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Enantiomer Fractions of Organic Chlorinated Pesticides in Arctic Marine Ice Fauna, Zooplankton, and Benthos

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Stereoisomers of chiral chlorinated pesticides (α-HCH (HCH = hexachlorocyclohexane), *trans*- and *cis*-chlordane, MC5, *o,p′*-DDT) were quantified in arctic marine invertebrates (ice-associated amphipods *Gammarus wilkitzkii*, pelagic copepods *Calanus hyperboreus*, krill *Thysanoessa inermis*, and amphipods *Themisto libellula*, and benthic amphipods *Paramphithoe hystrix*). Enantiomer fractions (EFs) were calculated to investigate the influence of habitat, geographic area, and diet on selective bioaccumulation of the (−)- or (+)-enantiomer. Depletion of the (+)-α-HCH enantionmer increased from ice fauna to zooplankton to benthos, corresponding to previous reports of EF variations with depth. Chlordanes and *o,p′*-DDT also showed the strongest enantioselective bioaccumulation in benthic amphipods and less so in zooplankton and ice fauna, which had closer to racemic EFs. Neither diet nor geographic area explained EF differences among samples. Nonracemic EFs in benthos may be related to stereoselective biotransformation, but is most likely reflecting vertical distribution of EFs in the water column and sediments, as demonstrated earlier for α-HCH in the Canadian and European Arctic.

Introduction

Chlorinated pesticides (CPs) such as hexachlorocyclohexanes (HCHs), chlordanes, and DDT have been heavily used worldwide in agriculture, forestry, and public health to control insect populations during the past half-century. Due to atmospheric and oceanic long-range transport, the insecticides have been transferred to regions far from their origins of use to the Arctic (*1*, *2*). Here the insecticides accumulate in organisms and reach concentrations that could potentially affect the organism's normal physiology and behavior (*3*).

Biological receptors are sensitive to the chemical's molecular structure. CPs such as α-HCH, *trans*-chlordane, *cis*-chlordane, octachlordane MC5, and *o,p′*-DDT are chiral compounds composed of two stereoisomers which are identical in atoms and bindings, but with different 3D structures that are not superimposable (*4*). The proportions of the two stereoisomers (enantiomers) in the technical mixtures are 1:1, i.e., racemic. Enantiomers have identical physicochemical properties and abiotic degradation rates, but because of different molecular configurations, they may differ in binding to structure-sensitive biological receptors and as a result undergo biotic degradation at different rates (*4*, *5*).

Studies of enantioselective bioaccumulation and degradation of CPs have become possible over the past 15 years due to the development of chiral chromatographic techniques that can separate the enantiomers (*4*). The chiral compound α-HCH undergoes enantioselective degradation in arctic seawater, but the degradation characteristics vary spatially and with depth. Depletion of the (−)-enantiomer was reported in surface water of the Bering−Chukchi Seas, while the (+)-enantiomer was selectively degraded in surface water of the Canada Basin and the eastern Arctic Ocean (including the Greenland Sea and north of Svalbard) (*1*, *6*, *7*) and in the Canadian Archipelago (*8*−*10*). Enantioselectivity increased with depth in the Canada Basin and eastern Arctic Ocean, with greater proportions of (+)-α-HCH being depleted below the polar surface water (PSW) (*6*, *7*). Preferential loss of (+)-α-HCH was also reported in arctic lakes and wetlands (*11*, *12*).

In addition to area-specific exposure to nonracemic chiral chemicals in water, biota may alter the enantiomeric proportions by selective uptake, biotransformation, and elimination (*5*, *9*, *13*−*15*). In the Canadian and Alaskan Arctic, marine zooplankton had (+)-α-HCH depletions similar to those of the water, suggesting no or limited biotransformation in these organisms (*9*, *10*). There are few data available on the enantiomer signatures of CPs in arctic marine invertebrates from other habitats, such as in association with sea ice (ice fauna) or the sea floor (benthos).

Given the documented change in (+)-α-HCH depletion with depth (*6*, *7*), and as some CP concentrations differ among ice fauna, zooplankton, and benthos (*16*−*18*), a closer investigation of animals from different habitats representing the water column is of interest. It is also of interest to study enantiomers of other chiral CPs such as *cis*- and *trans*-chlordane, MC5, and *o,p′*-DDT, for which there is presently little knowledge of distribution in arctic marine lower trophic levels as well as the abiotic compartments. The objectives of the present study were to investigate the influence of habitat, geographic area, and diet on enantioselective bioaccumulation of selected chiral CPs in European Arctic marine invertebrates. In addition, the relationship between CP concentration and enantioselective bioaccumulation was investigated.

Materials and Methods

Collection of Animals and Species Description. Ice fauna, zooplankton, and benthos were collected from Sept 25 to Oct 5, 1999, in the marginal ice zone northwest and northeast of Svalbard, and in the Greenland Sea (Table 1, Figure 1). Ice fauna (amphipods *Gammarus wilkitzkii* Birula 1897) were collected by scuba divers using an electric suction pump (*21*). Zooplankton (copepods *Calanus hyperboreus* Kröyer 1838, euphausiids/krill *Thysanoessa inermis* Kröyer 1846, amphipods *Themisto libellula* Lichtenstein 1822) were collected by vertical net hauls (WP-3 net and MEGA net, 1000 μm mesh) and a pelagic trawl (Tucker trawl, 1000 μm mesh). North of Svalbard, the first nets were hauled from 800 m to the surface; however, due to the higher abundance of animals in the upper water masses, most animals were collected from the upper 200−300 m. Benthic amphipods (*Paramphithoe hystrix* Ross 1835) were collected by bottom trawl. In the Greenland Sea, *T. libellula* was collected by bottom trawl.

