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Examination of the bioaccumulation of halogenated dimethyl bipyrroles in an Arctic marine food web using stable nitrogen isotope analysis

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"Capsule": *Except for ringed seals, halogenated dimethyl bipyrrole (HDBP) congeners biomagnified in a sample aquatic food web of invertebrate > fish > seabird.*

Abstract

Concentrations of four possibly naturally produced organohalogens — 1,1′-dimethyl-3,3′,4-tribromo-4,5,5′-trichloro-2,2′-bipyrrole (DBP-Br_3Cl_3), 1,1′-dimethyl-3,3′,4,4′-tetrabromo-5,5′-dichloro-2,2′-bipyrrole (DBP-Br_4Cl_2), 1,1′-dimethyl-3,3′,4,4′,5-pentabromo-5′-chloro-2,2′-bipyrrole (DBP-Br_5Cl) and 1,1′-dimethyl-3,3′,4,4′,5,5′-hexabromo-2,2′-bipyrrole (DBP-Br_6) — were quantitated and the extent of their magnification through an entire Arctic marine food web [measured as integrated trophic magnification factors (TMFs)] were calculated. The food web consisted of three zooplankton species (*Calanus hyperboreus, Mysis oculata*, and *Sagitta* sp.), one fish species [Arctic cod (*Boreogadus saida*)], four seabird species [dovekie (*Alle alle*), black guillemot (*Cepphus grylle*), black-legged kittiwake (*Rissa tridactyla*), and glaucous gull (*Larus hyperboreus*)], and one marine mammal species [ringed seal (*Phoca hispida*)]. Trophic levels in the food web were calculated from ratios of stable isotopes of nitrogen ($^{15}N/^{14}N$). All halogenated dimethyl bipyrrole (HDBP) congeners were found to significantly ($P < 0.02$) biomagnify, or increase in concentration with trophic level in the invertebrate — fish — seabird food web. DBP-Br_4Cl_2 (TMF = 14.6) was found to biomagnify to a greater extent than DBP-Br_3Cl_3 (TMF = 5.2), DBP-Br_5Cl (TMF = 6.9), or DBP-Br_6 (TMF = 7.0), even though the K_{ow} of DBP-Br_4Cl_2 was predicted to be lower than those of DBP-Br_5Cl and DBP-Br_6. None of the four HDBP congeners in ringed seals followed the general trend of increasing concentration with trophic level, which was possibly due to an ability of the seals to metabolize HDBPs. Crown Copyright © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Organohalogens; Arctic; Marine food web; Biomagnification; Metabolism

1. Introduction

Halogenated dimethyl bipyrroles (HDBPs) form a family of novel hexahalogenated heterocyclic compounds containing both chlorine and bromine. These compounds were first identified in marine seabirds from the Pacific coast of Canada (Tittlemier et al., 1999b). Their source is currently unknown, but evidence indicates that they are of biogenic origin. The mixed halogenation and predominance in marine rather than freshwater biota suggest that HDBPs do not have anthropogenic sources (Tittlemier et al., 1999b). The structures of the known HDBPs (Fig. 1) are also similar to that of a known natural marine product, hexabromo-2,2′-bipyrrole (Andersen et al., 1974).

Few data presently exist on environmental concentrations of HDBPs. However, the most abundant HDBP congener in Pacific Ocean biota, DBP-Br_4Cl_2, has been found at ppm concentrations in higher trophic level organisms such as bald eagles (*Haliaeetus leucocephalus*;

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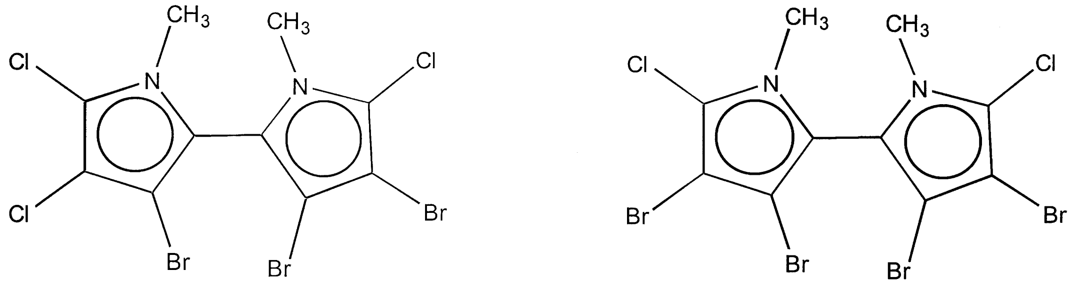
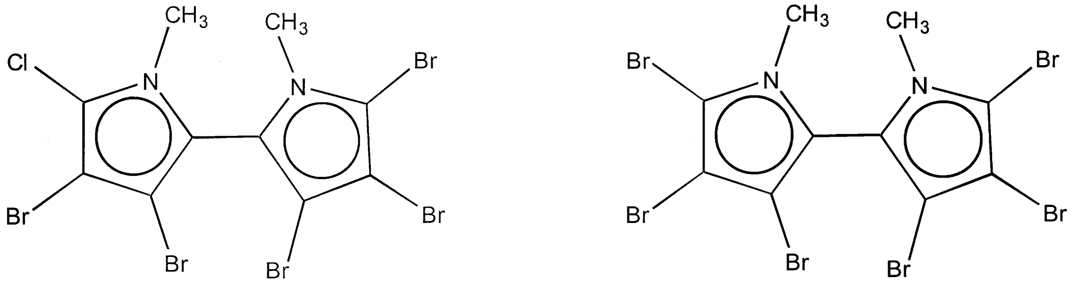


