Trophic Transfer of Contaminants in a Changing Arctic Marine Food Web: Cumberland Sound, Nunavut, Canada

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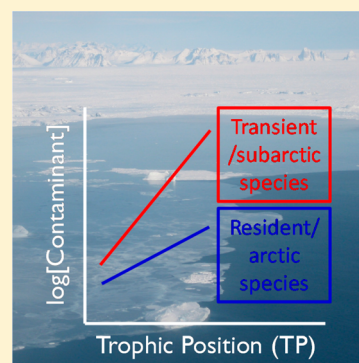[§]Fisheries and Oceans Canada, Winnipeg, MB R3T 2N6, Canada
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ⓢ *Supporting Information*

ABSTRACT: Contaminant dynamics in arctic marine food webs may be impacted by current climate-induced food web changes including increases in transient/subarctic species. We quantified food web organochlorine transfer in the Cumberland Sound (Nunavut, Canada) arctic marine food web in the presence of transient species using species-specific biomagnification factors (BMFs), trophic magnification factors (TMFs), and a multifactor model that included δ^{15}N-derived trophic position and species habitat range (transient versus resident), and also considered δ^{13}C-derived carbon source, thermoregulatory group, and season. Transient/subarctic species relative to residents had higher prey-to-predator BMFs of biomagnifying contaminants (1.4 to 62 for harp seal, Greenland shark, and narwhal versus 1.1 to 20 for ringed seal, arctic skate, and beluga whale, respectively). For contaminants that biomagnified in a transient-and-resident food web and a resident-only food web scenario, TMFs were higher in the former (2.3 to 10.1) versus the latter (1.7 to 4.0). Transient/subarctic species have higher tissue contaminant levels and greater BMFs likely due to higher energetic requirements associated with long-distance movements or consumption of more contaminated prey in regions outside of Cumberland Sound. These results demonstrate that, in addition to climate change-related long-range transport/deposition/revolatilization changes, increasing numbers of transient/subarctic animals may alter food web contaminant dynamics.

INTRODUCTION

Environmental contamination by persistent and bioaccumulative industrial, agricultural, and consumer-product chemicals is an ongoing global concern, including in regions far from source inputs such as the Arctic.[1−3] Persistent organic pollutants (POPs) enter arctic environments through atmospheric, aquatic, and biological transport and bioaccumulate in organisms, increasing in concentration relative to the surrounding environment.[4,5] Bioaccumulation can increase with each trophic step in the food web, biomagnifying contaminants to concentrations affecting arctic wildlife and human health.[6,7] Yet, concentrations of at least certain legacy POPs (which include polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs), chlordanes (CHLs), dieldrin, chlorobenzenes (ClBzs), and hexachlorocyclohexanes (HCHs)) have been effectively reduced in arctic wildlife over the last few decades through international agreements to restrict or eliminate the use of bioaccumulative substances.[8]

Arctic food webs are rapidly changing in response to warming air and ocean temperatures and related sea ice declines.[9,10] Climate changes may alter contaminant distribu-

tion, pathways, and fate through environmental changes impacting, for instance, contaminant transport, deposition, and revolatilization.[11−13] Climate-related ecological changes including changes in primary production, food web structure, habitat range, migration, and diets may also influence food web contaminant dynamics.[14−16] In fact, structural food web changes have the potential to impose a large influence on contaminant exposures relative to other factors, but there has only been limited empirical study of these changes to date.[17]

Cumberland Sound is a large, deep, seasonally sea ice-covered and biologically productive ocean inlet of southeast Baffin Island (Nunavut, Canada). It is home to the Inuit community of Pangnirtung, and an important feeding region for marine mammals and migratory seabirds.[18] As elsewhere in the Arctic, significant declines in sea ice extent (9.0% per decade) have been reported for this region.[19] Concurrently, there are reports in Cumberland Sound and various arctic

marine ecosystems of increasing numbers of pelagic, transient, and subarctic-associated species. A poleward range shift of these subarctic species and displacement of arctic species, particularly at higher trophic levels, may in fact constitute a widespread climate change impact on arctic marine ecosystems.[20] Harp seal (*Pagophilus groenlandicus*), which migrate between North Atlantic and Arctic waters, have increased in abundance.[21] Capelin (*Mallotus villosus*), also a migratory and subarctic-associated species, have increased and extended their range northward.[22] This phenomenon of subarctic forage fish moving into arctic waters under warmer conditions is also associated with shifts from benthic- to more pelagic-type arctic marine food webs.[10] Sightings of killer whale (*Orcinus orca*), a transient, actively sea ice-avoiding predator, have also increased.[18,23] Other transient species within Cumberland Sound include Greenland sharks (*Somniosus microcephalus*) (A. Fisk, unpublished data) and seasonally migratory narwhals[24] (*Monodon monoceros*), although both are considered arctic species. Species considered year-round residents include Cumberland Sound beluga whales (*Delphinapterus leucas*), in contrast to some other beluga populations which are known to undergo long-distance migrations.[25] Similarly, although sub-adult ringed seals (*Pusa hispida*) have shown occasional long-distance movements, there is no convincing evidence that adult ringed seals undergo long-distance seasonal migrations as do other seals like harp seals.[26−29] Here, we define a transient species as one that is present only intermittently in Cumberland Sound and is known to make substantial movements or migrations outside of the Sound (>1000 km), in contrast to a resident species that is assumed to reside year-round in Cumberland Sound.

Although many current and future climate change impacts on arctic marine ecosystems remain uncertain, those that have been documented have the potential to profoundly alter contaminant exposures in individual species, as well as overall biomagnification through food webs.[13] Here, we hypothesize that the presence of transient species substantially alters overall levels and, subsequently the levels trophically transferred within arctic marine food webs. Nitrogen (δ^{15}N) and carbon (δ^{13}C) stable isotope (SI) ratios may be useful tools to describe these changes as they have been used extensively to quantify food web structure and contaminant trophic transfer.[30] We used trophic magnification factors (TMFs) and biomagnification factors (BMFs) to study accumulation of major contaminants in extensive 2007−2008 samplings of the Cumberland Sound food web, which contains new or increasingly present transient species. In an overall model that considered established factors including δ^{15}N-derived trophic positions (TPs), thermoregulatory group (poikilotherms versus homeotherms), ice-covered versus ice-free season, and benthic versus pelagic δ^{13}C-derived carbon source, we tested the influence on food web contaminant accumulation of resident versus transient species habitat range. We determined the magnitude and direction of influence on contaminant accumulation to assess the importance of the presence of transient species in the food web relative to these other factors.

■ EXPERIMENTAL METHODS

Sample Collection. Major organisms in the Cumberland Sound food web were sampled in 2007−2008 (Table S1). Sampling sites and mixed zooplankton (mainly *Calanus* spp.) sampling ($n = 6$) were previously described.[31] Benthic scallop (*Chlamys islandica*; $n = 6$) and snail (*Buccinum cyaneum*; $n = 3$)

were sampled by ponar; Atlantic herring (*Clupea harengus*; $n = 1$), arctic char (*Salvelinus alpinus*; $n = 5$), and sculpin (*Myoxocephalus scorpioides*; $n = 9$) were sampled by gill net; capelin ($n = 5$) were collected by dip net, and turbot (*Reinhardtius hippoglossoides*; $n = 8$), arctic skate (*Amblyraja hyperborea*; $n = 5$), and Greenland sharks ($n = 11$) were collected by bottom long line. Marine mammals, harp seal ($n = 5$), ringed seal ($n = 5$), beluga whale ($n = 4$), and narwhal ($n = 7$), were captured during Inuit subsistence hunts.