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TABLE 1. Sampling, Biological Information (Mean ± SE (Minimum−Maximum)), Enantiomer Fractions, and Concentrations of Chlorinated Pesticides (ng·g^{-1} Extractable Organic Matter Adjusted, Mean ± 95 CI Adjusted for Sample Size) in Arctic Marine Invertebrates Collected in the Marginal Ice Zone from Sept 25 to Oct 5, 1999[a]

	Gammarus wilkitzkii		*Calanus hyperboreus*		*Thysanoessa inermis*	*Themisto libellula*		*Paramphithoe hysterix*
organism	gammarid amphipod		calanoid copepod		euphausiid (krill)	hyperiid amphipod		epimeriidae amphipod
habitat	sea ice underside		pelagic		pelagic	pelagic	epibenthic	benthic
location[b]	NOS	GS	NOS	GS	GS	NOS	GS	YP
sampling	suction pump		net/pelagic trawl		pelagic trawl	net/pelagic trawl	bottom trawl	bottom trawl
sampling depth (m)	∼0−5	∼0−5	∼0−300	∼0−150	∼0−150	∼0−300	∼309−319	∼560−570
station depth (m)	>3000	∼327	>3000	∼327	∼327	>3000	∼327	∼576
n[c]	5	4	6	5	4	1	3	3
N[d]	7−51	9−76	350−650	315−365	50	66	25	6
size[e] (mm)	19.5 ± 0.5 (12−44)	15.0 ± 0.6 (5−44)	(5−10)	(5−10)	25.6 ± 0.1 (21−30)	20.2 ± 0.6 (11−35)	38.9 ± 4.2 (31−49)	35.8 ± 6.2 (21−42)
diet[f]	OMNI	OMNI	HERB	HERB	HERB	OMNI	OMNI	OMNI
EOM[g] (%)	3.4 ± 0.4	4.3 ± 0.7	7.3 ± 0.4	12.3 ± 0.5	10.7 ± 0.4	3.5	6.6 ± 0.3	5.0 ± 0.6
enantiomer fractions								
α-HCH	0.447 ± 0.016	0.452 ± 0.005	0.432 ± 0.021	0.429 ± 0.023	0.415 ± 0.004	0.409	0.348 ± 0.009	0.277 ± 0.036
trans-chlordane	0.482 ± 0.017	0.480 ± 0.010	0.487 ± 0.013	0.505 ± 0.006	0.481 ± 0.007	0.481	0.478-0.481	0.445 ± 0.093
cis-chlordane	0.508 ± 0.009	0.510 ± 0.008	0.501 ± 0.014	0.493 ± 0.006	0.495 ± 0.003	0.497	0.498-0.502	0.617 ± 0.316
MC5	0.471 ± 0.127	0.458 ± 0.051	0.489	0.481 ± 0.004	0.476 ± 0.020	0.477	0.468	0.369 ± 0.085
o,p′ -DDT					0.511 ± 0.006	0.509	0.578 ± 0.040	0.793 ± 0.195
concns (ng·g^{-1} EOM)								
∑HCHs[h]	22.5 ± 2.1	63.8 ± 18.5[k]	15.1 ± 4.2	23.8 ± 12.2	26.1 ± 2.3	26.3	24.8 ± 15.2	357 ± 327
∑chlordanes[i]	46.2 ± 20.8	44.0 ± 25.0	14.3 ± 2.7	17.9 ± 5.0	18.6 ± 1.7	51.6	76.7 ± 17.6	799 ± 272
∑DDTs[j]	29.7 ± 13.4	21.9 ± 14.1	7.7 ± 2.1	8.0 ± 3.3	10.9 ± 1.8	37.5	72.3 ± 15.4	1836 ± 1792

[a] A missing SE or CI is due to a sample size of ≤2 for the respective EF, concentration, or measurement. [b] GS = location in the Greenland Sea: 76°45′N, 08°12′W. NOS = location north of Svalbard: 82°27′N, 35°55′E. YP = location at the Yermak Plateau: 81°16′N, 08°12′E. Location abbreviations correspond to the letters in Figure 1. [c] *n* = total number of samples analyzed. [d] *N* = number of individuals pooled per sample. [e] Size measured to nearest millimeter from anterior margin of head to the end of the uropod for amphipods and euphausiids. Length ranges for copepods are for copepodite stages C V and C VI (*52*). [f] Classified as omnivorous (OMNI) or herbivorous (HERB) according to the literature (*19, 20, 22, 25, 30, 31*). This coarse division is based on the main diet, although it is known that most of the species also feed on detritus, that, e.g., *Gammarus wilkitzkii* and *Themisto libellula* also feed on ice algae and phytoplankton, and that *Thysanoessa inermis* occasionally feed on copepods and other small zooplankton. [g] EOM = extractable organic matter using cyclohexane and acetone. Reported as a percent of the sample wet weight. Mainly composed of neutral lipids (triacylglycerols and wax esters, depending on the species). [h] Sum of α-, β-, and γ-hexachlorocyclohexanes. [i] Sum of oxychlordane, *cis*- and *trans*-chlordane, and *trans*-nonachlor. [j] Sum of *p,p′*-DDE, *p,p′*-DDT, and *p,p′*-DDD. [k] One sample was omitted from the estimation of the mean and CI due to extremely high values (3 times the reported mean).

