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Persistent Organic Pollutants at the Base of the Antarctic Marine Food Web

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Various organochlorine pesticides and brominated diphenyl ethers (BDE-47, -99, and -100) were measured in sea ice algae, water column plankton, and juvenile and adult krill collected in the Palmer Long-Term Ecological Research (LTER) region west of the Antarctic Peninsula during late austral winter and midsummer, 2001−2002. BDEs were 100−1000 times higher in ice algae and 2−10 times higher in phytoplankton than the most abundant organochlorine pesticide, hexachlorobenzene (HCB), reflecting the current production and use of BDEs versus organochlorine pesticides. However, concentrations of HCB and BDEs were significantly lower in summer plankton than in ice algae indicating lower atmospheric inputs, removal from the water column, and/or biodilution of persistent organic pollutants at the base of the food web during summer. Concentrations of HCB (juvenile and adult krill) and BDEs (juvenile krill) were not significantly different from their primary food source (ice algae, phytoplankton), and BDEs were significantly lower in adult krill versus phytoplankton, indicating no biomagnification of HCB or BDEs during transfer from plankton to krill. The high concentrations of BDEs and HCB in ice algae and associated juvenile krill illustrate the importance of sea ice as a vector for entry of POPs into the Antarctic marine ecosystem.

Introduction

Relatively volatile persistent organic pollutants (POPs) reach high latitude regions primarily via long-range atmospheric transport (*1*−*3*). The lipophilic nature and stability of these compounds allows efficient assimilation and accumulation in the body fat of organisms and subsequent biomagnification through the food web. Indeed, organochlorine contaminants (OCs) have long been detected in polar regions, particularly in high trophic level predators such as penguins, seals, whales, and polar bears (*4*−*7*). More recently, brominated diphenyl ethers (BDEs), organic compounds produced for use as flame retardants (*8*), have been found in fish-eating birds, the ringed seal (*Phoca hispida*), and Beluga whales (*Delphinapterus leucas*) from the Arctic Ocean (*9*, *10*). Due to the current production and use and long-range transport potential (*1*), the presence of BDEs in the Antarctic marine food web is also likely.

One mode of introduction of POPs into polar marine ecosystems is via atmospheric deposition onto the seasonal sea ice surface, primarily via falling snow, and subsequent percolation and incorporation into the underlying ice. Sea ice is a site of high biological productivity (*11*), with the bottom surfaces and interstices colonized by sea ice microbial communities (SIMCO; *12*), dominated by ice algae. POPs exhibit an enhanced association with particulate matter in the ice column (*13*, *14*); consequently ice algae are likely important in accumulating and concentrating these compounds. Moreover, in the Antarctic, sea ice biota are an important, and possibly the sole, food resource for over wintering juvenile krill (*Euphausia superba*) (*15*). Therefore, sea ice may serve as a conduit for the transfer of pollutants from long-range sources to the planktonic food web.

Antarctic krill is important in the diet of seabirds, seals, and penguins and is considered a keystone species in the region west of the Antarctic Peninsula (*16*, *17*). All Antarctic marine vertebrates depend either directly or indirectly on krill. This species is the most important macrozooplankton consumer in the Antarctic pelagic food web and, unlike during its juvenile stages, is supported in large numbers by blooms of phytoplankton (*18*). POPs released from the melting ice pack plus those deposited to surface waters during spring and summer may become sorbed to phytoplankton cells due to the hydrophobic nature of organic pollutants and the lipid-rich characteristics and relatively large surface area of plankton (*19*). Upon grazing of phytoplankton, POPs are partitioned to lipid-rich organelles and tissues of consumers (*20*), resulting in bioaccumulation and subsequent biomagnification. Lipid-normalized concentrations of POPs have been found to increase from Antarctic krill to fish as well as top predators including Adélie penguins (*Pygoscelis adeliae*), Weddell (*Leptonychotes weddellii*), and southern elephant seals (*Mirounga leonina*), proving that biomagnification of highly lipophilic pollutants (log octanol−water partition coefficient > 5) occurs (*21*).

This study focused on determining the presence of POPs in lower trophic levels of the Antarctic marine food web and on evaluating the role of both ice algae and phytoplankton in providing the first step in pollutant transport up the food chain.