Stable Isotopes Analysis. δ^{15}N and δ^{13}C were assessed in lipid-removed, powdered samples of whole zooplankton, soft tissues of scallop and snail, and muscle tissues of fish and marine mammals. Samples were combusted in an elemental combustion system and analyzed by a coupled Delta V Advantage isotope ratio mass spectrometer (Thermo Scientific, Waltham, MA, USA) as previously described.[32] Quality control details are provided in the Supporting Information.

Scallop and capelin SI were assessed in individuals other than those analyzed for contaminants, as there was not enough tissue to do both analyses on the same individuals. Thus, for those capelin and scallop samples analyzed for contaminants, their SI values were randomly generated within ±2 SE (i.e., within 95% confidence limits) of the mean of the SI values determined in the measured samples of the same species.

Contaminant Analysis. Contaminants were extracted and analyzed as described briefly in the Supporting Information and in detail elsewhere.[30] The same tissue-types were analyzed as for SI, except that blubber was analyzed for marine mammals. Marine mammal blubber was analyzed to best represent the majority of the POP body burden, as is generally done for marine mammal POP studies.[30,33,34] Quality control details are provided in the Supporting Information. Calculated concentrations were lipid normalized (concentration/percent lipid) because wet weight concentrations were correlated with percent lipid and for consistency with previous studies.[30,34]

Trophic Position and Carbon Source Determination. Nitrogen and carbon SI were used to assess different aspects of the food web structure. Consumer TPs were calculated from their δ^{15}N relative to zooplankton, assuming zooplankton occupy TP 2 and a constant 3.8 ‰ trophic enrichment factor.[30]

From δ^{13}C, we tested the relative contribution of benthic versus pelagic carbon source to food web contaminant bioaccumulation. If comparing carbon source of species at similar TPs, we could examine the relative pelagic/benthic carbon source using δ^{13}C directly.[35] However, since δ^{13}C, like δ^{15}N, is enriched through trophic positions and we were investigating carbon source across a broad spectrum of TPs, we eliminated the trophic influence on consumer δ^{13}C by calculating carbon source using a modified version of the two-source mixing model equation

$$\text{Carbon source} = 1 - \frac{\delta^{13}C_{\text{zooplankton}} - \delta^{13}C_{\text{consumer}} + \Delta\delta^{13}C(TP_{\text{consumer}} - TP_{\text{zooplankton}})}{\delta^{13}C_{\text{zooplankton}} - \delta^{13}C_{\text{scallop}}}$$

(1)

assuming that zooplankton represent the pelagic source, scallop represent the benthic source, and a constant trophic enrichment factor ($\Delta\delta^{13}$C) of 1.3‰ for consumers analyzed using muscle tissues.[36] The $\Delta\delta^{13}C(TP_{\text{consumer}} - TP_{\text{zooplankton}})$ term accounts for species occupying varying TPs higher than the sources and thus for δ^{13}C-enrichment between source and consumer depending on consumer TP relative to the source. Carbon source values closer to 1 indicate more pelagic feeding

and values closer to 0 indicate more benthic feeding. Although the magnitude of carbon source values is influenced by the choice of $\Delta\delta^{13}C$ (just as TPs are influenced by choice of $\Delta\delta^{15}N$), the relative carbon source (or TP) among individuals is not, making it a suitable variable for studying contaminant food web behavior.

Statistical Analyses of Contaminant–Food Web Relationships. Prior to statistical analyses, contaminant concentrations were log-transformed, improving normality and reducing heteroscedasticity between species, and checked for outliers (z-score tests). Statistical analysis (Statistica, version 10.0; Statsoft, Tulsa, OK, USA) and reporting only proceeded for major contaminants (those with concentrations comprising at least 2% of the total concentration of all analyzed contaminants), and ≤2.5% nondetect values to avoid biased comparisons between contaminants due to different sample sets. These major contaminants consisted of Cl_3–PCB, Cl_4–PCB, Cl_5–PCB, Cl_6–PCB, Cl_7–PCB, t-nonachlor, heptachlor epoxide, p,p′-DDE, dieldrin, hexachlorobenzene (HCB), and α-HCH. The probability of making a Type I error was set to $\alpha \leq 0.05$. Tests were two-tailed unless otherwise indicated.

Effects of TP, carbon source, thermal group (poikilotherms versus homeotherms), and habitat range (resident versus transient species) on contaminant concentrations and biomagnification were tested using a general linear model (Type III sum-of-squares, $n = 80$)

$$\log[\text{contaminant}] = b_0 + b_1\text{TP} + b_2\text{group} + b_3\text{range}$$
$$+ b_4\text{carbon source} + b_5\text{group} \times \text{TP}$$
$$+ b_6\text{range} \times \text{TP} + b_7\text{carbon source}$$
$$\times \text{TP} + \varepsilon \quad\quad (2)$$

where b_0–b_7 are constants and ε represents the error term, assumed to have a mean of zero and a constant variance. Predicted versus residual values for all individual contaminant models are provided in Figure S1, and normal probability plots are provided in Figure S2, for all reported contaminants. Tolerance for each effect in the GLM models was consistently ≥0.01, indicating that the model did not violate the assumption of non-multicollinearity. An initial model also included season (April versus August) and season × TP terms, but excluded cetacean samples not having specific April or August collections. However, season terms were not significant for any contaminants. Therefore, the subsequent model excluded season terms and included the cetacean samples. Only first-order interaction terms involving TP were included in eq 2, in order to study how the contaminant–TP relationship, i.e. the biomagnification, is influenced by thermal group, habitat range, and carbon source. According to eq 2, average contaminant concentrations would differ between homeotherms and poikilotherms if group were significant and between transients and residents if range were significant. If carbon source were significant, average concentrations would differ with relative contribution of benthic and pelagic carbon sources. TMFs would differ between homeotherms and poikilotherms if group × TP were significant and between transient and residents if range × TP were significant. If carbon source × TP were significant, then TMFs would differ with relative benthic versus pelagic source contribution. The Type III sum-of-squares evaluates the effect of each factor after accounting for all other factors. Thus, the impact of each factor on the log-[contaminant]–TP relationship was illustrated by using the

GLM intercept and b-coefficients for TP, the given factor of interest, and their interaction term, to generate the log-[contaminant] values for different scenarios (i.e., homeotherm or poikilotherm, resident or transient, and benthic or pelagic (carbon source set to 0 or 1, respectively).

Food web accumulation was additionally investigated using TMFs as

$$\text{TMF} = 10^{b_1} \quad\quad (3)$$

where b_1 is the slope of the contaminant–TP regression

$$\log[\text{contaminant}] = b_0 + b_1\text{TP} + \varepsilon \quad\quad (4)$$

considering a resident-only versus a resident-and-transient food web. TMFs significantly greater than 1 indicated a biomagnifying contaminant.