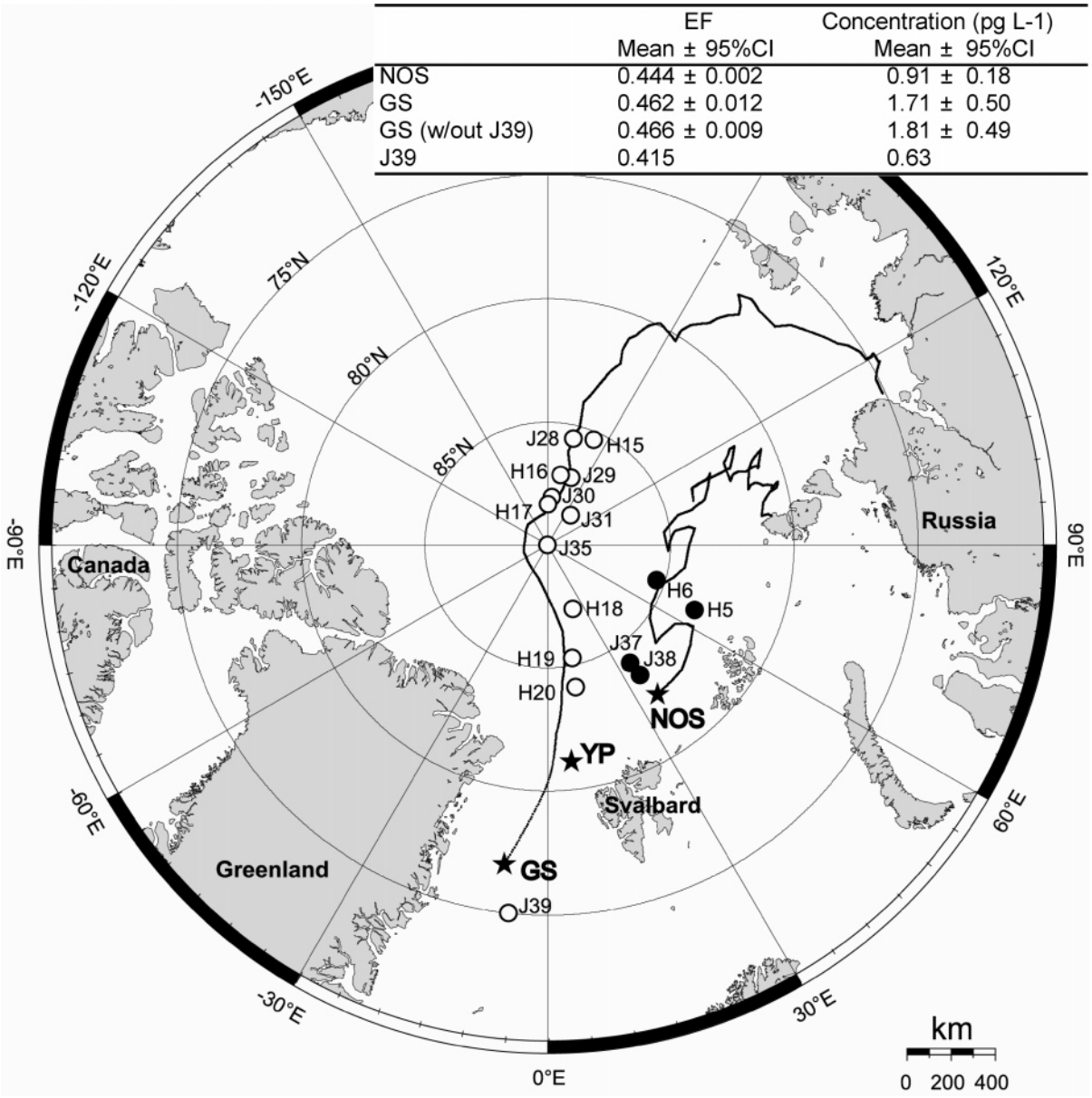

FIGURE 1. Sampling stations in the Arctic: stars, present study, Sept 25 to Oct 5, 1999; GS, Greenland Sea; YP, Yermak Plateau; NOS, north of Svalbard; lines, back-trajectories of ice drift to sampling stations in the GS and NOS (from ref *32*); circles, sampling stations of surface water for measurements of HCH concentrations and enantiomer signal in 1994 (from ref *6*) and 1996 (from ref *7*). Letters (J and H) and numbering refer to the respective water study and their station identification (*6, 7*). The table reports the mean ± 95% CI of α-HCH EFs in water (from refs *6* and *7*) along the respective transects: white circles to the GS, black circles to NOS.

The samples were assigned ice-associated, pelagic, or benthic in the statistical analyses depending on how they were sampled.

G. wilkitzkii are omnivorous amphipods living in association with the sea ice underside (*19*, *20*). They live up to 5−6 years and drift along with the sea ice across the Arctic Ocean (*21*). The pelagic copepods *C. hyperboreus* are predominantly herbivorous on phytoplankton (*22*). These arctic species have a 4−5 year life cycle, with the population core area in the Arctic Ocean, and they overwinter in an inactive state in the deeper layers of the sea (*23*, *24*). The pelagic krill *T. inermis* are predominantly herbivorous, but occasionally feed on microzooplankton (*25*). They have a life span of 3−4 years (*26*). The pelagic amphipod *T. libellula* is predatory on other zooplankton (*22*). They generally have a life cycle of 2−3 years (*27*, *28*). The benthic amphipod *P. hystrix* lives on deep-sea corals (*29*), and feeds on tissues of invertebrate hosts much larger than itself, including poriferans, hydrozoans, and echinoderms (*30*, *31*). Little is known of the general biology of this species.

The euphausiids' and amphipods' total stretched body length was measured to the nearest millimeter from the anterior margin of the head to the end of the uropod (Table 1). The organisms were pooled into samples and stored frozen (−20 °C) in polypropylene containers until chemical analyses.

Water Masses. Conductivity, temperature, and density (CTD) profiles in the water column were measured at each station with a CTD sensor (General Oceanics EG&G MARK-III C) (*32*). The water masses were determined by comparing conductivity, temperature, and density measurements from each station to water mass characteristics (*33*). The hydrographical data (CTD profiles) of the upper water column (below the meltwater layer) indicated an influence of PSW north of Svalbard and in the Greenland Sea. There, the cold and less saline PSW was separated by a pycnocline from warmer and more saline transformed Atlantic water (AW) in

the layers underneath. The AW is transformed and modified by other water masses on its way to and within the Arctic Ocean. At the Yermak Plateau, the deeper water masses where the benthic amphipods were collected were influenced by AW. Thus, ice fauna were collected in water of meltwater mixed with PSW, zooplankton were generally sampled from PSW, and *P. hystrix* and *T. libellula* collected with bottom trawl were collected from AW.

Chemical Analyses. Methods for the extraction and quantification of organic matter (EOM) and associated CPs with cyclohexane and acetone, at the Environmental Toxicology Laboratory at the Norwegian School of Veterinary Science, Oslo, Norway, are described in detail elsewhere (*17*, *34*), modified from Brevik (*35*). The CPs α-, β-, and γ-HCH (HCHs), oxychlordane, *cis*- and *trans*-chlordane, *trans*-nonachlor, and oxychlordane (chlordanes), *p*,*p*′-DDE, *p*,*p*′-DDD, and *p*,*p*′-DDT (DDTs) were separated by high-resolution gas chromatography (Agilent 6890 Plus GC system, Agilent Technologies). The gas chromatograph was equipped with two fused silica capillary columns of different polarities (SPB-5 and SPB-1701; 60 m, 0.25 mm i.d., 0.25 μm film; Supelco Inc.) and a ^{63}Ni micro electron capture detector (ECD; Agilent Technologies).