1,1'-dimethyl-3,3',4-tribromo-
4',5,5'-trichloro-2,2'-bipyrrole
(DBP-Br_3Cl_3)

1,1'-dimethyl-3,3',4,4'-tetrabromo-
5,5'-dichloro-2,2'-bipyrrole
(DBP-Br_4Cl_2)



1,1'-dimethyl-3,3',4,4',5-pentabromo-
5'-chloro-2,2'-bipyrrole
(DBP-Br_5Cl)

1,1'-dimethyl-3,3',4,4',5,5'-
hexabromo-2,2'-bipyrrole
(DBP-Br_6)

Fig. 1. Structures of halogenated dimethyl bipyrroles (HDBPs) found in marine biota.

Tittlemier et al., 1999b). These occurrences of high concentrations show that HDBPs are bioaccumulative, that is, they may be accumulated by an organism via uptake from food and water.

Physical property data for HDBPs, specifically high octanol/water partition coefficients (K_{ow}s), suggest that HDBPs may be transferred through aquatic food webs (Tittlemier et al., 1999a). Trophic transfer is the major exposure pathway of higher trophic level aquatic organisms to hydrophobic organohalogens (Thomann et al., 1992). In fact, the high K_{ow}s of these compounds suggest that they have the potential to biomagnify, or increase in concentration from one trophic level to the next provided that they are not metabolized. The degree of biomagnification of hydrophobic organochlorines in invertebrates and fish has been shown to be related to K_{ow} in a freshwater food web (Kidd et al., 1998).

Stable isotope analysis is often used to provide a continuous variable with which to assess both trophic level (Michener and Schell, 1994; Hobson et al., 1995) and trophic transfer of persistent organic pollutants (Kidd et al., 1998). In the case of stable nitrogen isotope analysis, the ratio of the heavier to lighter stable isotopes of nitrogen ($^{15}N/^{14}N$) is generally found to increase with trophic position in aquatic food webs. Trophic magnification factors (TMFs) can then be estimated from slopes of logarithmic concentration of contaminant vs. trophic level (Jarman et al., 1996). TMF differs from biomagnification factor (BMF) since it is a description of biomagnification over multiple, as opposed to just two trophic levels, of a food web.

In this study, three HDBP congeners of known structure — 1,1′-dimethyl-3,3′,4,4′-tetrabromo-5,5′-dichloro-2,2′-bipyrrole (DBP-Br_4Cl_2), 1,1′-dimethyl-3,3′,4,4′,5-pentabromo-5′-chloro-2,2′-bipyrrole (DBP-Br_5Cl) and 1,1′-dimethyl-3,3′,4,4′,5,5′-hexabromo-2,2′-bipyrrole (DBP-Br_6) — and the hypothesized 1,1′-dimethyl-3,3′,4-tribromo-4,5,5′-trichloro-2,2′-bipyrrole (DBP-Br_3Cl_3) were analyzed in an aquatic food web from the Northwater (NOW) polynya (Fig. 2). Polynyas are areas of year-round open water surrounded by sea ice. The NOW polynya supports a highly productive food web and provides an important habitat for marine mammals and seabirds, in some cases throughout the year. Trophic levels of the food web involving zooplankton, fish, seabirds, and marine mammals were characterized using stable nitrogen isotope analysis. Since little is known about HDBP distribution, study of their presence in the NOW will increase knowledge of the geographical occurrence and behaviour of what may be a ubiquitous naturally produced organohalogen.