Biomagnification was compared between individual transient and resident species that occupied similar TPs: harp seal versus ringed seal, narwhal versus beluga whale, and Greenland shark versus arctic skate. Species-specific BMFs were calculated from teleost fish prey to marine mammal or elasmobranch fish predator as

$$\text{BMF} = \frac{[\text{contaminant}]_{\text{predator,lipid weight}} / [\text{contaminant}]_{\text{teleost fish,lipid weight}}}{\text{TP}_{\text{predator}} / \text{TP}_{\text{teleost fish}}} \quad\quad (5)$$

where the prey were considered to be all lower trophic fish (herring, capelin, char, sculpin). Turbot were not considered prey fish since their TPs were higher than those of all other species investigated, likely due to a largely piscivorous diet.[37] A TMF or BMF statistically >1 indicated biomagnification through the food web or from prey-to-predator, respectively.

■ RESULTS AND DISCUSSION

Trophic Position, Carbon Source, and Contaminant Concentrations. Estimated TPs from $\delta^{15}N$ ranged from ≈2 in zooplankton (assigned to TP2) and scallop to ≈4 in Greenland shark and turbot (Figure 1). Carbon sources ranged from ≈0
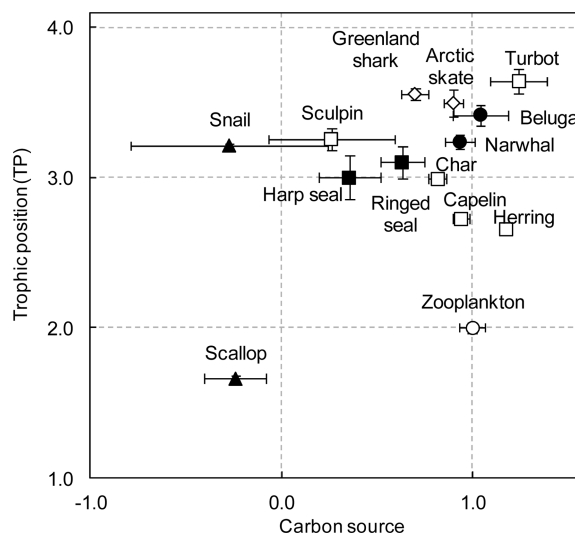

Figure 1. Trophic position (TP) versus carbon source for zooplankton (○), benthic invertebrates (▲; scallop, snail), teleost fishes (□; herring, capelin, char, sculpin, turbot), elasmobranch fishes (◇; arctic skate, Greenland shark), pinnipeds (■; harp seal, ringed seal), and cetaceans (●; beluga whale, narwhal) from the Cumberland Sound food web sampled in 2007–2008.

Table 1. Factors Influencing Pollutant Accumulation in the Cumberland Sound Food Web Sampled in 2007−2008

| | whole model[a] | | | parameter estimates: effect sizes (partial η^2), b-coefficients (*p < 0.05; **p < 0.01; ***p < 0.001) | | | | | | |
contaminant	r^2	p	df	TP	thermal group	thermal group × TP	range	range × TP	carbon source	carbon source × TP
Cl$_3$−PCB	0.19	0.03	7,72	0.08, 0.75*	0.07, 2.1*	0.07, −0.64*	0.00, 0.08	0.00, −0.07	0.02, −0.70	0.00, 0.10
Cl$_4$−PCB	0.45	<0.001	7,72	0.18, 1.0***	0.04, 1.4	0.05, −0.48	0.05, 0.95	0.07, −0.34*	0.05, −0.94*	0.01, 0.10
Cl$_5$−PCB	0.43	<0.001	7,72	0.12, 0.75**	0.01, 0.72	0.02, −0.25	0.06, 0.93*	0.08, −0.35*	0.08, −1.0*	0.03, 0.22
Cl$_6$−PCB	0.58	<0.001	7,72	0.07, 0.75*	0.01, −0.77	0.00, 0.13	0.19, 2.5***	0.24, −0.87***	0.07, −1.3*	0.05, 0.36
Cl$_7$−PCB	0.65	<0.001	7,71	0.12, 0.82**	0.00, −0.35	0.00, 0.02	0.23, 2.2***	0.29, −0.79***	0.02, −0.59	0.01, 0.13
t-nonachlor	0.76	<0.001	7,70	0.18, 1.0***	0.02, −0.97	0.01, 0.16	0.19, 1.9***	0.26, −0.72***	0.02, 0.48	0.01, −0.11
heptachlor epoxide	0.67	<0.001	7,70	0.10, 0.52*	0.00, −0.24	0.00, −0.02	0.22, 1.5***	0.27, −0.53***	0.07, −0.77*	0.04, 0.18
p,p′-DDE	0.76	<0.001	7,71	0.10, 0.96**	0.07, −2.5*	0.04, 0.58	0.27, 3.3***	0.34, −1.2***	0.00, −0.02	0.00, 0.12
dieldrin	0.42	<0.001	7,72	0.09, 0.60*	0.00, 0.09	0.00, −0.09	0.05, 0.86*	0.08, −0.32*	0.00, 0.14	0.00, −0.04
HCB	0.53	<0.001	7,70	0.10, 0.81**	0.00, −0.19	0.00, 0.00	0.02, 0.62	0.04, −0.26	0.04, 0.87	0.01, −0.17
α-HCH	0.38	<0.001	7,72	0.04, 0.31	0.02, 0.63	0.03, −0.25	0.00, 0.17	0.00, −0.00	0.04, 0.54	0.09, −0.27*

[a]General linear model (see Methods section), where the contaminant values are log-transformed ng/g lipid weight concentrations. The Cl$_3$−PCB, Cl$_4$−PCB, Cl$_5$−PCB, Cl$_6$−PCB, and Cl$_7$−PCB are the sum of tri-, tetra-, penta-, hexa-, and hepta-chlorinated PCB homologue group concentrations, respectively, representing on average 95% of the sum-PCB concentrations. Consumer trophic positions (TPs) were derived from δ^{15}N-values. Thermal groups were poikilotherms versus homeotherms. Habitat ranges were residents versus transients. Carbon sources were derived from δ^{13}C-values.

(more benthic-type feeding) in scallop and snail to ≈1 (more pelagic-type feeding) in zooplankton, Atlantic herring, capelin, arctic char, turbot, arctic skate, beluga whale, and narwhal. Species with intermediate values, suggesting input from benthic and pelagic sources, included in order of increasingly pelagic contribution: sculpin < harp seal < ringed seal < Greenland shark.

In the overall model, lipid weight contaminant concentrations except for α-HCH, were positively correlated with TP, indicating biomagnification through the food web (Table 1, Figure 2, Tables S2, S3). A statistically significant proportion (8% for the trichlorinated-PCBs (Cl$_3$−PCB) to 18% for t-nonachlor) of the explained variance in biomagnifying substance concentrations was explained by TP alone.