The extracts were divided for gravimetric determination of EOM and for cleanup of EOM by sulfuric acid. A part of the EOM-free extracts were shipped to the Meteorological Service of Canada, Toronto, Canada, for analysis of the enantiomer composition of chiral CPs. Enantiomer determinations were done by capillary gas chromatography−electron capture negative ion mass spectrometry using published conditions (*14*, *36*−*38*) or slight variations. Two ions were monitored for each compound, α-HCH 255/257, chlordanes 410/412, and *o*,*p*′-DDT 246/248. For a satisfactory analysis, the ion ratio for each enantiomer peak in a sample was required to be within the 95% confidence interval (CI) of the mean ratio for standards.

Several columns (15−30 m length × 0.25 mm i.d., 0.25 μm film thickness) containing different chiral stationary phases were used to carry out the required separations and confirm identities: BGB-172 (20% *tert*-butyldimethylsilylated β-cyclodextrin in OV-1701, BGB Analytik AG, Switzerland), Betadex-120 and Betadex-325 (BDX-120, 20% permethylated β-cyclodextrin in SPB-25; BDX-325, 25% 2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilylated β-cyclodextrin in SPB-20; both columns from Supelco Corp.), and Rt-βDEXcst (proprietary phase, Restek Corp.). The α-HCH enantiomer elution order is (+), (−) on BDX-120, BDX-325, and Rt-βDEXcst, and (−), (+) on BGB-172 (*12*, *36*). Elution orders of *trans*-chlordane (TC) and *cis*-chlordane (CC) enantiomers are (+)-TC, (−)-TC, (+)-CC, (−)-CC on BDX-120, and (+)-TC, (+)-CC, (−)-CC, (−)-TC on BGB-172 (*37*). Chlordane MC5 enantiomers are resolved only on BDX-120 (optical signs unknown) (*36*, *37*), and *o*,*p*′-DDT enantiomers are resolved only on BGB-172 with the elution order (−), (+) (*39*). Enantioenriched standards of (+)-α-HCH, (+)-TC, and (+)-CC (Ehrenstorfer Laboratories, Germany) were used in combination with racemic standards to confirm these elution orders; the order for *o*,*p*′-DDT was assumed to be the same as reported elsewhere (*39*).

The resulting data were quantified as the enantiomer fraction, EF, which is preferred over the enantiomer ratio (*40*, *41*). The EF was defined by the chromatographic peak areas of the (+)- and (−)-enantiomers for compounds with known optical rotations: EF = (+)/[(+) + (−)]. Thus, a racemic compound has an EF = 0.5, while EFs < 0.5 and > 0.5 indicate selective depletion of the (+)- and (−)-enantiomers, respectively. The EF of MC5 was defined as peak 1/[peak 1 + peak 2] as determined on the BDX-120 column, since its optical signs are not known (*37*). Agreement of the EFs determined on columns with dissimilar enantiomer elution orders agreed well. The EFs of α-HCH determined on two columns, BGB-172 and either BDX-325 or Rt-βDEXcst, were compared for 23 samples. None of the columns gave consistently higher or lower EF results than the others, and the (BGB-172 EF − column 2 EF)/mean EF averaged −1.4%, where column 2 was either BDX-325 or Rt-βDEXcst. Similarly, 20 samples were compared for the EFs of TC and CC on the BGB and BDX-120 columns. The (BGB-172 EF − BDX-120 EF)/mean EF averaged 0.3% for TC and 0.7% for CC. The mean EFs from multiple column determinations were used in the data treatment below. The EFs ± 95% CI (*n*) for racemic standards were (α-HCH) 0.502 ± 0.001 (62), (*trans*-chlordane) 0.501 ± 0.001 (86), (*cis*-chlordane) 0.501 ± 0.001 (82), (MC5) 0.499 ± 0.003 (16), and (*o*,*p*′-DDT) 0.500 ± 0.002 (36).

Data Treatment. The EFs of individual samples were considered racemic if they fell within the mean ± 95% CI of racemic standards ($t_{0.05,df}$, Student's *t* test; *42*). To analyze the effect of habitat, geographic area, and diet on EFs, analyses of variance (ANOVA type III SS, SAS V8; *43*) were carried out including only samples where EFs were determined. Nonsignificant variables were deleted, and Tukey's comparison of means was done on the habitat after removal of nonsignificant variables. *T. libellula* collected with a benthic trawl were characterized as benthic in the statistical analyses of the influence of habitat.

Principal component analysis (PCA) (*44*) was carried out on the variance−covariance matrix (EFs were centered, but not standardized) including the EFs quantified in all species (α-HCH, *cis*-chlordane, *trans*-chlordane, and MC5), and the EF scores were scaled by division by the standard deviation (CANOCO 4.5; *45*). For missing data (19 out of 120 values), the species' mean EF at the respective station was used as a replacement. As 12 of the 19 missing data points were for MC5, the PCA was carried out both with and without MC5 to control for the replacement of missing EFs. The resulting principal components (PCs) were highly correlated (adjusted $R^2 > 0.999$, $p < 0.0001$ for all PCs), and missing values were therefore included in the final analyses. Tukey's comparison of means was done to investigate differences in scores on PC1 and PC2 among species.

Spearman rank correlation was performed to investigate the relationship among EFs, PCs, EOM adjusted CP concentrations, and the relative proportion of the respective CP (α-HCH/∑HCH, *cis*- or *trans*-chlordane/∑chlordanes).

Results and Discussion

EFs in Arctic Marine Invertebrates. The mean EOM adjusted sums of chlorinated pesticide concentrations were 98−130 ng·g^{-1} in ice fauna, 37−56 ng·g^{-1} in herbivorous zooplankton, 115−174 ng·g^{-1} in omnivorous zooplankton, and 2992 ng·g^{-1} in benthic amphipods (Table 1). A presentation and discussion of CP concentrations in all species except *P. hystrix* can be found in Borgå et al. (*17*).