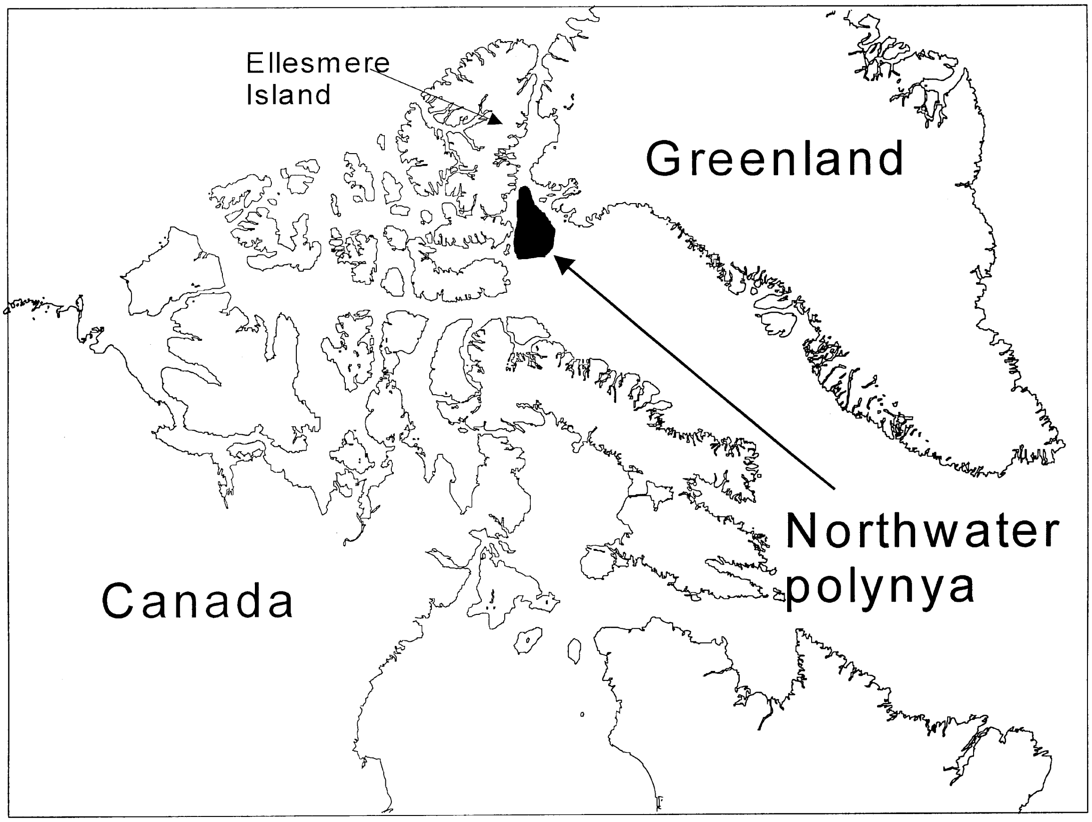


Fig. 2. Size and approximate location of the NOW polynya in May/June.

2. Materials and methods

2.1. Sample collection

All samples were collected in 1998. Sediment samples were taken in July from the sediment surface of box core samples. Zooplankton samples (*Calanus hyperboreus, Mysis oculata,* and *Sagitta* sp.) were collected between May and July using vertical tows of large zooplankton nets. Samples were sorted to species shortly after collection. In May, Arctic cod (*Boreogadus saida*) were opportunistically collected with hand-held nets. Seabirds [dovekie (*Alle alle*), black guillemot (*Cepphus grylle*), black-legged kittiwake (*Rissa tridactyla*), and glaucous gull (*Larus hyperboreus*)] were collected from the NOW polynya in May and June by shotgun. Samples of ringed seal (*Phoca hispida*) blubber were obtained from local hunters from Qaanaaq, Greenland during the same period. Seabirds and seals were dissected shortly after death, and muscle and liver samples were placed in Whirl Pak bags and frozen until analyzed isotopically.

2.2. Stable isotope analysis

Nitrogen stable isotope analysis was carried out according to the method described in Moisey et al. (2001). Prior to analysis, all tissue samples were washed in distilled water and then freeze-dried, powdered and treated with a 2:1 (v/v) chloroform/methanol solution to remove lipids. Whole body homogenates were the tissue substrates used for zooplankton, whereas muscle was analyzed for birds, fish, and seals.

Isotope assays were performed on subsamples of homogenized materials by loading into tin cups and combusting at 1800°C in a Robo-Prep elemental analyzer. Resultant N_2 gas was then analyzed using an interfaced Europa 20:20 continuous-flow isotope ratio mass spectrometer with every five unknowns separated by two laboratory standards (albumen).

Stable isotope abundances were expressed in δ notation as the deviation from a standard in parts per thousand ($^{\circ}/_{\circ\circ}$) according to the following equation:

$$\delta^{15}\mathrm{N} = \left[\left(R_{\mathrm{sample}}/R_{\mathrm{standard}}\right) - 1\right] \times 1000 \qquad (1)$$

where R is the ratio $^{15}\mathrm{N}/^{14}\mathrm{N}$. The R_{standard} values were based on atmospheric N_2 (AIR).