Materials and Methods

Winter Sample Collection. Ice and juvenile krill samples were collected in heavy pack ice (ca 1−5 m thickness and 80−100% cover) during the Austral late winter/early spring on the 2001 Palmer-LTER Ice Cruise (September 7−October 26) aboard the RVIB *Nathaniel B. Palmer*. Samples were collected at ice stations located west of the Antarctic Peninsula, southwest of Adelaide Island, at ca. 69° W, 68° S (Figure 1). Sea ice was sampled using a 1-m (3 in. diameter) barrel corer. Cores were taken after clearing the overlying snow from a ca. 2 m^2 area to expose the sea ice. Due to the variability in sea ice thickness and structure, and under rafting of the ice, not all cores reached the maximum thickness of the ice. Ice cores were cut into sections, placed into closed (air- and water-tight) 60-L, solvent-rinsed, stainless steel containers and transported back to the ship. Subsequently, ice samples were melted by placing the sealed containers in a warm water bath, and the thawed contents were filtered to collect particulate matter (SIMCO) on precombusted (4 h at 400 °C) 142 mm diameter glass fiber filters (Gelman Type A/E, nominal pore size 1 μm). Melted ice from three 60-L containers (≈100−130 L) was combined into one sample (n = 4). Filters were packed in prewashed and combusted (4 h at 400 °C) glass jars and frozen at −80 °C until analysis.

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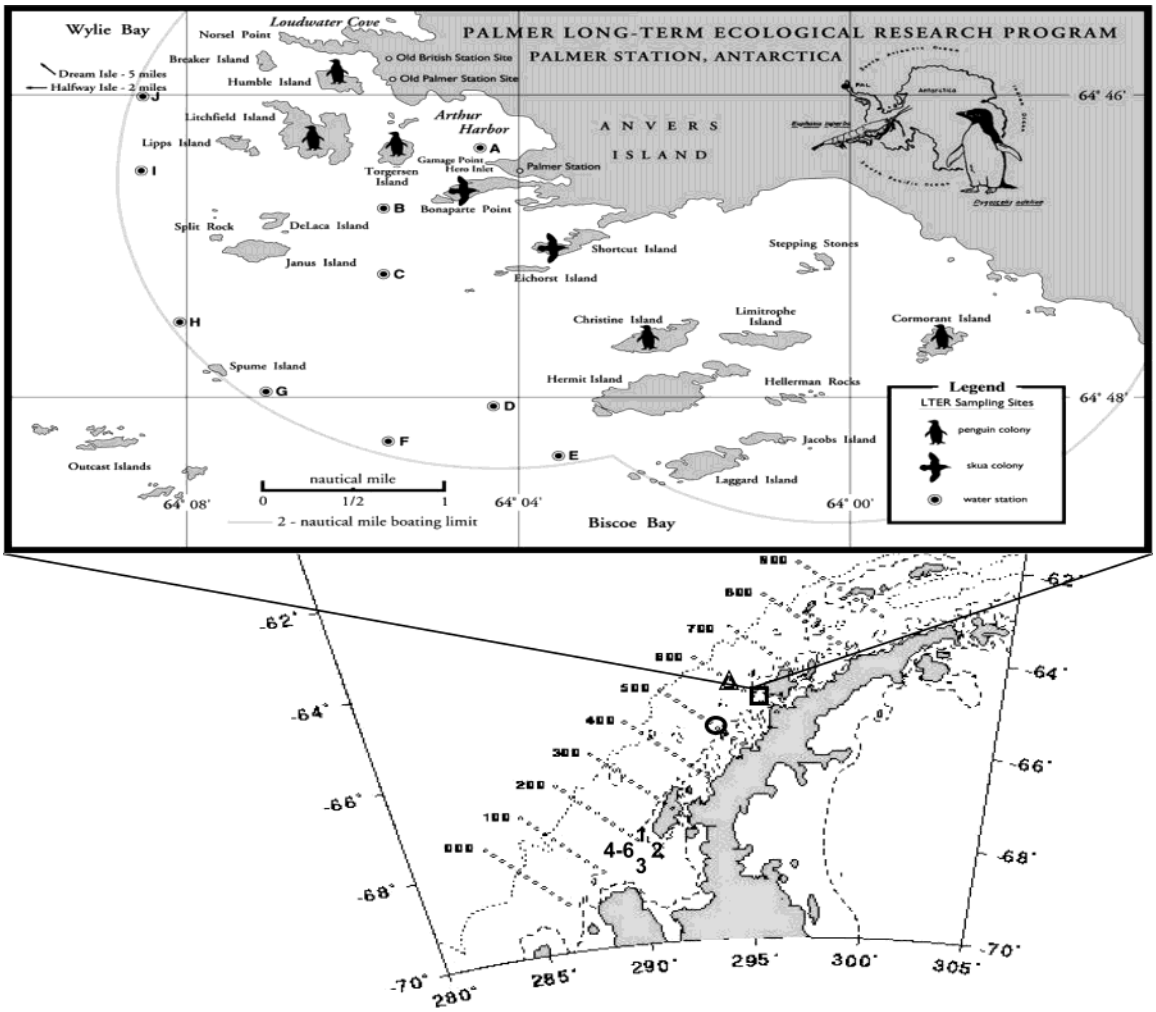

FIGURE 1. Locations of sea ice particulate matter and juvenile krill sampling stations (1−6) during winter (September−October 2001), and adult krill sampling stations (circle = station 500.060; square = station 600.040; triangle = station 600.120), during summer (January 2002), west of the Antarctic Peninsula. Inset map: plankton sampling sites (January−March 2002) in the vicinity of Palmer Station, Antarctica (64.7° S, 64.0° W).