EFs of α-HCH, *cis*- and *trans*-chlordane, and MC5 were determined in all species (Table 1), although not in all samples. The *o*,*p*′-DDT isomer was not found in copepods and ice-associated amphipods. When data for individual samples were compared with the 95% CI of the racemic standards, it was found that all samples had nonracemic EFs, except *trans*-chlordane in one copepod sample, and *cis*-chlordane in one copepod and one bottom-trawled *T. libellula* sample. The benthic amphipod (*P. hystrix*) had the most nonracemic EFs of all species for all compounds; the mean ± 95% CI ranged from 0.277 ± 0.036 for α-HCH to 0.793 ± 0.195 for *o*,*p*′-DDT (Table 1, Figure 2). They differed from the EFs for all other species, which were closer to racemic (Tables 1 and 2a, Figure 2). EFs in *P. hystrix* showed high variation, especially for *cis*- and *trans*-chlordane and *o*,*p*′-DDT, compared to those in the other species (Figure 2). Increasing nonracemic *o*,*p*′-DDT EFs correlated with in-

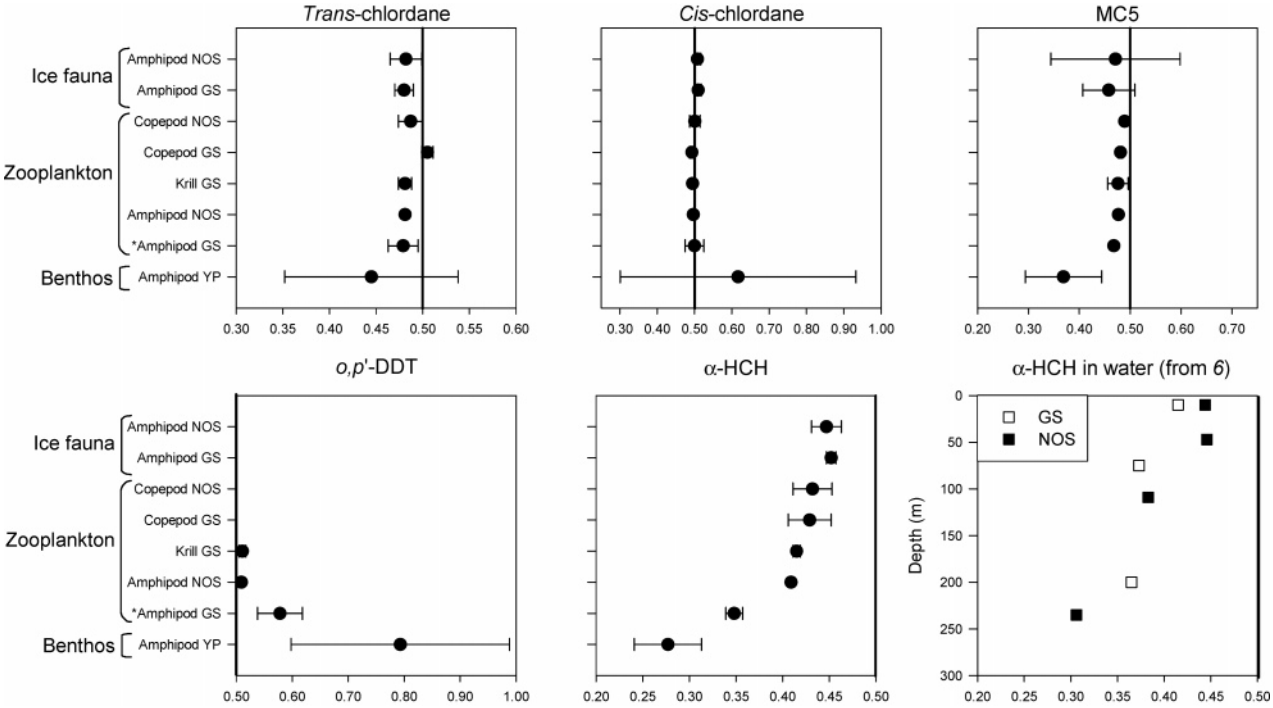

FIGURE 2. Enantiomer fractions (mean ± 95% CI) of chlorinated pesticides in ice fauna (amphipods *Gammarus wilkitzkii*), zooplankton (copepods *Calanus hyperboreus*, krill *Thysanoessa inermis*, amphipods *Themisto libellula*) collected northeast of Svalbard (NOS), and in the Greenland Sea (GS). Benthic amphipods (*Paramphithoe hysterix*) were collected from the Yermak Plateau (YP). The asterisk indicates *Themisto libellula* collected with a benthic trawl. The line at 0.5 indicates racemic EF. The α-HCH EF seawater depth profiles are from Jantunen and Bidleman (*6*).

creasing nonracemity of the other pesticides, except for *cis*-chlordane (Table 2b). Similarly, increasing nonracemic *trans*-chlordane EFs correlated with increasing MC5 nonracemity (Table 2b). This may imply that the process leading to nonracemic bioaccumulation of these chiral CPs is through the same mechanism.

Only a few published data on chiral CPs in marine invertebrates are available for comparison with the data of the present study. The EFs of α-HCH in calanoid copepods in the present study (0.431) were lower than in the coastal Beaufort−Chukchi Seas (0.48) (*9*), but more similar to EFs from the Northwater Polynya (0.42) (*10*). Both Hoekstra et al. (*9*) and Moisey et al. (*10*) reported α-HCH EFs in zooplankton similar to those in water, suggesting nonenantioselective bioaccumulation. The EFs of α-HCH in pelagic *T. libellula* in the present study (0.409) were lower than EFs from the Northwater Polynya (EF = 0.43, *10*), which were both higher than in present *T. libellula* collected by bottom trawl (EF = 0.348).

EFs of *trans*-chlordane in seawater, and of *cis*-chlordane in seawater and copepods, from the coastal Beaufort−Chukchi Seas were all considered racemic (*9*). *trans*-Chlordane and *cis*-chlordane were racemic also in European and North American arctic waters (*1*), and Arctic cod (*Boreogadus saida*) (*9*, *14*).