Trophic levels were determined using equations modified slightly from those reported in Hobson et al. (1995). Trophic level was determined relative to the copepod *Calanus hyperboreus*, which was assumed to occupy trophic level 2 since it is an obligate herbivore. Trophic level (TL) was determined for each individual sample of zooplankton, fish and marine mammal using the relationship:

$$\mathrm{TL}_{\mathrm{organism}} = 2 + \left(\frac{\delta^{15}\mathrm{N}_{\mathrm{organism}} - \delta^{15}\mathrm{N}_{C.\ hyperboreus}}{3.8}\right) \quad (2)$$

where $\mathrm{TL}_{\mathrm{organism}}$ is trophic level of the organism, $\delta^{15}\mathrm{N}_{C.\ hyperboreus}$ is equal to 9.0±0.2‰, and 3.8 is the isotopic trophic enrichment factor in parts per thousand (Hobson et al., 2001).

For birds, there is evidence that trophic enrichment values differ from other marine organisms. Avian captive-rearing studies suggest an isotopic enrichment factor of +2.4‰ for muscle tissue to account for this difference (Hobson and Clark, 1992). Thus, Eq. (2) was modified using the relationships in (3) and (4) to result in an equation which describes the trophic level of seabirds in the NOW polynya (5):

$$\mathrm{TL}_{\mathrm{bird}} = \mathrm{TL}_{\mathrm{prey}} + 1 \quad (3)$$

$$\delta^{15}\mathrm{N}_{\mathrm{bird}} = \delta^{15}\mathrm{N}_{\mathrm{prey}} + 2.4 \quad (4)$$

$$\mathrm{TL}_{\mathrm{bird}} = 3 + \left(\frac{\delta^{15}\mathrm{N}_{\mathrm{bird}} - 11.4}{3.8}\right) \quad (5)$$

Eqs. (2) and (5) are somewhat arbitrary, but are based on current knowledge of how δ^{15}N values behave in Arctic marine food webs and adequately describe seabird trophic level in the NOW (Hobson et al., 2001).

2.3. Organohalogen analysis

The following tissues were analyzed for organohalogens: zooplankton (whole body), Arctic cod (whole body), seabirds (liver), and ringed seal (blubber). Sediment and zooplankton samples were freeze-dried, spiked with an internal standard, and extracted with 1:1 (v/v) dichloromethane (DCM)/hexane using a Dionex ASE 200 accelerated solvent extractor. All cod, seabird, and seal samples were extracted according to a similar method described in Norstrom et al. (1988). Briefly, a known amount of tissue was ground with anhydrous Na_2SO_4, spiked with an internal standard [mixture of $^{13}C_{12}$-PCBs (polychlorinated biphenyls)] and extracted with 1:1 DCM/hexane. Lipid amounts were determined gravimetrically, and the lipids were subsequently removed from the sample by gel permeation chromatography. Sulfur containing compounds were removed from the sediment samples by the addition of reduced copper. The lipid-free (biota) and sulfur-free (sediment) extracts were reduced and applied to a Florisil column (8 g, 1.2% deactivated). For the sediment, zooplankton, cod, and seabird samples, organohalogens were recovered by consecutive elution with 35 ml hexane [Fraction 1 (F1)], 38 ml of 85% hexane: 15% DCM (F2), and 52 ml of 1:1 DCM/hexane (F3). For seals, organohalogens were eluted by a single elution of 100 ml of 1:1 DCM/hexane. All fractions were rotary evaporated, solvent exchanged into isooctane, and reduced under a gentle N_2 stream. Volume correction standard ($^{13}C_{12}$-CB 138) was added prior to analysis.

HDBPs were analyzed as described in Tittlemier et al. (1999b) using a Hewlett Packard 5987B mass spectrometer coupled via a 5988 GC/MS direct interface to a 5890 Series II GC. The GC was equipped with a 30 m×0.25 mm i.d. DB5-MS column with a film thickness of 0.25 μm. HDBPs were analyzed in the electron capture negative ionization single ion monitoring mode. Methane (99.97%) was used as the moderating gas. The sediment, zooplankton, cod, and seabird F2 Florisil fractions, and the combined ringed seal Florisil fractions, were analyzed for HDBPs. Synthesized HDBPs (Tittlemier et al., 2000) were used as external standards to quantitate the four congeners in the samples.

3. Results and discussion

3.1. HDBP concentrations

Concentrations of HDBPs were normalized to the average $^{13}C_{12}$-PCB recovery since average recoveries of the internal standards ranged from 60 to 110%. The recovery corrected and lipid normalized concentrations of the HDBP congeners and results of the ^{15}N stable isotope analysis are given in Table 1.

HDBPs were detected in all of the samples studied from the NOW polynya. As shown in Table 2, levels of DBP-Br_4Cl_2 were generally similar to those recorded in seabird samples occupying similar ecological niches from Atlantic Canada (Tittlemier et al., 1999b). For this comparison, the DBP-Br_4Cl_2 egg wet weight concentrations were transformed to lipid normalized liver concentrations using an egg-to-liver organochlorine ratio calculated from Braune and Norstrom (1989). Such a comparison cannot be made for the other congeners since the present study contains the first reported concentration data for these congeners.

