⁸⁾. Lipid-normalized concentrations ($[PCB]_{lipid}$ & $[OCP]_{lipid}$) enable comparison of contaminant levels in various biota. The lowest $\Sigma_{ICES}[PCB]_{lipid}$ (0.84 ng/g lipid) was found in the *Molpadia* from site 1, which is the only subsurface deposit feeder species collected. It is less selective about its food resource than other species reported here. The more selective surface deposit feeder *Bathyplores* found at the same site had a higher $\Sigma_{ICES}[PCB]_{lipid}$ of 2.7 ng/g lipid. This may result from the different feeding strategy and exposure to contaminants in the overlying water column. The highest concentration of $\Sigma_{ICES}[PCB]_{lipid}$ was found in the *Protelpidia* (10.3 ng/g lipid) from site 2 where highest $\Sigma_{ICES}[PCB]_{sediment}$ was detected. The dominant PCBs in these biota samples were hexa-Cl congeners (PCB 138 and 153) accounting for an average of 49% in the detected $\Sigma_{ICES}[PCB]_{lipid}$. Next came penta-Cl congeners (PCB 101 and 118) which made up of 24% of the total $\Sigma_{ICES}[PCB]_{lipid}$ on average. To further compare the congener profiles in various holothurians at different sites, a

hierarchical cluster analysis was conducted using a similarity profile test (SIMPROF). The details of this test can be found in SI on page 9.

HCB (0.87 ± 0.34 ng/g lipid), TC (0.17 ± 0.12 ng/g lipid), CC (0.13 ± 0.06 ng/g lipid), and p,p'-DDE (0.26 ± 0.15 ng/g lipid) were detected in all of the holothurians with smaller intra-space and species differences in concentrations compared to PCBs. Although there have been several studies on POPs in Antarctic pelagic food web species ^(24, 29, 30, 33), this is the first comprehensive report on PCB and OCP concentrations in benthic holothurians at the Western Antarctic Peninsula. Comparisons on concentrations were thus made between holothurians and other species on the similar trophic level in the Antarctic food web. The sinking particulate organic matter (POM) at the WAP was dominated by quickly-sinking diatom aggregates (phytodetritus) and fecal pellets of krill (*Euphausia superba*) ^(63, 64). These sinking POM are the major food source for benthic holothurians. Thus, the krill and benthic holothurians are considered to be on a similar trophic level. In addition, $\delta^{15}\text{N}$ values were similar in the krill ($11.2 \pm 0.5\text{‰}$) ⁽⁶⁵⁾ and benthic holothurians ($8.0\text{--}10.2\text{‰}$) ⁽⁵⁵⁾. $\delta^{15}\text{N}$ has been used to characterize trophic levels with levels of POPs in organisms ⁽⁶⁶⁾. Concentrations of PCBs and OCPs were comparable to other lipid-normalized low trophic level biota concentrations in the Antarctic ^(24, 27, 29, 30, 33). Detailed comparison can be found in SI on page 10 (Table SI-5)

Partitioning between Sediments and Porewater

Predicted partitioning coefficients based on the classic model (equation □) which considers absorption into organic carbon (OC) dominating the partitioning

behavior of hydrophobic POPs in the sediments, underestimated the distribution of all PCB congeners by 10-100 times (Fig 2A). Several previous studies have found that observed distribution coefficients (K_D) can not be explained by partitioning into OC alone ^(47, 67, 68), suggesting there was an additional sediment fraction present (i.e., BC or another recalcitrant carbon fraction) with a higher sorption capacity of hydrophobic POPs than OC ⁽⁴⁸⁾. The Freundlich distribution model (Equation □) has been employed to account for both OC and BC sorption of POPs in the sediments. The Freundlich exponent n is determined by both the characterization of the sorption sites on BC as well as the hydrophobic structure of POPs ^(69, 70), which was taken a value of 0.7 from previous studies ⁽⁴⁸⁾. K_{BC} LFER relationship was chosen from Koelmans et al ⁽⁷⁰⁾.

$$\log K_{BC} = 1.1016 * \log K_{OW} + 0.2469 \quad \square$$

Other reported K_{BC} LFER relationships generated very similar K_{BC} values with differences less than 0.3 log unit ^(35, 71). With the above chosen parameters, the dual-mode model (Equation ▢) produced a better prediction (less than a factor of 10 from the observed K_D values, Figure 2B) than the model with OC alone (Figure 2A). This probably means that the value of Freundlich exponent n needs to be adjusted based on the composition of different black carbons. Since BC is composed of a mixture of various reduced and aromatic OC, n could vary between different locations. The $\delta^{13}C$ of black carbon revealed that the black carbon at site 1 were different from site 2 and 3 (Table 1), which probably will have different n values. When we chose smaller n values (0.68 for site1, 0.57 for

site 2, and 0.58 for site3), the predictions were less a factor of 3 for PCBs compared to observed values (Fig SI-4).