It bears noting that here, as in previous studies, we generated stable isotope ratios from fish and marine mammal lipid-free muscle samples to characterize food web structure. Yet, lipophilic substances are preferentially deposited in lipid-rich tissues. There are two potential issues with such an approach. In marine food webs, dietary consumption consists mainly of proteins and lipids, the proportions of which vary between prey items. Thus, due to isotopic routing, estimated TPs and carbon sources based on lipid-free muscle may reflect the protein portion of the diet, but not necessarily the overall diet.[38] For example, we could have underestimated Greenland shark TPs because consumption of lipid-rich seals versus more proteinaceous fish would not be fully reflected in muscle stable isotope ratios. The result would be higher contaminant concentrations than expected based on δ^{15}N-derived TPs. The second issue is that nitrogen and carbon turnover rates in muscle may be faster than the turnover rate of contaminants. Overall then, muscle stable isotope ratios may represent more recent feeding and more proteinaceous dietary items, whereas contaminant levels may reflect diets integrated over longer time periods and also the more lipid-rich dietary items.

Habitat Range. Aside from TP, transient versus resident habitat range was the most important factor explaining contaminant concentrations and TMFs. This factor accounted for 5% (dieldrin) to 27% (p,p′-DDE, a DDT metabolite) of explained variance in concentrations and 7% (Cl$_4$−PCB) to 34% (p,p′-DDE) of the variance for TMFs (Table 1). Where TP ranges overlapped (∼ TP 2.6−3.8) in the resident and

transient data sets, average concentrations and TMFs of higher-chlorinated PCBs, dieldrin, p,p′-DDE, t-nonachlor, and heptachlor epoxide (a CHL), were significantly higher in transients (herring, capelin, Greenland shark, harp seal, narwhal) than in residents (zooplankton, scallop, snail, arctic char, sculpin, turbot, arctic skate, ringed seal, beluga) (Figure 3a, additional panels in Figure S3). While t-nonachlor, p,p′-DDE, dieldrin, and hexachlorobenzene (HCB) biomagnified in a resident-only food web, TMFs were consistently higher in a transient-and-resident scenario (Figure 4, Table S4). For instance, p,p′-DDE concentrations increased on average by 10.1 per TP (TMF of 10.1) in the resident-and-transient food web and just 4.0 in the resident-only food web. Moreover, Cl$_4$− to Cl$_7$−PCB and heptachlor epoxide significantly biomagnified only when transients were included. Additionally, BMFs were often substantially higher in migratory harp seals, Greenland sharks, and narwhals than in resident ringed seals, arctic skates, and belugas, respectively, despite being at comparable TPs (Figure 5). These similar TP−individual species BMF comparisons confirm that higher TMFs with transients in the food web were not simply due to the data set containing greater numbers of higher-TP transients than residents. Thus, our results suggest that an increasing presence of transient species within arctic ecosystems would increase overall food web contaminant levels relative to levels if transient species were not present.

Transient species may have higher tissue contaminant levels and greater TMFs due to higher energetic requirements associated with long-distance movements. These requirements are met through higher feeding rates, which ultimately may lead to higher contaminant accumulation.[30] Harp seal, capelin, and herring are migratory, moving vast distances between North Atlantic and Subarctic/Arctic waters. Greenland sharks can move great distances (>2000 km) as well, based on satellite tracking data, although not necessarily in a fixed migratory pattern (A. Fisk, unpublished data). Tracking data suggest that Cumberland Sound narwhals are seasonal transients and undergo large annual migrations (>1000 km).[24]

Another explanation, and not mutually exclusive, for transient species having elevated concentrations and TMFs is consumption of more contaminated prey in regions outside of Cumberland Sound. Harp seals overwinter in the northwestern
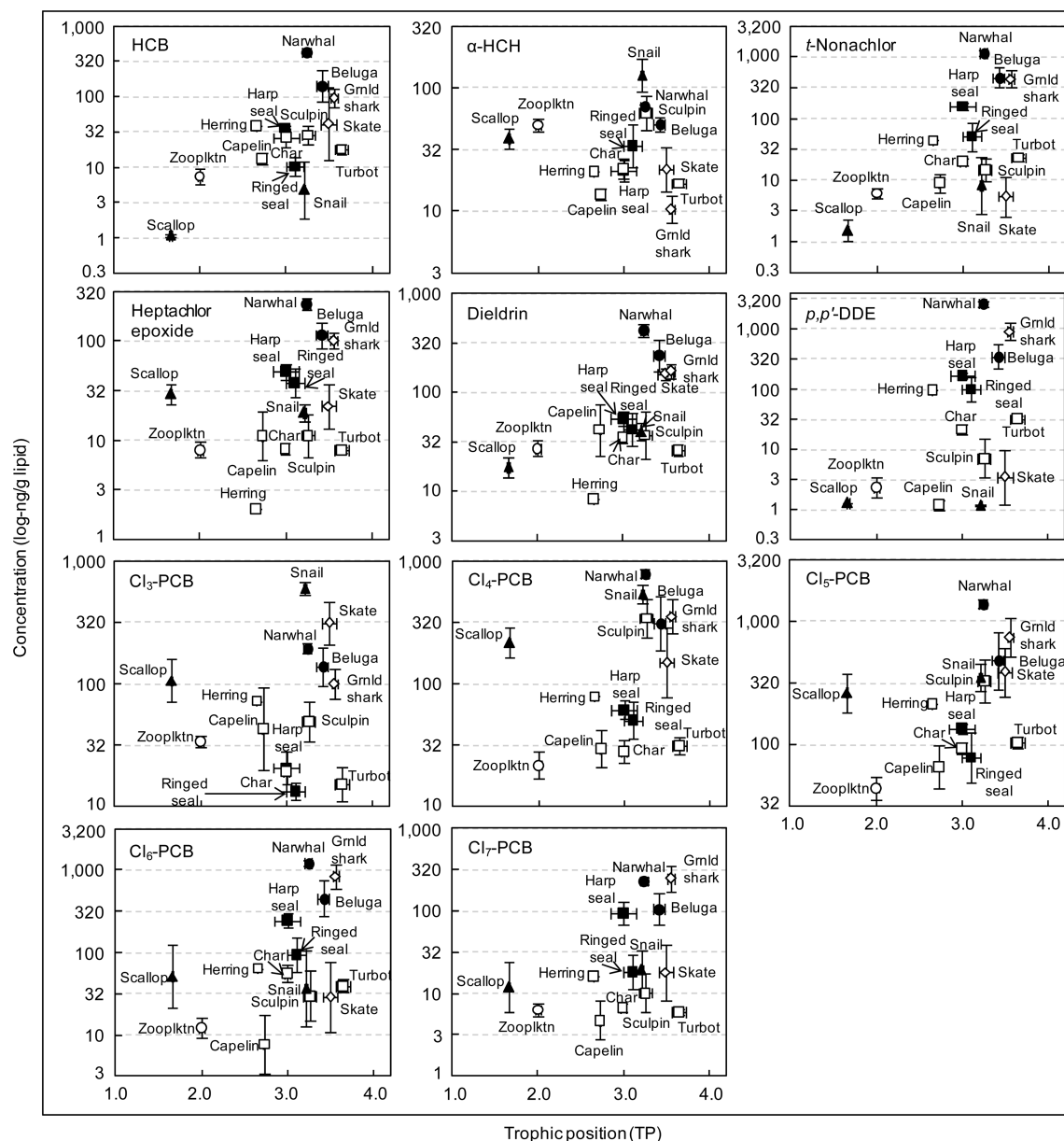
Figure 2. Contaminant concentration versus trophic position (TP) for zooplankton (O; zooplktn), benthic invertebrates (▲; scallop, snail), teleost fishes (□; herring, capelin, char, sculpin, turbot), elasmobranch fishes (◇; skate, Greenland shark (Grnld shark)), pinnipeds (■; harp seal, ringed seal) and cetaceans (●; beluga whale, narwhal) from the Cumberland Sound food web sampled in 2007−2008.