Concentrations of DBP-Br_4Cl_2 in the offshore surface and omnivorous feeders from the NOW were on the same order of magnitude as similar species from Atlantic Canada. It should be noted that the diet of the glaucous gulls in the NOW likely reflects a more carnivorous feeding strategy than that of the herring gulls from Newfoundland and Nova Scotia (Nettleship et al., 1990). This would account for the higher DBP-Br_4Cl_2 levels observed in the glaucous gulls.

Dovekies provide the single clear exception to the similarities between the NOW and previously published Atlantic seabird data (Tittlemier et al., 1999b). Dovekie DBP-Br_4Cl_2 concentrations (1.76 ppb) are approximately 10 times lower than those of the Atlantic puffin (*Fratercula artica*, 20 ppb), a species which has a similar

Table 1
HDBP congener and stable isotope analysis results, arithmetic mean ± standard deviation

Organism[a]	*n*	δ^{15}N (‰)	TL[b]	DBP-Br_3Cl_3	DBP-Br_4Cl_2	DBP-Br_5Cl	DBP-Br_6
SED	2	na[c]	na	<0.006[d]	0.0020±0.0002	<0.002	0.028±0.028
CH	3	9.0±0.2	2.0±0.05	<0.003	0.021±0.02	<0.001	<0.001
MO	3	10.8±0.4	2.5±0.09	0.11±0.10	0.22±0.03	0.017±0.002	0.58±0.23
SS	3	10.9±0.2	2.5±0.04	<0.003	0.057±0.027	<0.001	<0.001
DOVE	3	11.9±0.9	3.1±0.2	0.55±0.15	1.8±0.3	0.16±0.04	0.69±0.33
COD	5	14.1±0.5	3.3±0.1	0.17±0.28	0.38±0.39	0.05±0.05	0.53±0.60
BLKI	5	13.2±0.4	3.5±0.1	3.3±1.5	15±6	1.1±0.4	13±23
BLGU	6	14.9±0.7	3.9±0.2	0.62±0.44	1.9±1.5	0.18±0.07	6.9±4.7
GLGU	4	16.0±0.8	4.2±0.2	11±7	42±28	1.8±0.9	13±4
SEAL	10	17.4±0.5	4.2±0.2	0.027±0.022	0.017±0.008	<0.02	0.046±0.044

[a] SED, sediment; CH, *Calanus hyperboreus*; MO, *Mysis oculata*; SS, *Sagitta* sp.; DOVE, dovekie; COD, Arctic cod; BLKI, black-legged kittiwake; BLGU, black guillemot; GLGU, glaucous gull; SEAL, ringed seal. Biota concentrations are on a lipid weight basis, ng/g.

[b] Trophic level.

[c] Not applicable.

[d] Estimated method detection limit.

Table 2
Comparison of DBP-Br_4Cl_2 concentrations in seabird species from the NOW polynya and Atlantic Canada (Tittlemier et al., 1999b)

Species[a]	*n* (*n* in pool)	Location	Mean ± S.D.[b] DBP-Br_4Cl_2 lipid weight (ng/g) in liver
Offshore surface feeders			
BLKI	5	NOW polynya	15±6
LSP	(10)	Gull Island, NF	55
LSP	(10)	Kent Island, NB	58
Offshore subsurface feeders			
DOVE	3	NOW polynya	1.8±0.3
ATPU	(10)	Gull Island, NF	20
ATPU	(10)	Machias Seal Island, NB	32
Omnivores			
GLGU	4	NOW polynya	42±28
HERG	(4)	Gull Island, NF	11
HERG	(10)	Sable Island, NS	28

[a] BLKI, black-legged kittiwake; LSP, Leach's storm-petrel; DOVE,dovekie; ATPU, Atlantic puffin; GLGU, glaucous gull; HERG = herring gull.

[b] S.D., standard deviation.

winter habitat but a more piscivorous diet. The difference in concentrations would be driven by the dovekies feeding at a lower trophic position than the puffins. A change in dovekie diet just prior to their collection in early summer (Fisk et al., 2001b) may also contribute to the differences in DBP-Br_4Cl_2 concentrations. During late spring, as dovekies return to the NOW polynya from the St. Lawrence Estuary and Atlantic Canada, they feed exclusively on lipid-rich relatively uncontaminated zooplankton, rather than fish (N. Karnovsky, unpublished data).