The sorption mechanisms for POPs to BC is an adsorptive process and nonlinearly depends on the porewater concentration ($[POP]_{\text{porewater}}$), whereas the absorption into OC represents a linear process. The lower the porewater concentration is, the larger the contribution of BC to the overall partitioning process⁽³⁷⁾. In this study, the $[POP]_{\text{porewater}}$ for both PCBs and OCPs were on the level of sub-picogram per liter which resulted in a large portion of the PCBs and OCPs being adsorbed onto BC. For very hydrophobic hexa-Cl PCBs up to 94% were sorbed with BC, even for less hydrophobic di-Cl PCBs (PCB 8) 63% of them were affiliated with BC according to calculation obtained from Equation 7. Thus, the majority of PCBs and OCPs were not available as part of the organic carbon pool due to their sorption with BC. This greatly reduced the porewater concentrations of PCBs and OCPs in the sediments and resulted in reduced bioavailability of POPs through passive exposure at these locations.

The one-carbon model (TOC) approach can also generate a better prediction of partitioning behavior of PCBs between sediment and porewater than OC alone (Figure 2A&C). We chose the median values of the $\log K_{\text{TOC}}$ compiled by Hawthorne et al⁽³⁶⁾ from 53 different sediments historically contaminated with PCBs and plotted them against observed K_D values (Figure 2C). The $f_{\text{TOC}} K_{\text{TOC}}$ predictions fell within one order of magnitude with the observed K_D . Importantly, both the two-carbon and one-carbon model predicted the partitioning coefficients of PCBs within a factor of ten from the observed ones. The one-carbon model

tends to underestimate the K_D values for high-chlorinated PCBs and overestimate those for low-chlorinated PCBs, whereas the two-carbon (OC and BC) generally predicts lower K_D values compared to observed ones. The main advantage of the TOC-model is that only 1 parameter; only f_{TOC} is needed to make a decent prediction of overall partitioning. On the other hand, there are mechanistic advantages to the OC-BC model. First of all, our measurement (see QA/QC in SI for details) and other studies did find black carbon exist in the sediments in Antarctic ⁽⁷²⁾, which may be resulted from local activities and long-range transport. Geochemically speaking, the existence of 2 carbon pools (organic vs black carbon) is widely accepted, though the exact cut-off of the two pools is under debate ⁽⁷³⁾. Second, the sorption strength to OC (adsorption) and BC (adsorption) have been measured independently in laboratory and field studies ⁽⁴⁷⁾. In contrast, there is no lab/field measurement of a coal tar type of TOC to our best knowledge. Yet, the TOC model works surprisingly well considering it covered a wide range of different sediments.

Partitioning between Biota and Porewater

Benthic holothurians are deposit feeders which take up POPs passively through physical contact with porewater (bioconcentration) as well as actively through ingestion of sediment particles. The bioaccumulation of POPs by deposit feeder oligochaete can be explained by equilibrium partitioning of POPs between porewater and the lipids of the oligochaete according to Kraaij et al ⁽⁷⁴⁾ regardless of their uptaking pathway. Following their approach, the lipid-porewater partitioning coefficients (K_{lipid}) of benthic holothurians were calculated based on

equation □ and plotted against with corresponding K_{OW} (Fig. 3). Regression analysis suggested the obtained relationships were significantly linear; the standard errors were much smaller than the slopes (Table SI-5). In other words, the bioaccumulation of PCBs up to $\log K_{OW}$ 7.7 in our sampling sites at WAP can be described by equilibrium partitioning between the lipids of benthic holothurians and porewater. The K_{lipid} equals the bioconcentration factor in this case. The body burden of PCBs in sediment dwelling holothurians can be estimated on the basis of PCB concentrations in porewater and their bioconcentration factors. Statistical analysis on regressions revealed that obtained K_{lipid} - K_{OW} relationships of site 1 *Molpadia* and *Bathyplores* were not significantly different from each other ($p < 0.05$) but were significantly different from *Protelpedia* at Site 2. The difference could be attributed to the fact that they were different biota species with different feeding strategies (sub-surface vs surface) and different food selectivity, which probably lead to different lipid composition in their bodies. Previous study indicated different lipid pools (storage vs. membrane) can have distinguished K_{lipid} ^(75, 76). The obtained K_{lipid} - K_{OW} relationships for *Protelpedia* at site 2 and 3 were not significantly different from each other (Fig 3). The regression of average K_{lipid} - K_{OW} ($\log K_{lipid} = 0.949 * K_{OW} + 0.06$) was very close to literature values (Table SI-4).