Atlantic, a more contaminated area relative to arctic regions.[39] These seals may pick up a more contaminated North Atlantic-type signature during winter-feeding and transport it to the Arctic during summer migration northwards. This biovector hypothesis[5] was supported by harp seal BMF patterns versus ringed seal (Figure 5). The specific contaminants that showed higher BMFs in harp seal (higher-chlorinated PCBs and *t*-nonachlor) are consistent with a more temperate region-type signature. Thus, increasing abundance of harp seal in Cumberland Sound has implications for contaminant exposures in top predators that opportunistically feed on marine mammals, such as polar bears, if they are shifting their diets to greater consumption of harp seals.[40] The increasing presence of migratory forage fish such as capelin and herring could similarly act as a contaminant biovector into arctic marine food webs from lower latitudes and directly influence contaminant concentrations in forage-fish consuming marine mammals and

seabirds. Regardless of transient species acting as biovectors through higher accumulation (energetic requirements of greater movement) or higher exposures (in areas outside Cumberland Sound), the overall ecosystem contamination and the amount that is passed from one trophic position to the next (i.e., trophic transfer) is higher, on average, than if these species were not present.[5,41]

Differences in BMF patterns between elasmobranchs and cetaceans versus pinnipeds suggested that other additional factors could also influence the BMFs. Unlike seals, both parent contaminant (*t*-nonachlor) and metabolite (heptachlor epoxide, *p,p'*-DDE) BMFs were higher in Greenland sharks and narwhals versus arctic skates and belugas, respectively (Figure 5). Although Greenland sharks and narwhals undergo extensive movements, these movements do not clearly bring them to more contaminated feeding grounds, supporting the bioenergetics versus biovector hypothesis for these transients. Yet,
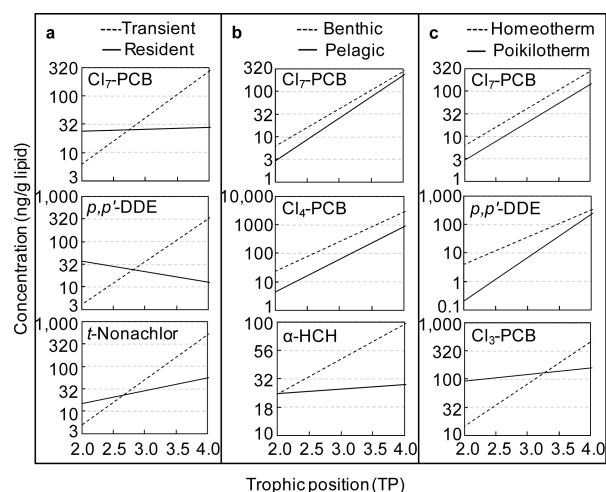
Figure 3. Relationship to TP of contaminant concentrations (ng/g/lipid) (i.e., trophic magnification factors) in the Cumberland Sound food web. Relationships are illustrated for (a) transients versus residents, (b) benthic versus pelagic carbon source, and (c) homeotherms versus poikilotherms. Each relationship was generated from variable coefficients in the GLM Type III sum-of-squares model, i.e., corrected for all other factors (Table 1). Raw log-contaminant–TP relationships are provided elsewhere (Figure 2). Note different y-axes scales.
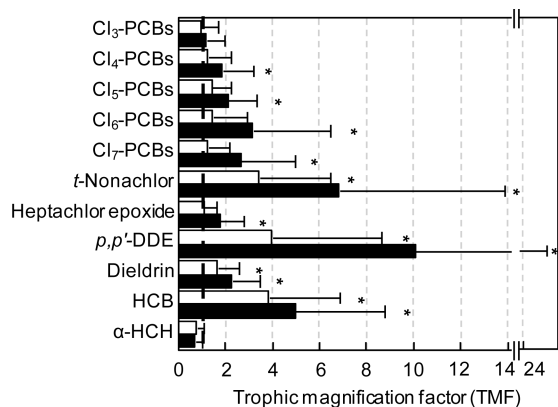

Figure 4. Calculated contaminant TMFs in a Cumberland Sound resident species-only (white bars) versus resident-and-transient species (black bars) marine food web. TMFs (+ 95% CI) are the antilog of the log[contaminant]–trophic position regression slope. Thick dashed line indicates TMF = 1. Asterisks indicate statistically significant biomagnification, i.e., TMF > 1 (see Table S4).
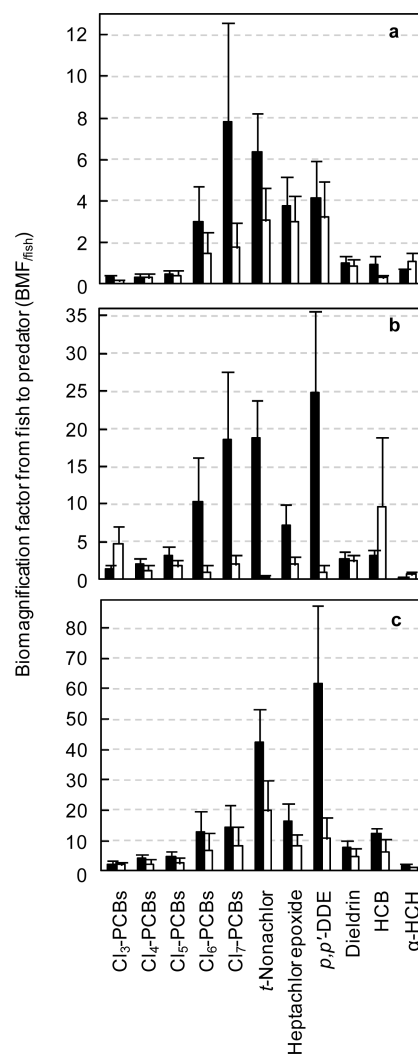

Figure 5. Calculated trophic position-adjusted contaminant BMFs (+SE) in Cumberland Sound transient (black bars) versus resident (white bars) species. Relationships are illustrated for (a) pinnipeds (harp versus ringed seals), (b) elasmobranchs (Greenland sharks versus arctic skates), and (c) cetaceans (narwhals versus belugas). BMFs are the ratio of the lipid weight contaminant concentration in a predator to its prey divided by the ratio of the TP of the predator to its prey. Biomagnification indicated by BMFs > 1. Note different y-axes scales.