Relative amounts of each HDBP congener varied among species (Fig. 3). In the majority of the bird species, *Calanus hyperboreus*, and *Sagitta* sp. DBP-Br_4Cl_2 was the predominant congener. These species are primarily pelagic, and therefore likely to reflect the HDBP pattern in the water column. The apparent absence of the other congeners in the zooplankton is probably due to concentrations being very near the detection limit. DBP-Br_4Cl_2 was also the major congener in seabird samples analyzed previously (Tittlemier et al., 1999b). The exception occurred with black guillemots, where DBP-Br_6 was the most abundant congener. This may be due to black guillemots feeding on benthic organisms during part of the year (Gaston and Jones, 1998). Benthic organisms are more likely to contain DBP-Br_6 as the predominant congener since it was the most abundant in sediment samples. Assuming that predominance of DBP-Br_6 indicates a benthic contribution, the HDBP congener pattern for *M. oculata* suggests that those zooplankton feed on benthic organisms as well. *M. oculata* is considered a suprabenthic organism,

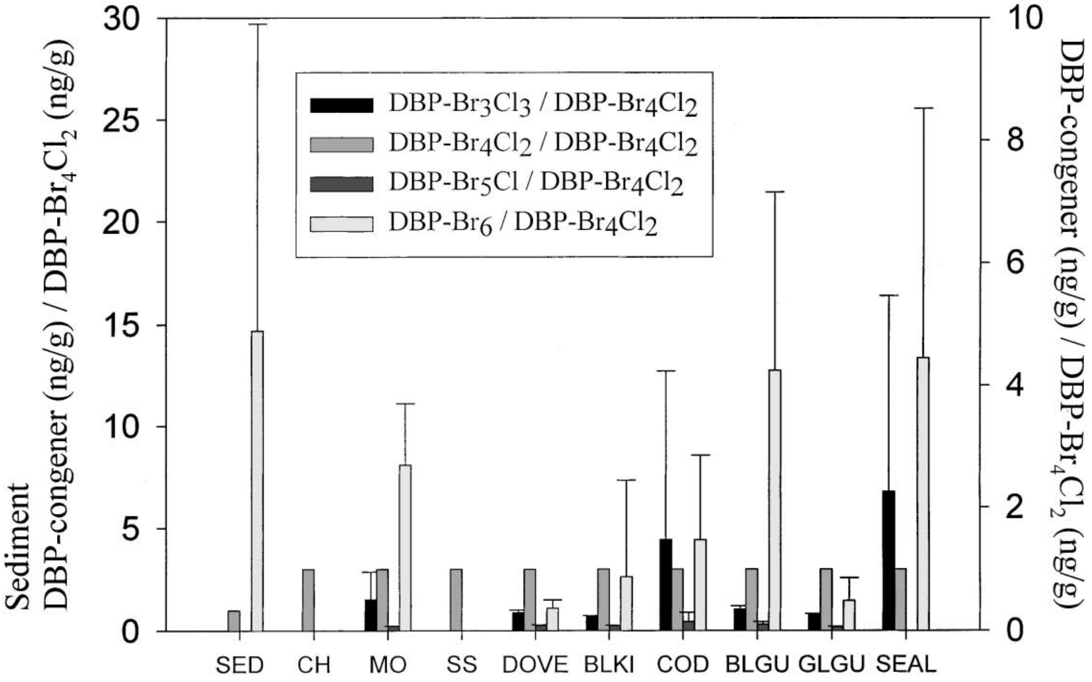


Fig. 3. Abundances of HDBP congeners relative to DBP-Br_4Cl_2. Species data labels are the same as those used in Table 1.

feeding on the sediment surface but also spending some time in the water column. Therefore it is likely that there is a benthic component to its diet (Hobson et al., 2001).

DBP-Br_3Cl_3 and DBP-Br_6 were the predominant congeners in the cod and seal samples. The patterns in the two species resembled each other, which is consistent with the importance of Arctic cod in the ringed seal diet (Welch et al., 1992). The HDBP congener patterns found in the cod and seal samples appeared more similar to those in the benthic than the pelagic species, apart from the dominance of the DBP-Br_3Cl_3.

It is interesting to speculate why there are such differences in patterns of HDBPs in such a closely integrated ecosystem as found in the NOW polynya. It is very unlikely that any HDBP congener can be converted to another by any of the species in this study. The bipyrrole rings are fully halogenated in all four congeners, so such a conversion would require replacement of chlorine by bromine, or the reverse. *Calanus hyperboreus* is one of the most abundant herbivorous zooplankton species in the polynya, and therefore is representative of the bottom of the pelagic food web. Concentrations of anthropogenic organochlorine compounds in *Calanus hyperboreus* appear to be governed by water concentrations (Fisk et al., 2001). It is therefore expected that species such as Arctic cod ca. 1–2 trophic levels higher than *Calanus hyperboreus* would have a similar HDBP pattern, assuming that cod do not significantly metabolize HDBPs. This is the case for PCB congeners (Fisk et al., 2001a). Most cod samples followed the ln concentration vs. trophic level relationship (Fig. 4), suggesting that metabolism is slow if it occurs at all. One plausible hypothesis is that cod are more connected to the benthic food web than has been assumed, which would account for the relatively high concentration of DBP-Br_6. The high relative level of DBP-Br_3Cl_3 in cod compared with *M. oculata* and dovekie may be due to greater efficiency of absorption of this congener from the diet by fish, since it has the lowest log K_{OW} and smallest molecular size of the four congeners.