Juvenile krill samples ($n = 2$) were collected with clean aquarium nets from the undersides and between rafted surfaces of the sea ice by divers. Samples were frozen in precleaned glass jars at −80 °C until analysis.

Summer Sample Collection. Summer sampling took place between January 7 and March 14, 2002, in open water in the vicinity of Palmer Station, Antarctica (64.7° S, 64.0° W), located southwest of Anvers Island (Figure 1). Net tows were used to collect plankton from the surface water community. Plankton samples ($n = 24$) were collected weekly at three stations (A, B, and E; see Figure 1) on the LTER in-shore sampling grid located within 2 mi of Palmer Station. Horizontal tows were done via Zodiak using a 153-μm net, followed by 2-mm sieving to separate out krill and other large grazers. A subsample of plankton was examined under 10−20× magnification using a compound microscope following each tow. Plankton samples were found to be composed mainly of diatoms, with a large proportion of the species *Thalassiosira*. Plankton samples were frozen in precleaned glass jars at −80 °C until analysis.

Adult krill samples ($n = 3$) were collected at stations on the Palmer-LTER regional grid (Figure 1) using a 505-μm, 2-m ring net during the LTER summer cruise (January 2002). Krill were frozen in precleaned glass jars at −80 °C until analysis.

Chemical Analyses. Plankton, krill, and sea ice particulate matter (ice algae) were extracted following identical procedures, although preparation of each sample type for extraction differed. Plankton samples were centrifuged at 1800 rpm for 30 min, and the supernatant was decanted to remove excess water prior to extraction. Individual krill were picked from each sample for analysis and homogenized using a Virtis 45 tissue homogenizer prior to extraction. Filters containing sea ice particulate matter were torn into pieces using clean stainless steel forceps prior to extraction. Each plankton sample (40−100 g wet wt), krill sample (≈14−15 g wet wt), and filter sample was thoroughly mixed with precombusted (4 h at 450 °C) Varian Chem Tube−Hydromatrix to remove water and extracted with 65:35 (v:v) dichloromethane (DCM): methanol via accelerated solvent extraction (2000 psi; 100 °C; Dionex ASE 200 accelerated solvent extractor) following addition of a surrogate standard mixture containing deuterated α-hexachlorocyclohexane (α-HCH) and 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (OCB). Hydromatrix alone was extracted as a laboratory blank. For each sample or blank, the extract was brought to 1:1:0.9 DCM:methanol:water by addition of methanol and 20% NaCl in hexane-extracted water and back-extracted 3 times into hexane via agitation for 3 min.

The hexane extracts were reduced in volume to ≈5 mL by turbo- and/or rotoevaporation, followed by blow down with purified N_2. The total lipid extract (fraction of lipids by weight in the hexane extract) was determined gravimetrically for each sample in triplicate by weighing the ≈5-mL extract and 0.1 mL (≈2%) of the extract before and after solvent

evaporation at 65 °C. The remaining hexane extract was vortexed with 1 mL of H_2SO_4 (3−6×) to remove lipids, and the hexane layer was removed after settling. The acidified hexane fraction was blown down under ultrahigh-purity N_2 to 1 mL and passed through a column containing 10 g of precleaned (Soxhlet extraction with DCM for 24 h) deactivated silica (mesh size 100−200), topped with 1 in. precombusted (4 h at 450 °C) $NaSO_4$ for further removal of interfering substances. Both 25 mL of hexane and 40:10 mL DCM:hexane eluents were collected and reduced by rotoevaporation followed by nitrogen blow down to 1 mL. An internal standard containing deuterated lindane was added, and the extract was further reduced to ≈100 μL under N_2 for analysis.