Greenland sharks could also have higher BMFs from feeding on higher TP marine mammals or greater accumulation over longer life spans.[42] Another explanation may involve using a constant trophic enrichment factor to assess TPs, whereas species-specific factors may be more appropriate.[43] In the cetacean comparison, differences could partly be because the narwhals were all males, whereas only one of four belugas was a male. In fact, limited indications from other published studies have suggested similar narwhal and beluga organic contaminant levels.[44] Yet, differences between their contaminant levels here appeared larger than what would likely be explained by sex differences alone,[45] and sex differences in diet have not been identified for either species.[46] Moreover, Cumberland Sound belugas are known to be residents, whereas all other high latitude (>60° N) populations are known to migrate

considerable distances.[47] Another possible issue is that for some species, certain age classes may exhibit long-distance movements, whereas others do not. For example, some juvenile ringed seals are known to migrate long distances, whereas evidence suggests that adult ringed seals show a much more restricted range.[26−29] We were not able to obtain ages for all of the samples in this study, but it would be worthwhile in future work to investigate the consequences of these age-related habitat use differences on POP burdens.

Season. Season did not significantly influence contaminant concentrations (Table S5). Low statistical power to detect differences or interyear variation may partly explain why no significant seasonal effect was observed. Although samples were collected in 2007 and 2008, the influence of interyear variation in contaminant concentrations could not be assessed in the current data set. Annual changes in arctic marine animal legacy contaminant concentrations are generally less than 2%/year,

although higher for DDTs, HCHs, and ClBzs.[48] Nonetheless, food web concentrations were generally higher in the ice-free versus ice-covered season. In the Northwater Polynya, $\sum$ClBz, $\sum$HCH, and $\sum$CHL, but not $\sum$PCB and $\sum$DDT concentrations, increased from April to July in herbivorous zooplankton.[49] Possible explanations for these patterns include seasonal changes in hydrophobic organic contaminant aquatic concentrations related to particulate organic matter concentrations or source water variation into the region, in addition to lipid dynamics and food availability differences between seasons. Significant seasonal concentration differences were also reported for a Norwegian Arctic marine food web.[50] However, the species composition of the food web differed between seasons. For instance, higher concentrations and TMFs were generally found in July, but greater numbers of subarctic-type zooplankton and fish including capelin were sampled in July. Thus, the observed concentration change may partly be related to seasonal changes in species abundances, including transient species.

These findings may suggest that climate-associated shifts to more prolonged ice-free periods would not have a substantial direct impact on food web contaminant concentrations or TMFs. However, greater ice-free periods may lead to other indirect changes, such as increased volatilization from surface reservoirs and increased primary production.[11,14] In the latter case, this would generally lead to decreased bioaccumulation due to decreased bioavailability from higher particulate organic carbon levels.[14] Our data suggest that a main concern with respect to greater ice-free periods is increased abundance of more contaminated ice-avoiding transient or subarctic species.

Carbon Source. Carbon source was not a major factor explaining most contaminant concentrations or TMFs (Table 1). The exceptions were a small, but significant, main effect of carbon source for Cl_4–PCB to Cl_6–PCB and heptachlor epoxide concentrations. That is, TMFs were not significantly different for benthic versus pelagic carbon source, but across TPs, benthic source was associated with higher concentrations of these substances. For α-HCH concentrations, there was no main effect of carbon source, but significant interaction with TP showed that the TMF was higher for a benthic versus pelagic carbon source (Figure 3b).

Higher benthic concentrations for lower-chlorinated PCBs and heptachlor epoxide, and TMF for α-HCH, may be related to differing water-solubilities compared to other contaminants. Species having benthic-type carbon source values were collected in near-shore, shallow waters. Surface waters contain the highest concentrations of lower-chlorinated PCB and HCH, which decline with depth.[51] Conversely, more hydrophobic contaminants undergo greater particle scavenging, allowing rapid deep water transport and more homogeneous water column distributions.[51] So, differences in benthic versus pelagic α-HCH, heptachlor epoxide, and lower-chlorinated PCB concentrations may be related to higher concentrations of these more surface-associated contaminants in shallow water, near-shore species.

Based on these findings, possible climate-associated shifts to increasingly pelagic-type food webs would not necessarily increase food web contaminant concentrations and TMFs. This speculation does not take into account other potential differences in pelagic replacement species, such as migration patterns or other changes in trophic relationships. Nonetheless, we would expect slightly lower food web concentrations of more water-soluble contaminants under increasingly pelagic-

type food web regimes. Higher concentrations of these contaminants have also been found in surface water-associated sympagic amphipods than pelagic zooplankton.[52] Therefore, shifts from benthic/nearshore and ice-associated food webs to pelagic-type food webs could potentially additively contribute to reducing food web concentrations of these contaminants, but would not necessarily have substantial impacts on the more recalcitrant and environmentally predominant higher-chlorinated PCBs and DDTs.

Thermoregulation. The inclusion of homeotherms and poikilotherms generally had no significant effect on contaminant concentrations or TMFs (Table 1, Figure 3c). The exceptions were small, but significant, relationships of p,p'-DDE to thermal group and of Cl_3–PCB to thermal group and group $\times$ TP. Higher p,p'-DDE concentrations, and a similar though not statistically significant pattern for other recalcitrant pollutants, in homeotherms than in poikilotherms was likely related to higher energetic requirements, longevity, and lack of water-exchange as an elimination route in homeotherms.[30] Concentrations of Cl_3–PCB increased with TP, but the TMF differed between homeotherms and poikilotherms, related to different metabolic capacity toward lower-chlorinated PCBs.[50]

It will be important, but logistically and financially challenging, to develop long-term temporal, full food web data sets to further consider the influence of ecosystem changes, and to consider these changes in combination with direct changes in concentrations in abiotic compartments (air, seawater) due to climate warming and changing emissions. Nonetheless, we have shown here that the presence of transient species may be a strongly influential factor given its importance relative to other established factors influencing bioaccumulation of persistent pollutants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Contaminant analysis, quality control, biological and collection data, TP and carbon source, raw contaminant concentrations, results of contaminant−TP correlations (TMFs), general linear model results including season factor, residual versus predicted values and normal probability plots for the GLM, additional panels showing relationship to TP of contaminant concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Letcher, R. J.; Bustnes, J. O.; Dietz, R.; Jenssen, B. M.; Jørgensen, E. H.; Sonne, C.; Verreault, J.; Vijayan, M. M.; Gabrielsen, G. W. Exposure and effects assessment of persistent organohalogen contaminants in arctic wildlife and fish. *Sci. Total Environ.* **2010**, *408*, 2995–3043.

(2) de Wit, C. A.; Herzke, D.; Vorkamp, K. Brominated flame retardants in the Arctic environment – trends and new candidates. *Sci. Total Environ.* **2010**, *408*, 2885–2918.

(3) Butt, C. M.; Berger, U.; Bossi, R.; Tomy, G. T. Levels and trends of poly- and perfluorinated compounds in the arctic environment. *Sci. Total Environ.* **2010**, *408*, 2936–2965.

(4) Macdonald, R. W.; Barrie, L. A.; Bidleman, T. F.; Diamond, M. L.; Gregor, D. J.; Semkin, R. G.; Strachan, W. M. J.; Li, Y. F.; Wania, F.; Alaee, M.; Alexeeva, L. B.; Backus, S. M.; Bailey, R.; Bewers, J. M.; Gobeil, C.; Halsall, C. J.; Harner, T.; Hoff, J. T.; Jantunen, L. M. M.; Lockhart, W. L.; Mackay, D.; Muir, D. C. G.; Pudykiewicz, J.; Reimer, K. J.; Smith, J. N.; Stern, G. A.; Schroeder, W. H.; Wagemann, R.; Yunker, M. B. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. *Sci. Total Environ.* **2000**, *254*, 93–234.