Implications

Our results suggest that recalcitrant carbon (possibly black carbon) reduces the availability of sedimentary POPs even in the most remote region of the planet. Partitioning model developed including both organic carbon and black carbon in

impacted sediments from the northern hemisphere gave good results for predicting porewater concentrations of POPs in the remote region. Using the recently postulated one-carbon (TOC) model resulted in predictions that were similarly within an order of magnitude of observed partitioning coefficient (K_D) values. The partitioning behavior of various chlorinated organic pollutants into benthic invertebrates was very similar between our remote sites and impacted sites elsewhere.

There is evidence of more and warmer Circumpolar Deep Water intrusion on the WAP continental shelf ⁽⁷⁷⁾, which could bring not only anthropogenic pollutants to the WAP in the future, but also nutrients to the surface ocean through upwelling which could increase surface primary production and enhance sedimentation. The increased amount of sinking organic matter would bring more lipophilic POPs from the surface ocean to the shelf sediments. The increased temperature in the projected climate change scenario could also aid to mobilize the previously deposited POPs in the vicinity of scientific research stations throughout the Antarctica by water current and atmospheric transport.

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Supporting Information Available

Additional information on results comparison, figures, and tables were included in the Supporting Information section. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

Table 1. Sampling locations, sediments and benthic biota characteristics. Sites 1 to 5 in this study are corresponding to site AA, B, E, F, and G in the FOODBANCS-2 project ⁽⁴²⁾.

Station No.	1	2	3	4	5			
Latitude	-63.05	-64.80	-65.98	-66.98	-68.13			
Longitude	-61.60	-65.33	-67.28	-69.72	-71.00			
Sampling date	Jul-25-2008	Jul-28-2008	Jul-20-2008	Jul-19-2008	Jul-15-2008			
Depth (m)	578	578	597	590	582			
Sediments	f _{TOC} (%)	0.46%	0.87%	1.02%	0.62%	0.55%		
	f _{BC} (%)	0.094%	0.104%	0.102%	0.099%	0.112%		
	BC/TOC (%)	19.95%	12.25%	10.21%	16.21%	21.47%		
	δ ¹³ C TOC	-24.9	-24.0	-23.3	-23.1	-21.9		
	δ ¹³ C BC	-18.2	-14.7	-14.1	-13.6	-14.3		
	δ ¹³ C OC	-26.5	-25.4	-24.3	-24.9	-24.0		
Biota	species	Molpadia	Bathyploce	Protelpidia	Protelpidia	Protelpidia	Peniagone	Peniagone
	sub-surface	surface deposit feeding holothurians						
	lipid (%)	4.5%	5.5%	3.3%	2.8%	3.0%	2.6%	3.1%

Figure 1. A. Map of Antarctic with Major Scientific Research Stations. B. Sampling Sites 1-5 (O). Selected Scientific Research Stations (*). Palmer Long Term Ecological Research (LTER) grids (•). Sites 1 to 5 in this study are corresponding to site AA, B, E, F, and G in the FOODBANCS-2 project ⁽⁴²⁾

Figure 2. Observed distribution coefficients (K_D) compared to predicted partitioning based on equations (□ and □) in sediments from site 1-3. The black line represents 1:1 log/log relationship. A. predicted values derived from equation □ when organic carbon was considered as the solely partitioning medium in the sediments. B. predicted values derived from equation □ when both organic carbon and black carbon were taken into account for controlling the partitioning process. n was chosen as 0.7. C. predicted values derived from modified equation □ with Log K_{TOC} chosen from Hawthorne et al (2011)

Figure 3 Regressions for K_{lipid} - K_{ow} relationships for benthic holothurians at different sites. Average K_{lipid} values were also plotted against K_{ow} (blackline) with a linear relationship of $\log K_{lipid} = 0.95 \cdot \log K_{ow} + 0.06$. Literature reported relationships were also plotted for comparison; Endo et al 2011 (.....) and Schwarzenbach et al 2003 (-----).

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TOC figure