Samples were analyzed via gas chromatography/negative chemical ionization mass spectrometry (Hewlett-Packard 6890 series GC and 5973 mass selective (MS) detector) using a J&W DB-35MS wide bore capillary column (30 m length, 0.25 mm diameter, 0.25 μm film thickness) and selective ion monitoring. Method parameters for pesticide analysis were as follows: 70 °C initial hold time of 1 min; 70−150 °C at 20 °C min^{-1}; 150−280 °C at 4 °C min^{-1}, hold for 15 min; 280−295 °C at 5 °C min^{-1}, hold for 2 min; source temperature 150 °C. The temperature program for BDE analysis was 50 °C initial hold time of 1 min; 50−130 °C at 20 °C min^{-1}; 130−300 °C at 5 °C min^{-1}, hold for 6 min; and the source temperature was 150 °C. The carrier gas for both methods was helium at 1.0 mL min^{-1} with a velocity of 39 cm s^{-1}. Surrogate standard recoveries (± standard deviation) were 78 (±17)%, 90 (±8)%, and 75 (±17)% for plankton, krill, and SIMCO, respectively.

OCs and BDEs were quantified relative to the surrogate standards and concentrations are reported per unit of lipid biomass (ng/g_{lipid}). Method detection limits (MDLs) in plankton based on the average blank and lipid values were 1.5, 0.2−0.3, and 0.03−0.06 ng/g_{lipid} for BDE-47 and -99; HCB, heptachlor, and BDE-100; and the other OC pesticides, respectively. The MDLs for adult krill, juvenile krill, and SIMCO were 1/2, 2×, and 10× the plankton values, respectively, due to varying lipid contents of the samples. Average values (± standard error) were only reported if compounds were quantified in at least two-thirds of the samples. The average hexachlorobenzene (HCB) concentration in plankton was calculated substituting a lipid-normalized blank value for values that were not quantifiable (NQ, values that were below 3× the field blank (SIMCO filters) or lab blank (plankton and krill)). The average γ-HCH concentration in adult krill was calculated using a value of zero for NQ, because this compound was not detected in blanks. Unpaired or paired (where appropriate) *t*-tests were performed on log-transformed data to compare average values.

Results and Discussion

Sea Ice Algae and Phytoplankton. Concentrations of HCB and BDE-47, -99, and -100 averaged 15.9 ± 6.2, 5460 ± 3840, 7110 ± 5910, and 1350 ± 1070 ng/g_{lipid}, respectively, in sea ice particulate matter. Note that the BDEs were present in ice algae at concentrations between 100 and 1000 times higher than HCB (Figure 2; $p < 0.05$; df = 3). One possible reason for this difference is that BDEs are currently produced and used in large quantities. In 1999, the North American market demand for the penta-BDE commercial mixture (of which BDE-47, -99, and -100 are major components) was 8290 t or 97.5% of the global demand (*22*). In comparison, HCB is not currently manufactured or used as a commercial end product in the United States, although it is formed as a byproduct in the production of several chlorinated chemicals and is a contaminant in some pesticides. Moreover, HCB has a higher vapor pressure as compared to the BDEs (*23*, *24*) and was detected in relatively high concentrations in winter air samples as compared to the other POPs during the study period (*25*). The lower vapor pressures of BDEs versus HCB render the former more easily condensed out of the atmosphere (*2*) and incorporated into sea ice.

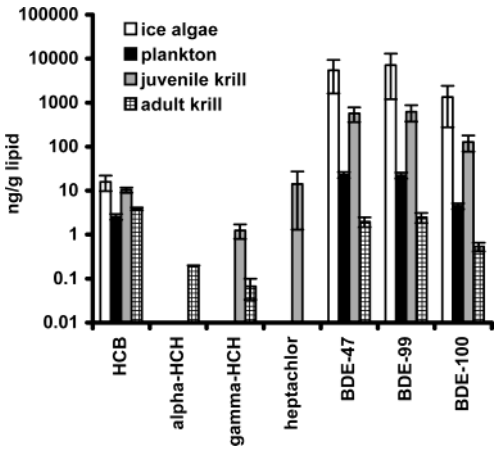

FIGURE 2. Average lipid-normalized concentrations ± standard error of selected organochlorine pesticides and BDEs in sea ice algae ($n = 4$), summer plankton ($n = 24$), juvenile krill ($n = 2$), and adult ($n = 3$) krill samples. Heptachlor, α-HCH, and γ-HCH were detected in less than two-thirds of the plankton samples; heptachlor was detected in only one ice algae sample; and other missing values were not detected in the samples (see Supporting Information).

Concentrations of α- and γ-hexachlorocyclohexane (HCH), heptachlor epoxide, and the DDT compounds were below the level of quantification in sea ice particulate matter, and heptachlor was only quantified (12 ng/g_{lipid}) in one of four samples. Nonquantifiable concentrations of these OCs are likely a reflection of reductions in use in lower latitude regions, leading to low atmospheric concentrations and reduced deposition onto sea ice. For example, lower atmospheric DDT concentrations compared to those reported a decade earlier indicated that atmospheric DDT levels over the Southern Ocean had dropped 200−300× between 1980 and 1990 (*26*, *27*). Likewise, quantifiable concentrations of *p*,*p*′-DDE and DDT associated with sea ice diatoms were observed during the 1986−1987 season in the Antarctic Peninsula region (*28*) in contrast to this study.