3.2. Trophic magnification of HDBPs

In general, the natural logarithm of concentrations of HDBPs were found to increase linearly with a corresponding increase in trophic level (Table 1). However, ringed seals did not follow this trend. Concentrations of organochlorines (OCs) and PCBs quantitated in the same samples also deviated from the ecosystem trophic magnification relationship. This was found to be due to the concentration differences between male and female samples (Fisk et al., 2001a). Females generally have lower concentrations of OCs and PCBs because they have increased elimination capacities through maternal transfer and lactation (Weis and Muir, 1997). There was no significant difference ($P < 0.06$) between HDBP concentrations in the male and female seals, indicating that lactation is not the most important route of excretion. A more plausible explanation is that ringed seals are more proficient than birds at metabolizing HDBPs. Seals generally have a higher capability than zooplankton, fish, and cetaceans, but lower than birds and terrestrial mammals, for metabolism of organohalogen pesticides

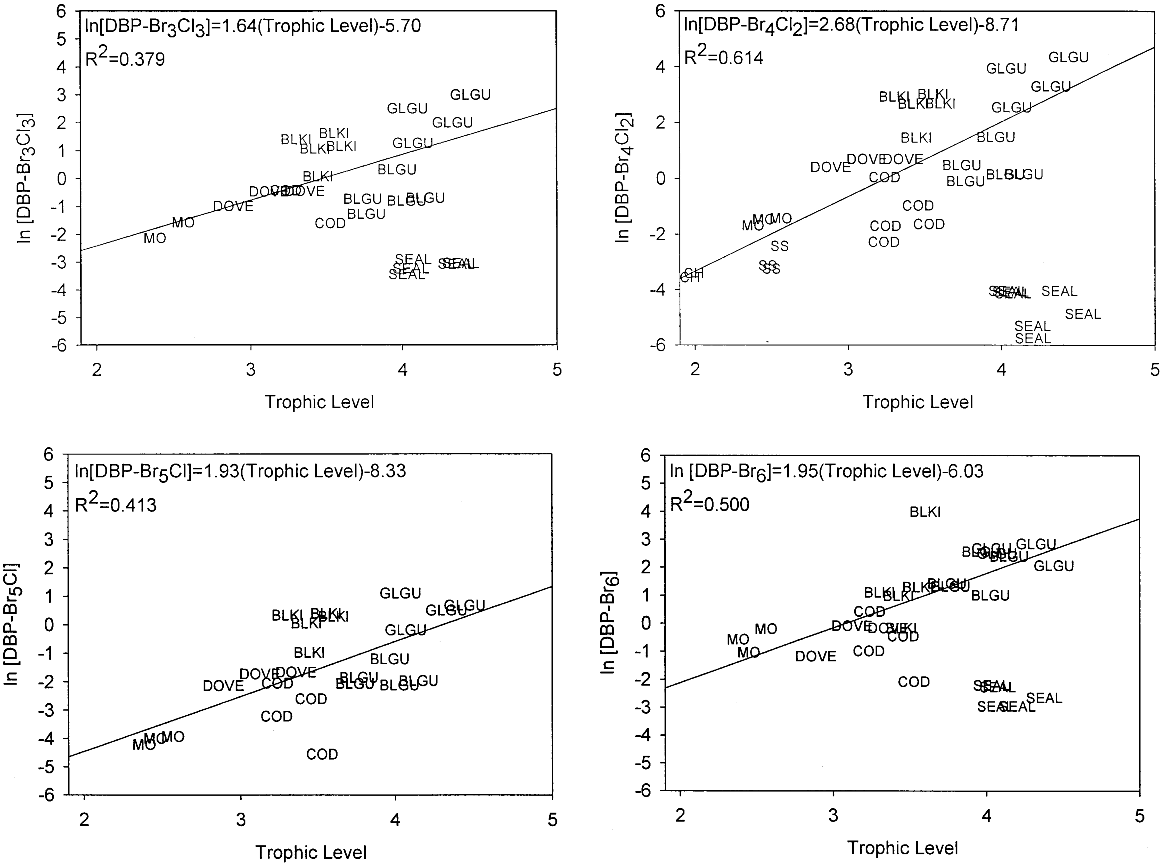


Fig. 4. Relationship between HDBP congener concentration and trophic level. Seal data was not included in the linear regressions. Species data labels are the same as those used in Table 1.