(5) Krümmel, E. M.; Macdonald, R. W.; Kimpe, L. E.; Gregory-Eaves, I.; Demers, M. J.; Smol, J. P.; Finney, B.; Blais, J. M. Delivery of pollutants by spawning salmon. *Nature* **2003**, *425*, 255–256.

(6) Borgå, K.; Kidd, K. A.; Muir, D. C. G.; Berglund, O.; Conder, J. M.; Gobas, F. A. P. C.; Kucklick, J. R.; Malm, O.; Powell, D. E. Trophic magnification factors: Considerations of ecology, ecosystems, and study design. *Integr. Environ. Assess. Manage.* **2011**, *8*, 64–84.

(7) Sonne, C. Health effects from long-range transported contaminants in Arctic top predators: An integrated review based on studies of polar bears and relevant model species. *Environ. Int.* **2010**, *36*, 461–491.

(8) Rigét, F. F.; Braune, B. M.; Bignert, A.; Wilson, S.; Aars, J.; Born, E. W.; Dam, M.; Dietz, R.; Evans, M. S.; Evans, T. J.; Gamberg, M.; Gantner, N.; Green, N.; Gunnlaugsdöttir, H.; Kannan, K.; Letcher, R.; Muir, D. C. G.; Roach, P.; Sonne, C.; Stern, G. A.; Wiig, Ø. Temporal trends of Hg in Arctic biota, an update. *Sci. Total Environ.* **2011**, *409*, 3520–3526.

(9) Post, E.; Forchhammer, M. C.; Bret-Harte, M. S.; Callaghan, T. V.; Christensen, T. R.; Elberling, B.; Fox, A. D.; Gilg, O.; Hik, D. S.; Høye, T. T.; Ims, R. A.; Jeppesen, E.; Klein, D. R.; Madsen, J.; McGuire, A. D.; Rysgaard, S.; Schindler, D. E.; Stirling, I.; Tamstorf, M. P.; Tyler, N. J. C.; van der Wal, R.; Welker, J.; Wookey, P. A.; Schmidt, N. M.; Aastrup, P. Ecological dynamics across the Arctic associated with recent climate change. *Science* **2009**, *325*, 1355–1358.

(10) Grebmeier, J. M.; Overland, J. E.; Moore, S. E.; Farley, E. V.; Carmack, E. C.; Cooper, L. W.; Frey, K. E.; Helle, J. H.; McLaughlin, F. A.; Mcnutt, S. L. A major ecosystem shift in the northern Bering Sea. *Science* **2006**, *311*, 1461–1464.

(11) Ma, J. M.; Hung, H. L.; Tian, C.; Kallenborn, R. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. *Nature Clim. Change* **2011**, *1*, 255–260.

(12) Bustnes, J. O.; Gabrielsen, G. W.; Verreault, J. Climate variability and temporal trends of persistent organic pollutants in the Arctic: A study of glaucous gulls. *Environ. Sci. Technol.* **2010**, *44*, 3155–3161.

(13) Macdonald, R. W.; Harner, T.; Fyfe, J. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *Sci. Total Environ.* **2005**, *342*, 5–86.

(14) Borgå, K.; Saloranta, T. M.; Ruus, A. Simulating climate change-induced alterations in bioaccumulation of organic contaminants in an arctic marine food web. *Environ. Toxicol. Chem.* **2010**, *29*, 1349–1357.

(15) McKinney, M. A.; Peacock, E.; Letcher, R. J. Sea ice-associated diet change increases the levels of chlorinated and brominated contaminants in polar bears. *Environ. Sci. Technol.* **2009**, *43*, 4334–4339.

(16) Gaden, A.; Ferguson, S. H.; Harwood, L.; Melling, H.; Alikamik, J.; Stern, G. A. Western Canadian Arctic ringed seal organic contaminant trends in relation to sea ice break-up. *Environ. Sci. Technol.* **2012**, *46*, 4427–4433.

(17) Armitage, J. M.; Quinn, C. L.; Wania, F. Global climate change and contaminants-an overview of opportunities and priorities for modelling the potential implications for long-term human exposure to organic compounds in the Arctic. *J. Environ. Monit.* **2011**, *13*, 1532–1546.

(18) Diemer, K.; Conroy, M.; Ferguson, S. H.; Hauser, D.; Grgicak-Mannion, A.; Fisk, A. T. Marine mammal and seabird summer distribution and abundance in the fjords of northeast Cumberland Sound of Baffin Island, Nunavut, Canada. *Polar Biol.* **2011**, *34*, 41–48.

(19) Perovich, D. K.; Richter-Menge, J. A. Loss of sea ice in the Arctic. *Ann. Rev. Mar. Sci.* **2009**, *1*, 417–441.

(20) Wassmann, P.; Duarte, C. M.; Agusti, S.; Sejr, M. K. Footprints of climate change in the Arctic marine ecosystem. *Glob. Change Biol.* **2011**, *17*, 1235–1249.

(21) DFO. *Current Status of Northwest Atlantic Harp Seals, (Pagophilus groenlandicus)*; DFO Can. Sci. Advis. Sec. Sci. Advis. Rep. 2011-050, 2011.

(22) Gaston, A. J.; Bertram, D. F.; Boyne, A. W.; Chardine, J. W.; Davoren, G.; Diamond, A. W.; Hedd, A.; Montevecchi, W. A.; Hipfner, J. M.; Lemon, M. J.; Mallory, M. L.; Rail, J. F.; Robertson, G. J. Changes in Canadian seabird populations and ecology since 1970 in relation to changes in oceanography and food webs. *Environ. Rev.* **2009**, *17*, 267–286.

(23) Higdon, J. W.; Ferguson, S. H. Loss of Arctic sea ice causing punctuated change in sightings of killer whales (*Orcinus orca*) over the past century. *Ecol. Appl.* **2009**, *19*, 1365–1375.

(24) Dietz, R.; Heide-Jorgensen, M. P.; Richard, P.; Orr, J.; Laidre, K.; Schmidt, H. C. Movements of narwhals (*Monodon monoceros*) from Admiralty Inlet monitored by satellite telemetry. *Polar Biol.* **2008**, *31*, 1295–1306.

(25) Laidre, K. L.; Stirling, I.; Lowry, L. F.; Wiig, Ø.; Heide-Jorgensen, M. P.; Ferguson, S. H. Quantifying the sensitivity of arctic marine mammals to climate-induced habitat change. *Ecol. Appl.* **2008**, *18*, S97–S125.

(26) Harwood, L. A.; Smith, T. G.; Auld, J. C. Fall migration of ringed seals (*Phoca hispida*) through the Beaufort and Chukchi Seas, 2001–02. *Arctic* **2012**, *65*, 35–44.

(27) Teilmann, J.; Born, E. W.; Acquarone, M. Behaviour of ringed seals tagged with satellite transmitters in the North Water polynya during fast-ice formation. *Can. J. Zool.* **1999**, *77*, 1934–1946.