Concentrations of HCB and BDE-47, -99, and -100 averaged 2.5 ± 0.4, 22.9 ± 3.5, 22.3 ± 3.4, and 4.5 ± 0.7 ng/g_{lipid}, respectively, in plankton collected during the austral summer (January−March) in the vicinity of Palmer Station. HCHs (<0.06−5.6 ng/g_{lipid}), heptachlor (<0.3−10.9 ng/g_{lipid}), heptachlor epoxide (<0.04−5.5 ng/g_{lipid}), and the DDT compounds (<0.04−16.7 ng/g_{lipid}) were below the level of quantification in more than half of the samples (see Supporting Information); thus, average concentrations were not calculated. The presence of POPs in plankton suggests retention of POPs introduced during snow and ice melt and/or atmospheric deposition and subsequent uptake by plankton of these contaminants during summer. However, BDEs were only ∼2−10 times higher than HCB in summer plankton (Figure 2), suggesting lower atmospheric deposition or continuous removal of these POPs from the water column in summer as compared to winter.

The concentrations of HCB and BDEs (μg/g_{lipid}) in summer plankton were significantly lower than in ice algae ($p < 0.05$; df = 26) (Figure 2). One mechanism responsible for this decrease could be removal of particle-associated POPs from the euphotic zone via sedimentation following ice retreat. Phytoplankton blooms in the marginal ice zone around the Antarctic Peninsula are followed by high rates of particulate organic carbon export (*29*). For example, in the nearby Bransfield Strait, more than 90% of the annual sedimentation is concentrated in a short period during December and

TABLE 1. Concentrations (ng/L) of Particulate- and Dissolved-Phase Pesticides and BDEs in Glacier Runoff Samples Collected in the Vicinity of Palmer Station, January−February 2002[a]

station	α-HCH	γ-HCH	*p,p′* DDE	*o,p′* DDD	*o,p′* DDT	*p,p′* DDD	*p,p′* DDT
particulate							
runoff 1	NQ	nd	NQ	NQ	nd	0.006	0.005
runoff 2	NQ	NQ	NQ	0.01	0.004	0.01	0.02
dissolved							
runoff 1	nd	nd	0.02	0.03	0.01	0.078	nd
runoff 2	0.01	0.04	nd	0.05	0.01	0.47	0.03

[a] NQ (not quantifiable) = levels below 3× field blank; nd = no peak detected on GC/MS.

January (*30*). Sinking of pollutants sorbed to organic particulates is important in the sequestration of POPs in marine environments. In the Mediterranean Sea, the seasonality of PCB flux corresponded to cycles of zooplankton biomass and primary productivity in surface waters (*31*). Given the seasonal flux of particulate matter in the Antarctic Peninsula region, a large portion of POPs deposited onto sea ice is likely removed in a relatively short period of time following ice melt.

The high standing stocks observed in the summer water column (up to ~300 mg m^{-2} chl-*a*; *32*) compared to winter (up to 23 mg m^{-2} chl-*a* for sea ice algae; *11*) likely also play a role in the observed seasonal decrease in plankton-associated POPs. An increase in the biomass of plankton cells can lead to a decrease in contaminant concentration on a per mass basis (*33*). Thus, contaminants retained in the upper water column until summer and those added via atmospheric input would be diluted in comparison to concentrations in ice algal communities resulting in lower POP levels per g_{lipid}.

Finally, lower atmospheric deposition fluxes or efflux out of surface waters during spring and summer may also contribute to the lower levels of POPs observed in phytoplankton during that period. Total atmospheric fallout of POPs is lower during summer (*27*), with higher air temperatures during summer resulting in less condensation of gas-phase POPs (*2*). Volatilization of contaminants from the water to the air may also occur in the absence of sea ice. Although this process is more likely for the more volatile HCB, it may also be possible for the lower brominated BDE congeners. Hargrave et al. (*34*) noted a high potential for sea to air flux following ice melt in the Arctic in June and reported an outgassing of HCB during the ice-free period that could have removed 20% of the surface layer inventory of this compound. Gregor (*35*) suggested volatilization as a mechanism responsible for the summertime loss of a major portion of the OCs deposited in the Arctic snowpack during winter. Thus, lower atmospheric deposition or volatilization of POPs in summer may be responsible in part for the lower POP concentrations observed in summer plankton than in ice algae.