and *m,p*-substituted PCBs (Boon et al., 1989). Metabolism of these compounds is mediated by CYP2B-like enzymes, therefore it is unlikely that these enzymes are responsible for HDBP metabolism in seals. Metabolic indices have suggested that seals have potentially higher CYP1A-type enzyme activities than birds and cetaceans, but less than terrestrial mammals, depending on level of exposure to compounds that are Ah receptor agonists, such as 2,3,7,8-TCDD and CB-126 (Tanabe et al., 1988; Nakata et al., 1998). However, since the Arctic ringed seals are not expected to contain high levels of dioxin-like CYP1A inducers (Norstrom et al., 1990), metabolism of HDBPs by CYP1A is also an unlikely scenario. Differences in HDBP concentrations between birds and ringed seals could be due to mediation of HDBP metabolism by constitutive enzymes which are not involved in metabolism of persistent xenobiotic organohalogen compounds.

TMFs were calculated over all trophic levels of the food web excluding the seals. TMFs are defined as e^{slope} of the linear regressions of the natural logarithm of concentration vs. trophic level. The linear regressions for HDBPs are shown in Fig. 4. Slopes for the HDBPs were not significantly different, but it does appear that DBP-Br_4Cl_2 has a higher TMF (14.6) than DBP-Br_3Cl_3 (5.2), DBP-Br_5Cl (6.9), and DBP-Br_6 (7.0). DBP-Br_4Cl_2 would thus be expected to biomagnify through the NOW food web to a greater extent than the other congeners. The TMF values were similar to those for recalcitrant compounds such as CB-153 (TMF = 9.8) and *p,p′*-DDE (TMF = 13.9) determined for the same food web (Fisk et al., 2001a). This similarity suggests that, with the exception of seals, HDBPs are metabolized slowly or not at all in this food web.

It has been demonstrated that TMFs tend to increase with an increase in recalcitrance and K_{ow} (Kidd et al., 1998). Feeding studies with rainbow trout have also shown such a relationship between TMF and K_{ow} (Fisk et al., 1998). However, in this case differences in HDBP K_{ow}s may not be large enough to show differences in TMFs and therefore a relationship between K_{ow} and TMF. Log K_{ow}s of the four HDBP congeners were estimated to be 6.9 for DBP-Br_3Cl_3, 7.0 for DBP-Br_4Cl_2, 7.2 for DBP-Br_5Cl, and 7.3 for DBP-Br_6 using the fragment constant method (Lyman, 1982), indicating a narrow range of values for the four congeners. The log K_{ow} for DBP-Br_6 has also been experimentally determined using the slow-stirring method to be 8.9±0.3 (Tittlemier et al., 1999a). Even though log K_{ow} for DBP-Br_6 differs by one order of magnitude from the estimated value, the narrow range of values for the HDBP congeners is not expected to differ since all congeners are hexahalogenated.

4. Conclusions

This study is the first to report the presence of HDBPs in the Arctic marine ecosystem. Their presence in plankton, fish, seabirds, and seals provides more evidence for their widespread occurrence and expands their known distribution to include Pacific, Atlantic, and Arctic Ocean biota. The distribution of HDBPs indicates that they are formed in wide ranging marine environments, or are subject to long range transport from regions of formation. Neither possibility rules out a biogenic source. However, the first suggests that the source is a common organism with a wide occurrence. The second scenario implies HDBPs are formed by an organism whose range is limited. There is evidence from analysis of seabird eggs that HDBP concentrations are higher in the North Pacific Ocean than elsewhere indicating the source may be located here. Absence in Great Lakes seabirds suggests that atmospheric transport is not their major mode of movement. HDBPs may therefore be circulated globally via ocean currents. In some cases HDBP congener patterns in NOW polynya biota were consistent with known predator–prey relationships, such as for ringed seal and cod. However, there appeared to be significant differences in HDBP congener patterns in benthic- and pelagic-based food webs, which were dominated by DBP-Br_6 and DBP-Br_4Cl_2, respectively. Benthic and pelagic signatures appeared to be mixed in some species at higher trophic levels.

In addition, results showed that the four, possibly naturally produced, organohalogen compounds biomagnify in a marine food web. All HDBP congeners were found to magnify with trophic level as determined by stable nitrogen isotope analysis, except in ringed seals, which appear more capable than birds of metabolizing HDBPs. This order of metabolic capability is reversed to what is usually observed with xenobiotic organohalogens. The TMFs of HDBPs determined from the slope of the ln concentration vs. trophic level regressions ranged from 5 to 15, which is the same range as recalcitrant organochlorine compounds such as 2,2′,4,4′,5,5′-hexachlorobiphenyl (CB-153). It is conceivable that due to their metabolism, HDBPs will not be found to bioaccumulate in other mammals to the relatively high levels found for recalcitrant xenobiotic organohalogens.

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