(28) Born, E. W.; Teilmann, J.; Acquarone, M.; Riget, F. F. Habitat use of ringed seals (*Phoca hispida*) in the North Water Area (North Baffin Bay). *Arctic* **2004**, *57*, 129–142.

(29) Crawford, J. A.; Frost, K. J.; Quakenbush, L. T.; Whiting, A. Different habitat use strategies by subadult and adult ringed seals (*Phoca hispida*) in the Bering and Chukchi seas. *Polar Biol.* **2012**, *35*, 241–255.

(30) Fisk, A. T.; Hobson, K. A.; Norstrom, R. J. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. *Environ. Sci. Technol.* **2001**, *35*, 732–738.

(31) McMeans, B. C.; Arts, M. T.; Rush, S. A.; Fisk, A. T. Seasonal patterns in fatty acids of *Calanus hyperboreus* (Copepoda, Calanoida) from Cumberland Sound, Baffin Island, Nunavut. *Mar. Biol.* **2012**, *159*, 1095–1105.

(32) McMeans, B. C.; Olin, J. A.; Benz, G. W. Stable-isotope comparisons between embryos and mothers of a placentatrophic shark species. *J. Fish Biol.* **2009**, *75*, 2464–2474.

(33) Hop, H.; Borgå, K.; Gabrielsen, G. W.; Kleivane, L.; Skaare, J. U. Food web magnification of persistent organic pollutants in poikilotherms and homeotherms from the Barents Sea. *Environ. Sci. Technol.* **2002**, *36*, 2589–2597.

(34) Hoekstra, P. F.; O'Hara, T. M.; Fisk, A. T.; Borgå, K.; Solomon, K. R.; Muir, D. C. G. Trophic transfer of persistent organochlorine contaminants (OCs) within an Arctic marine food web from the southern Beaufort-Chukchi Seas. *Environ. Pollut.* **2003**, *124*, 509–522.

(35) Fisk, A. T.; Hoekstra, P. F.; Gagnon, J. M.; Duffe, J.; Norstrom, R. J.; Hobson, K. A.; Kwan, M.; Muir, D. C. G. Influence of habitat, trophic ecology and lipids on, and spatial trends of, organochlorine

contaminants in Arctic marine invertebrates. *Mar. Ecol.: Prog. Ser.* **2003**, *262*, 201−214.

(36) McCutchan, J. H.; Lewis, W. M.; Kendall, C.; McGrath, C. C. Variation in trophic shift for stable isotope ratios of carbon, nitrogen, and sulfur. *Oikos* **2003**, *102*, 378−390.

(37) Dennard, S. T.; McMeans, B. C.; Fisk, A. T. Preliminary assessment of Greenland halibut diet in Cumberland Sound using stable isotopes. *Polar Biol.* **2009**, *32*, 941−945.

(38) Cherry, S. G.; Derocher, A. E.; Hobson, K. A.; Stirling, I.; Thiemann, G. W. Quantifying dietary pathways of proteins and lipids to tissues of a marine predator. *J. Appl. Ecol.* **2011**, *48*, 373−381.

(39) Beck, G. G.; Smith, R. G.; Addison, R. F. Organochlorine residues in harp seals, *Phoca groenlandica*, from the Gulf of St. Lawrence and Hudson Strait: An evaluation of contaminant concentrations and burdens. *Can. J. Zool.* **1994**, *72*, 174−182.

(40) Kleivane, L.; Severinsen, T.; Skaare, J. U. Biological transport and mammal to mammal transfer of organochlorines in Arctic fauna. *Mar. Environ. Res.* **2000**, *49*, 343−357.

(41) Blais, J. M.; Kimpe, L. E.; McMahon, D.; Keatley, B. E.; Mattory, M. L.; Douglas, M. S. V.; Smol, J. P. Arctic seabirds transport marine-derived contaminants. *Science* **2005**, *309*, 445.

(42) Fisk, A. T.; Tittlemier, S. A.; Pranschke, J. L.; Norstrom, R. J. Using anthropogenic contaminants and stable isotopes to assess the feeding ecology of Greenland sharks. *Ecology* **2002**, *83*, 2162−2172.

(43) Hussey, N. E.; Brush, J.; McCarthy, I. D.; Fisk, A. T. δ^{15}N and δ^{13}C diet-tissue discrimination factors for large sharks under semi-controlled conditions. *Comp. Biochem. Physiol. A* **2010**, *155*, 445−453.

(44) Ford, C. A.; Muir, D. C. G.; Norstrom, R. J.; Simon, M.; Mulvihill, M. J. Development of a semiautomated method for non-*ortho* PCBs - Application to Canadian Arctic marine mammal tissues. *Chemosphere* **1993**, *26*, 1981−1991.

(45) Stern, G. A.; MacDonald, C. R.; Armstrong, D.; Dunn, B.; Fuchs, C.; Harwood, L.; Muir, D. C. G.; Rosenberg, B. Spatial trends and factors affecting variation of organochlorine contaminants levels in Canadian Arctic beluga (*Delphinapterus leucas*). *Sci. Total Environ.* **2005**, *351*, 344−368.

(46) Gaden, A.; Stern, G. A. Temporal trends in beluga, narwhal and walrus mercury levels: Links to climate change. In *A Little Less Arctic: Top Predators in the World'S Largest Northern Inland Sea, Hudson Bay*; Ferguson, S. H., Loseto, L. L., Mallory, M. L., Eds.; Springer: New York, 2010; pp 197−216.

(47) Luque, S. P.; Ferguson, S. H. Age structure, growth, mortality, and density of belugas (*Delphinapterus leucas*) in the Canadian Arctic: Responses to environment? *Polar Biol.* **2010**, *33*, 163−178.

(48) Rigét, F. F.; Bignert, A.; Braune, B.; Stow, J.; Wilson, S. Temporal trends of legacy POPs in arctic biota, an update. *Sci. Total Environ.* **2010**, *408*, 2874−2884.

(49) Fisk, A. T.; Stern, G. A.; Hobson, K. A.; Strachan, W. J.; Loewen, M. D.; Norstrom, R. J. Persistent organic pollutants (POPs) in a small, herbivorous, arctic marine zooplankton (*Calanus hyperboreus*): Trends from April to July and the influence of lipids and trophic transfer. *Mar. Pollut. Bull.* **2001**, *43*, 93−101.

(50) Hallanger, I. G.; Warner, N. A.; Ruus, A.; Evenset, A.; Christensen, G.; Herzke, D.; Gabrielsen, G. W.; Borgå, K. Seasonality in contaminant accumulation in Arctic marine pelagic food webs using trophic magnification factor as a measure of bioaccumulation. *Environ. Toxicol. Chem.* **2011**, *30*, 1026−1035.

(51) Dachs, J.; Lohmann, R.; Ockenden, W. A.; Mejanelle, L.; Eisenreich, S. J.; Jones, K. C. Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4229−4237.

(52) Borgå, K.; Gabrielsen, G. W.; Skaare, J. U. Differences in contamination load between pelagic and sympagic invertebrates in the Arctic marginal ice zone: Influence of habitat, diet and geography. *Mar. Ecol.: Prog. Ser.* **2002**, *235*, 157−169.