Impact of Glacial Melting. Glaciers accumulate atmospherically deposited contaminants (*36*), and melting glacial ice provides a source of contaminants to surface waters during the spring and summer seasons (*28*, *37*, *38*). DDTs were deposited in Antarctica during the 1960s and 1970s, and from 0.5 to 4 ng/L of DDT was found in ice layers down to 6.0 m below the glacier surface in the vicinity of Anvers Island during a 1975 study (*39*). In our study, the highest levels of α- and γ-HCH, heptachlor, heptachlor epoxide, and the DDTs in plankton were measured during the first sampling week (January 15, 2002) at station A, ≈5 m from shore in Arthur Harbor, an area directly influenced by melting glacier ice during summer. In addition, glacier runoff samples collected during this study contained DDTs and, to a lesser extent, α- and γ-HCH, largely in the dissolved phase (Table 1). α- and γ-HCH and heptachlor were all found in air in the vicinity of Palmer Station (*25*), indicating continued cycling of these POPs between air and water and promoting accumulation by plankton. However, DDTs were not detected in air, suggesting some other source to summer plankton. Consequently, runoff from glacier ice previously contaminated with DDTs could have resulted in the presence of DDT compounds in the near-shore plankton samples.

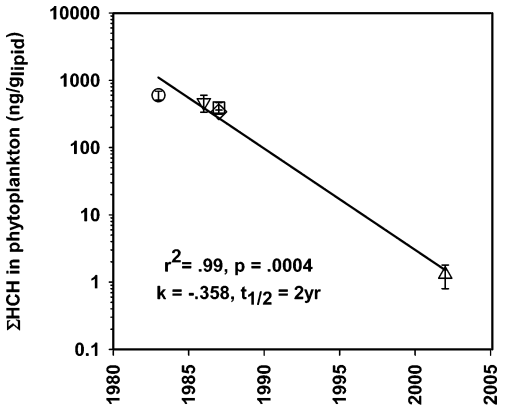

FIGURE 3. Average ∑HCH (α- + γ-HCH) concentrations ± standard error in plankton collected in the vicinity of Palmer Station, 2002 (△), and data from previous studies: (○) ref *37*, (▽, □) ref *28*, and (◇) ref *42*. The average value for this study was calculated using only those samples in which α- or γ-HCH was quantifiable. Therefore, the calculated half-life is a conservative estimate.

Temporal Trends. Levels of γ-HCH (<0.06−5.6 ng/g_{lipid}), heptachlor epoxide (<0.04−5.5 ng/g_{lipid}), *p,p′*-DDT (<0.04−16.4 ng/g_{lipid}), and *p,p′*-DDE (<0.03−5.2 ng/g_{lipid}) in plankton measured in this study were almost 2 orders of magnitude lower than concentrations previously reported for plankton samples taken during 1987 in the Indian Ocean sector of the Antarctic (*40*). Similarly, lower concentrations of α- and γ-HCH and the DDTs were measured in phytoplankton in this study than previously in the Antarctic Peninsula region (*28*, *37*). The reduced frequency of occurrence and concentrations of pesticides in Antarctic plankton can be attributed to decreases in use and atmospheric concentrations over the past few decades. The decline in ∑HCH (α- + γ-HCH) in Antarctic plankton over time yields an estimated environmental half-life of 2 yr for HCHs in coastal Antarctic surface waters (Figure 3).

Juvenile and Adult Krill. Average concentrations of HCB (10.3 ± 1.4 ng/g_{lipid}) and BDEs (568 ± 209, 622 ± 253, and 128 ± 50.5 ng/g_{lipid} for BDE-47, -99, and -100, respectively) in juvenile krill were not significantly different from those found in ice algae ($p > 0.05$; df = 4; Figure 2), suggesting uptake of these compounds by juvenile krill feeding on ice algae but no biomagnification between trophic levels. γ-HCH and heptachlor were also quantified in juvenile krill, at average concentrations of 1.3 ± 0.5 and 14.2 ± 12.9 ng/g_{lipid}, respectively. Heptachlor was quantified in one ice algal sample at a similar concentration as in juvenile krill (12 ng/

g_{lipid}), but otherwise, levels of γ-HCH and heptachlor were not quantifiable in ice algae.

The average concentration of HCB (3.8 ± 0.3 ng/g_{lipid}) in adult krill was not significantly different from that in summer plankton ($p > 0.05$; df = 25; Figure 2). Average concentrations of BDEs in adult krill (2.0 ± 0.5, 2.5 ± 0.6, and 0.5 ± 0.1 ng/g_{lipid} for BDE-47, -99, and -100, respectively), in comparison, were significantly lower than in plankton ($p < 0.05$; df = 25; Figure 2). As with juvenile krill and ice algae, no biomagnification of POPs was found between plankton and adult krill.