Spatial Variation in EFs. Geography was not a significant variable in the ANOVA for any of the EFs (Table 2a). Although little is known about the environmental stability of EFs in the Arctic, it was surprising that α-HCH EFs were similar in animals from north of Svalbard and the Greenland Sea, as EFs in water differed between these areas in the mid-1990s (*6*, *7*) (Figure 1). In addition, both ice fauna and copepods from the Greenland Sea had higher α-HCH concentrations compared to those from north of Svalbard (*17*, *34*). Ice amphipods from the Greenland Sea were associated with ice that had drifted across the ice-dense central Arctic Ocean, while those from north of Svalbard were on ice that had drifted a more southern route in dispersed ice (*32*) (Figure 1). The month prior to sampling, sea ice at the Greenland Sea station had drifted south at least 360 km from 79°72′N, 01°55′W, whereas sea ice at the station north of Svalbard had drifted west at least 80 km from 82°51′N, 41°89′E (*17*). By averaging surface water α-HCH EFs from Jantunen and Bidleman (*6*) and Harner et al. (*7*) along the respective ice trajectories, α-HCH EF from the north of Svalbard ice trajectory was lower than the EF along the Greenland Sea ice trajectory (Figure 1). The EF in water along the north of Svalbard trajectory was within the range found in copepods and ice amphipods (Table 1, Figure 1), whereas Greenland Sea copepod and ice amphipod EFs were between the EFs in water along the Greenland Sea trajectory and at Station 39 (Table 1, Figure 1). The variance in α-HCH water concentrations was higher along the trajectory to the Greenland Sea than to north of Svalbard (Figure 1) (*6*, *7*). Thus, assuming that the seawater α-HCH conditions were comparable in the mid-1990s and late 1990s, ice amphipods collected north of Svalbard experienced a rather uniform exposure of α-HCH EFs and concentrations from water, whereas those collected from the Greenland Sea were exposed to a wider range of concentrations and EFs as the ice moved through the central Arctic Ocean and down into the Fram Strait (Figure 1). Until reaching the sampling station in the Greenland Sea, the animals were exposed to higher water concentrations and higher EFs, and may not yet have reached equilibrium with the Greenland Sea water. Copepods in the Greenland Sea are advected from the core area in the Arctic Ocean (*46*), and may have followed relatively similar trajectories and water masses as the ice fauna. The copepods' α-HCH EFs in the Greenland Sea were lower than the ice amphipods' EFs, and they were closer to the EF in water at Station 39.

The principal component analyses of the samples' EFs resulted in three PCs which together accounted for 98.2% of the total variance (PC1 and PC2 shown in Figure 3a). Whereas

TABLE 2. Summary of (a) ANOVA Type III Sum of Squares and Tukey's Test of the Enantiomer Fraction (EF) Comparison among Samples and (b) Spearman Rank Correlation among Samples[a]

(a) ANOVA Type III Sum of Squares and Tukey's Test of the Enantiomer Fraction (EF) Comparison among Samples

	α-HCH	*trans*-chlordane	*cis*-chlordane	MC5	*o,p′*-DDT
EF = habitat + diet	$n = 29$	$n = 24$	$n = 25$	$n = 18$	$n = 11$
habitat	**$F = 74.59$, $p = 0.0001$**	$F = 2.56$, $p = 0.10$	$F = 2.70$, $p = 0.09$	**$F = 7.96$, $p = 0.0049$**	$F = 2.6$, $p = 0.15$
diet	$F = 0.59$, $p = 0.45$	$F = 0.24$, $p = 0.63$	$F = 0.00$, $p = 0.99$	$F = 0.00$, $p = 0.93$	$F = 0.00$, $p = 0.98$
EF = habitat	**$F = 82.9$, $p < 0.0001$**	**$F = 5.8$, $p = 0.0103$**	**$F = 4.38$, $p = 0.0251$**	**$F = 14.01$, $p = 0.0004$**	**$F = 9.15$, $p = 0.0144$**
ice-associated	A	AB	AB	B	
pelagic	B	A	A	B	A
benthic	C	B	B	A	B
EF = habitat + area	$n = 18$	$n = 14$	$n = 15$	$n = 9$	
habitat	**$F = 8.9$, $p = 0.0091$**	**$F = 10.61$, $p = 0.0076$**	**$F = 12.5$, $p = 0.0041$**	**$F = 5.38$, $p = 0.0595$**	
area	$F = 0.03$, $p = 0.85$	$F = 2.56$, $p = 0.14$	$F = 0.37$, $p = 0.5550$	$F = 1.33$, $p = 0.2930$	

(b) Spearman Rank Correlation among Samples

	α-HCH EF	*trans*-chlordane EF	*cis*-chlordane EF	MC5 EF	*o,p′*-DDT EF
α-HCH EF		$n = 23$, $r = 0.28$, $p = 0.2$	$n = 24$, $r = 0.29$, $p = 0.16$	$n = 18$, $r = 0.27$, $p = 0.3$	**$n = 11$, $r = -0.91$, $p = 0.0001$**
trans-chlordane EF			$n = 24$, $r = -0.40$, $p = 0.053$	**$n = 18$, $r = 0.71$, $p = 0.001$**	**$n = 10$, $r = -0.78$, $p = 0.008$**
cis-chlordane EF				$n = 18$, $r = -0.42$, $p = 0.09$	$n = 10$, $r = 0.58$, $p = 0.08$
MC5 EF					**$n = 9$, $r = -0.73$, $p = 0.02$**
α-HCH concn (ng g^{-1} lw)	$n = 29$, $r = -0.16$, $p = 0.4$				
trans-chlordane concn (ng g^{-1} lw)		$n = 22$, $r = -0.35$, $p = 0.11$			
cis-chlordane concn (ng g^{-1} lw)			**$n = 23$, $r = 0.53$, $p = 0.009$**		
α-HCH/∑HCH	$n = 29$, $r = -0.2$, $p = 0.29$				
trans-chlordane/∑chlordanes		**$n = 0.22$, r = 0.48, $p = 0.024$**			
cis-chlordane/∑chlordanes			$n = 23$, $r = 0.34$, $p = 0.12$		

[a] The mean EF differs significantly among habitats when the letters differ (Tukey's test). The sample size (n) differs among analyses as not all samples could be included in all comparisons or correlations due to missing values. Significant comparisons ($\alpha = 0.05$) are in bold.