Concentrations of HCB and BDEs were significantly lower in adult than juvenile krill ($p < 0.05$; df = 3; Figure 2). Heptachlor was also detected in juvenile krill, but it was below quantifiable levels in adult krill (Figure 2).Therefore, POP accumulation by juvenile krill during their first year when they are feeding on ice algae appears to exceed that for adult krill.

Concentrations of HCB and BDEs were significantly higher on a per lipid basis in ice algae as compared to summer water column plankton ($p < 0.05$; df = 26; Figure 2). Thus, the significant difference in POP levels between juvenile and adult krill may be a reflection of contaminant levels in their food source or of acquisition of contaminants during the egg stage. Eggs of zooplankton are lipid-rich, and PCB concentrations in *Acartia tonsa* eggs have been found to be ~4 times higher than the original concentration in the body of the female (*41*). Juvenile stages of zooplankton generally have high OC levels after yolk absorption, and higher levels of hydrocarbons have been found in juvenile krill as compared to adult males on a wet weight basis (*42*). Thus, some portion of POPs in juvenile krill may have been acquired during the egg stage rather than by accumulation via consumption or absorption.

The average HCB concentration (0.11 ng/$g_{wet\ wt}$) in the adult krill samples observed in this study is comparable with the HCB concentration (0.2 ng/$g_{wet\ wt}$) previously found in krill collected between 1994 and 1996 from the Ross Sea, Antarctica (*43*). However, the average concentration of $\sum$HCH (0.009 ng/$g_{wet\ wt}$) in our adult krill samples was much lower ($\approx 8\times$) than that found by Gupta et al. (*44*) for samples collected from December 1987 to January 1988. This contrast may be due to differences in the sampling region or time. HCH concentrations in air close to the sampling site of Gupta et al. (*44*) were 10 times higher (*27*) than for air samples collected during this study (*25*). The decline in Antarctic HCH concentrations with time is also reflected in plankton (Figure 3).

While a number of studies have shown biomagnification of POPs between plankton and fish (*21*, *45*, *46*), increases in contaminant concentrations within lower planktonic trophic levels are less often seen. For example, no biomagnification and OC concentrations reflective of equilibrium partitioning with water have been observed for various plankton species in the Arctic (*47*−*49*). However, an increase in PCB concentration with age for organisms with a life span greater than 1 yr (fish) has been observed (*45*), and longer life spans have been suggested to lead to increased biomagnification in fish and other marine organisms. Given the long life span of krill (6−7 yr) as compared to other zooplankton (*50*), we expected to see POP biomagnification in adult krill.

The absence of biomagnification for HCB is more likely than for the BDEs, given the relatively low octanol−water partition coefficient (K_{ow}) of this compound. Although POPs in general are hydrophobic and lipophilic, characteristics that affect POP bioaccumulation vary. For example, chemicals with log $K_{ow} > 6.3$ were observed to be biomagnified in a food web containing zooplankton, benthic invertebrates, and fish, while chemicals with log $K_{ow} \leq 5.5$ (including HCB, log $K_{ow} = 5.5$) were not biomagnified (*51*). Similarly, HCHs (log $K_{ow} = 3.8$) and HCB, despite being the most abundant OCs in air and seawater samples from the Canadian Arctic, were present in low concentrations in biota (*52*). Consistent with our results, meso- and macrozooplankton in the Arctic were found to contain similar amounts of α-HCH as ice algae and phytoplankton on a per lipid basis (*47*).

Lack of biomagnification for HCB may reflect the uptake mechanisms of this contaminant. Zooplankton, including crustaceans, can accumulate POPs through ingestion of contaminated food or by passive accumulation from water into internal lipid pools. The mode of uptake varies depending on the characteristics of each contaminant, with lower K_{ow}, more water-soluble compounds, bioavailable via passive uptake from water (*48*, *49*). If krill accumulate POPs primarily by equilibrium absorption into their lipids from water, we would expect to see similar concentrations in plankton and krill on a per lipid basis. This was observed for HCB in plankton and adult krill, suggesting passive uptake by equilibrium partitioning as the primary mechanism of uptake of this contaminant by krill.

Despite no difference in BDE concentrations between ice algae and juvenile krill (Figure 2), equilibrium partitioning of these contaminants between water and juvenile krill is unlikely because of the high K_{ow} values (log $K_{ow} > 6.5$) and, consequently, low solubilities of these contaminants. Lack of equilibrium partitioning of high K_{ow} OCs has also been observed between zooplankton and water in the Arctic (*48*, *49*). Likewise, the low solubility of BDEs does not suggest a high dissolved under-ice or water column concentration for these compounds. Instead, BDEs would likely be more bioavailable absorbed to ice algae or plankton and would be taken up by juvenile and adult krill via ingestion. Biomagnification would therefore be more likely for BDEs. Also, since biomagnification of POPs increases with age, it would be more likely to be observed in adult krill. A number of factors may account for the lack of biomagnification for BDEs between ice algae and juvenile krill and especially for the significant decrease in BDE concentrations between plankton and adult krill.

First, it is important to note that our sampling method may have led to higher contaminant concentrations for ice algae than were actually present in the ice column. Because melted ice samples were passed through a GFF filter for particulate matter collection, dissolved-phase compounds in ice may have absorbed to particles during filtration causing an over-representation of the fraction associated with ice algae. However, this potential over-collection would only occur if contaminant partitioning between ice and ice algae were not already at equilibrium. Under low temperature, slow growth conditions, algae have been observed to reach equilibrium with PCBs in water after about 20 d (*54*). Given the environmental conditions associated with sea ice, it is likely that the ice algae were under slow growth conditions and had presumably reached equilibrium with contaminants in sea ice prior to our sampling at the end of winter. Thus, it is unlikely that the measured ice algae concentrations were influenced by the collection method. Moreover, this potential sampling artifact would not have been a factor controlling the significantly lower BDE concentrations in adult krill compared to phytoplankton (Figure 2).

Increasing lipid content in adult krill during summer could lead to biodilution of contaminants during trophic transfer. In the Arctic, zooplankton synthesize lipids during summer as energy reserves (*55*). Seasonal accumulation of lipids during summer by Antarctic krill has also been observed (*56*). An increase in lipid reserves in Arctic zooplankton has been hypothesized to lead to a dilution of PCBs and was suggested to explain lower PCB concentrations in the zooplankton than particulate matter on a lipid weight basis (*53*). A lower PCB concentration in zooplankton as compared

to particulate matter on a lipid weight basis has also been attributed to a dilution of contaminants in autogenically formed lipids (*57*). Since these lipids are contaminant free, an increase in lipid reserves at a faster rate than contaminant uptake by krill feeding on plankton may have played a role in diluting contaminants, particularly the BDEs, during this initial trophic transfer. Accumulation of lipid reserves in adult krill during summer may also explain the apparent dilution of BDEs in adult as compared to juvenile krill collected in winter (Figure 2). Likewise, growth dilution may account for the decreases in POP concentrations between juvenile and adult krill. Growth dilution of POPs occurs when the growth rate of the organism is faster than the uptake rate of POPs, resulting in a dilution of the pollutant in the growing biomass and a decreased concentration per unit of lipid biomass. Growth dilution has been suggested as an explanation for the inverse relationship between krill length and mercury concentration (*58*).

Biomagnification factors less than one also occur when the rate of elimination exceeds that for uptake of a compound and may explain the lower levels of BDEs in adult krill compared to plankton. Organisms at higher trophic levels (i.e., mammals) generally have a higher capacity to metabolize persistent organochlorines. This capability is also suggested for longer-lived plankton (*52*) and may be likely for krill given their relatively long life span. It can be hypothesized that this process would be more important for elimination of BDEs as compared to HCB since BDEs have vicinal C−H pairs that would allow for biodegradation via the monooxygenase pathway (*59*), whereas HCB does not. However, egestion is another mechanism by which zooplankton can eliminate contaminants. PCB concentrations in krill fecal pellets have been found to be 10−1000× higher than in euphausiid bodies or molts (*60*). Given the similarity of BDE structure to PCBs, this suggests that egestion may account for some of the decrease observed for BDEs in adult krill compared to their food source and for the lack of biomagnification between ice algae and juvenile krill.

The absence of POP biomagnification between plankton and krill samples was surprising, given the long life span of krill. The significant decrease for BDEs between plankton and adult krill was particularly surprising, given the high potential for biomagnification of these compounds. It is also interesting that, while the average BDE concentration was significantly higher than the HCB concentration in ice algae and plankton, this contrast was not the case in krill. Thus, BDEs may not be efficiently transferred to higher trophic levels despite the apparently higher input of these contaminants to the Antarctic coastal ecosystem and higher concentration in the lowest trophic levels.

Our results further suggest that sea ice contributes contaminants to higher trophic levels in polar food webs. This occurs directly via feeding by juvenile krill on ice algae but may also include contaminant uptake by plankton and adult krill following ice melt. Therefore, sea ice appears to provide a controlling vector for entry of POPs into the Antarctic marine environment and food web.

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Supporting Information Available

Table S1 includes concentration data (ng/g_{lipid}) for OCs and BDEs measured in all Antarctic plankton, sea ice algae, juvenile and adult krill samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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