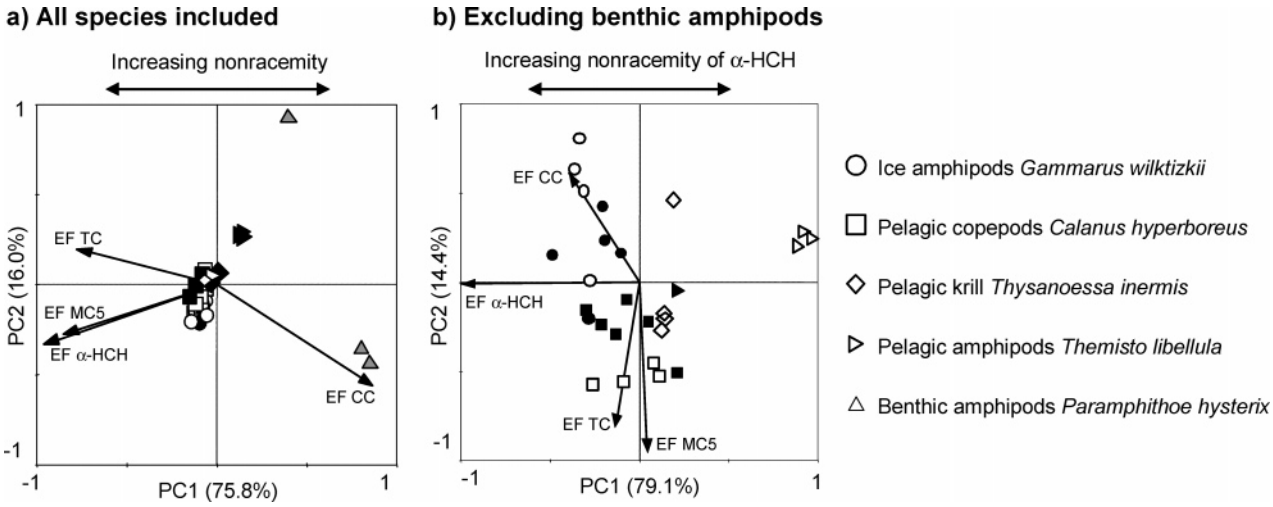

FIGURE 3. Principal component analysis of enantiomer fractions (EFs) of the chiral chlorinated pesticides α-HCH, MC5, *cis*-chlordane (CC), and *trans*-chlordane (TC) in the individual samples: (a) including all samples, (b) excluding *Paramphithoe hysterix* from the analysis, (black symbols) north of Svalbard, (white symbols) Greenland Sea, (gray symbols) Yermak Plateau. The EFs' arrows are pointing in the direction of increasing values.

cis-chlordane EF correlated positively with PC1, the other EFs correlated negatively (all loadings >|0.76| on PC1); therefore, increasing positive and negative values on PC1 indicate increasing enantioselective bioaccumulation (Figure 3a). All EFs had low correlation with PC2 and PC3 (loadings <|0.33|), except *cis*-chlordane on PC2 (−0.54) and MC5 on PC3 (−0.51). Due to the nonracemic EF composition (higher *cis*-chlordane EFs, and lower *trans*-chlordane, MC5, and α-HCH EFs), benthic amphipods had the highest PC1 values (Tukey, $p < 0.05$), whereas the other species were closer to the origin due to more racemic EFs (Figure 3a). Habitat was the only variable that significantly explained the samples' separation along PC1 and PC3 (PC1, $F_{2,23} = 17.48$, $p < 0.0001$; PC3, $F_{2,23} = 4.32$, $p = 0.0256$), whereas no variables significantly explained the variation along PC2. When *P. hystrix* were removed from the PCA (Figure 3b), the zooplankton and ice fauna were better separated, with bottom trawl collected *T. libellula* being separated from the rest of the samples. Although copepods and ice amphipods were separated along PC2 by species and due to the geographic sampling site, α-HCH EF per se was not significant in this separation, as it correlated with PC1.

Habitat-Related Variation in EFs. α-HCH was the only compound with a distinct decrease in the animals' EFs with depth, from ice fauna through zooplankton to benthic amphipods, whereas the other compounds showed gradually increased deviation from racemic with depth (Figures 2 and 3, Table 2a). The enantioselective bioaccumulation of α-HCH increased (thus decreasing the EFs) from ice fauna (*G. wilkitzkii*) to krill (*T. inermis*), and further to pelagic (*T. libellula*) and benthic (*P. hystrix*) amphipods (Figure 2). The α-HCH EF decrease in biota reflects the EFs in water, which decreased with depth (*6*) (Figure 2). Several explanations have been proposed for the change in α-HCH EFs with depth: a stronger nonracemic signal has been observed in sediments and suspended particulate matter than in the dissolved phase (*1*, *9*, *10*), which may be due to transport of HCH on sinking particles, and enantioselective degradation on those particles and in the sediments. However, this does not explain the prevalence of nonracemic α-HCH in the dissolved phase as sorption of HCHs onto particles is not strong; more than 88% of the HCHs in surface water are in the dissolved phase (*1*). Lower α-HCH EFs in subsurface water may be caused by the isolation of AW from atmospheric exchange as saline and warm inflowing surface AW is forced below the less saline and colder PSW north of Svalbard. Degradation of dissolved HCHs then proceeds in the AW without new atmospheric input, whereas the nearly racemic EF signal in the PSW is influenced by exchange with the atmosphere (*7*). The present study supports the isolation of AW as a source of increased deviation from racemic in benthos, as the water masses from where organisms were collected by bottom trawl were influenced by warmer, more saline water. Benthic amphipods have been exposed to incoming AW at the Yermak Plateau, whereas *T. libellula* had been exposed to outflowing AW on the shelf of the Greenland Sea.

The other CPs also showed significant EF differences among habitats (Figures 2 and 3, Table 2a), with higher enantioselective bioaccumulation in animals collected with the bottom trawl. Compared to bottom-trawled *T. libellula*, the one sample of pelagic *T. libellula* collected with net hauls/pelagic trawls had a higher α-HCH EF (0.348 ± 0.009 versus 0.409, respectively), being more comparable to the α-HCH EF in ice amphipods and calanoid copepods (Table 1, Figures 2 and 3). Generally, *T. libellula* are distributed in the upper pelagic zone of the water column (*28*), and not in the deeper waters, whereas older individuals are living close to the seabed but feeding from the pelagic zone. Although the bottom-trawled *T. libellula* were larger individuals, the size ranges overlapped with the pelagically collected ones; thus, the difference in EFs between the two is most likely due to habitat differences in exposure rather than other size-specific characteristics such as diet or age. It is notable that the CP concentrations were relatively comparable between the bottom trawl and pelagically collected *T. libellula* (Table 1). As discussed in detail elsewhere (*17*, *34*), samples from the Greenland Sea have a higher α-HCH concentration and a higher relative contribution of α-HCH to ∑HCH. Whereas the isomeric relative proportions of HCHs followed this geographic pattern, and therefore differed between the two *T. libellula* groups, the chlordane and DDT relative proportions did not differ between pelagically and benthic collected *T. libellula* (Figure 4). Both the HCH and chlordane relative proportions in benthic amphipods differed from those of the other species, with more α-HCH, less β-HCH, less *trans*- and *cis*-chlordane, and more *trans*-nonachlor in *P. hystrix* than all the other species (Tukey, $p < 0.05$) (Figure 4).

Diet and Biotransformation. Although detritus, primary producers, and other diet items of the invertebrates were not included in the present study, dietary influence on the invertebrates' EFs was investigated with diet (herbivore/

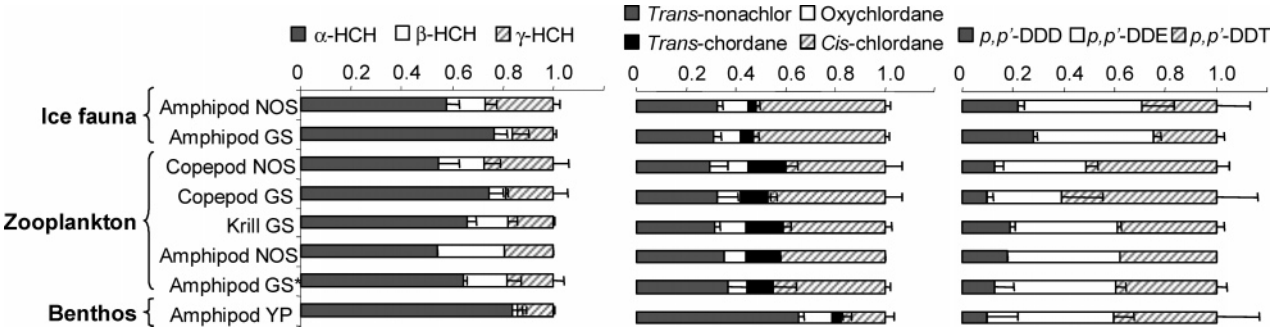

FIGURE 4. Relative proportions of chlorinated pesticides hexachlorocyclohexane (HCH), chlordane compounds, and DDTs in ice fauna (amphipod *Gammarus wilkitzkii*), zooplankton (copepod *Calanus hyperboreus*, krill *Thysanoessa inermis*, amphipod *Themisto libellula*) collected north of Svalbard (NOS), and in the Greenland Sea (GS) (mean + 95% CI). Benthic amphipods (*Paramphithoe hysterix*) were collected from the Yermak Plateau (YP). The asterisk indicates *Themisto libellula* collected with a benthic trawl.

omnivore) as one of the explanatory variables in the ANOVA. Diet did not explain any of the variation among the samples' EFs when the effect of habitat (ice-associated, pelagic, benthic) was accounted for, and was therefore deleted from the ANOVA (Table 2a). In the Great Lakes, chiral PCBs had racemic signals in lower trophic levels (algae and bulk zooplankton), and a higher degree of nonracemity in higher trophic levels (mysids *Mysis relicta*) (*15*). An explanation for the nonracemic EF composition of chiral PCBs in mysids may be enantioselective biotransformation (*15*), although mysids have a low ability to biotransform other nonchiral PCBs (*47*), and the authors could not rule out the possibility that the animals obtained nonracemic residues by feeding on organic-rich suspended particles and sediment detritus (*15*). In the present study, biotransformation seems unlikely to have influenced the observed EFs not only due to low biotransformation ability in arctic marine invertebrates (their EFs and isomeric relative proportions highly resemble those in water; see, e.g., *9*, *10*), but also since samples of *T. libellula*, in which biotransformation should be comparable, differ in EFs depending on the habitat (Figure 2). It is not likely that EF differences in *T. libellula* are due to different trophic levels, as their achiral CP concentrations are comparable (Table 1). Thus, although the possible influence of diet and biotransformation on invertebrates' EFs cannot be ruled out, the present study suggests that it is minor in terms of explaining variation in the animals' EFs, compared to other factors such as habitat (ice fauna, zooplankton, or benthos).

Law et al. (*12*) reported a higher degree of enantiomeric degradation of α-HCH in aquatic systems with a high chemical−sediment contact and a high chemical concentration. In the present study, although the animals living closer to the sediments (benthos) show a higher degree of enantioselective bioaccumulation, no correlation was found between either α-HCH or *trans*-chlordane concentration and their respective EFs (Table 2b). *cis*-Chlordane was the only compound with its EFs correlated with its achiral concentration (Table 2b), due to high concentration and high nonracemity in benthic amphipods. *trans*-Chlordane was the only compound where the EFs correlated with its relative proportion, with increasing EFs with increasing relative contribution of *trans*-chlordane to ∑chlordanes (Table 2b).

Nonracemic EFs in Benthic Amphipods. *P. hystrix* showed stronger enantioselective bioaccumulation of all CPs, as well as higher CP concentrations, than the other species (Table 1). Benthos might be directly exposed to more nonracemic chiral CP than zooplankton and ice fauna, as discussed for α-HCH above. Nonracemic EFs and elevated concentrations may result from contaminant accumulation in sediments and elevated nonracemic EFs due to microbial enantioselective degradation, as seen for α-HCH in the Arctic Ocean (*6*, *7*). In the Northwater Polynya at the northern end of Baffin Bay, detritivore benthic basket stars collected at ca. 320 m depth had an α-HCH EF of 0.41 (*10*), which is in the range of those of the present study's pelagic samples. These benthic sea stars were collected from an area in which the entire water column is dominated by a strong southward flow of cold water with low salinity from the Arctic Ocean (*48*).

Previous studies have reported high concentrations of organochlorines in benthic amphipods (*Eurythenes gryllus* and *Anonyx nugax*), suggestively due to occasional feeding on dead higher trophic level animals that eventually sink to the sea floor (*16*, *18*, *49*). It is not known if also *P. hystrix* occasionally feed on dead higher trophic level animals, such as fish or seals. However, the chlordane EFs, high concentrations, and chlordane compound pattern with low relative contribution of *cis*-chlordane might suggest so. *P. hystrix* are often found on corals, and they are known feeders on sponges (*31*). Sponges accumulate polychlorinated biphenyls (PCBs) at levels higher than those of mussels (*50*), and sponges show a high concentration of some halogenated metabolites which are produced either by the sponges themselves or by bacteria and algae associated with the sponge (*51*). If sponges or their associated bacteria or algae have the capacity for enantioselective degradation of chiral CPs, they may function as a transfer pathway in the accumulation of nonracemic EFs and elevated CP concentrations in their predators.

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