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CURRENT-USE PESTICIDES IN SEAWATER AND THEIR BIOACCUMULATION IN POLAR BEAR–RINGED SEAL FOOD CHAINS OF THE CANADIAN ARCTIC

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Abstract: The distribution of current-use pesticides (CUPs) in seawater and their trophodynamics were investigated in 3 Canadian Arctic marine food chains. The greatest ranges of dissolved-phase concentrations in seawater for each CUP were endosulfan sulfate (less than method detection limit (MDL) to 19 pg L^{-1}) > dacthal (0.76–15 pg L^{-1}) > chlorpyrifos (less than MDL to 8.1 pg L^{-1}) > pentachloronitrobenzene (less than MDL to 2.6 pg L^{-1}) > α-endosulfan (0.20–2.3 pg L^{-1}). Bioaccumulation factors (BAFs, water-respiring organisms) were greatest in plankton, including chlorothalonil (log BAF = 7.4 ± 7.1 L kg^{-1}, mean ± standard error), chlorpyrifos (log BAF = 6.9 ± 6.7 L kg^{-1}), and α-endosulfan (log BAF = 6.5 ± 6.0 L kg^{-1}). The largest biomagnification factors (BMFs) were found for dacthal in the capelin:plankton trophic relationship (BMF = 13 ± 5.0) at Cumberland Sound (Nunvavut), and for β-endosulfan (BMF = 16 ± 4.9) and α-endosulfan (BMF = 9.3 ± 2.8) in the polar bear—ringed seal relationship at Barrow and Rae Strait (NU), respectively. Concentrations of endosulfan sulfate exhibited trophic magnification (increasing concentrations with increasing trophic level) in the poikilothermic portion of the food web (trophic magnification factor = 1.4), but all of the CUPs underwent trophic dilution in the marine mammal food web, despite some trophic level–specific biomagnification. Together, these observations are most likely indicative of metabolism of these CUPs in mammals. *Environ Toxicol Chem* 2016;9999:1–13. © 2016 SETAC

Keywords: Current-use pesticide Marine mammal Food chain Trophic dilution Bioaccumulation

INTRODUCTION

Current-use pesticides (CUPs) of the organochlorine and organophosphorus classes are large-scale replacements for globally banned legacy organochlorine pesticides and have been monitored in the Arctic Ocean since the mid-1990s [1,2]. Current-use pesticides vary in their physical–chemical properties and have a wide range of crop-protection uses and modes of action [2–4]. The CUPs endosulfan (a legacy-type organochlorine pesticide) and dacthal (a chlorinated herbicide) have recently been reported in Arctic seawater in the Chukchi and Bering Seas [5] and in the Devon Island ice cap (Nunavut, Canada) [6]. Most recently, endosulfan, dacthal, chlorothalonil (a chlorinated fungicide and preservative), and chlorpyrifos (an organothiophosphate insecticide) were reported in the western Canadian Arctic and central Arctic Archipelago at concentrations comparable with some legacy organochlorine pesticides such as dieldrin, the chlordane isomers, chlorobenzenes, and heptachlor epoxide (typically all in the low picograms per liter range) [7].

Though studies of CUPs in arctic biota are relatively rare, they have been reported in a vegetation–caribou–wolf food chain in northern Canada [3], in some marine organisms from Greenland [8], and in terrestrial biota from national parks in Alaska [9]. Bioaccumulation hypotheses, modeling, and some (limited) field studies suggest that organic contaminants with intermediate octanol–water (K_{OW}) and octanol–air (K_{OA}) partition coefficients ($10^2 < K_{OW} < 10^{10}$ and $K_{OA} \geq 10^6$), such as the CUPs, will bioaccumulate to greater degrees in mammalian food chains relative to food chains containing exclusively water-respiring organisms (when metabolism of the contaminants is insignificant). This is largely due to increased dietary absorption, combined with reduced respiratory and renal elimination of these contaminants in mammals [10–12].

Several CUPs with these intermediate K_{OW} and K_{OA} properties (endosulfans, dacthal, chlorothalonil, chlorpyrifos, pentachloronitrobenzene [PCNB]) have been shown to bioaccumulate in all trophic levels of the vegetation–caribou–wolf food chain [3]. There was little significant biomagnification of these CUPs in the terrestrial consumers, and they underwent trophic dilution, decreasing in concentration with increasing trophic level, when assessed throughout the food chain [3]. These same current-use pesticides were also quickly metabolized in experimental mammals [13–17], which is significant because metabolism can reduce the biomagnification potential of organic contaminants, as was observed for metabolizable organochlorine pesticides in Arctic wolf food chains [18]. Whether these observations are also true for CUPs in marine food webs has not yet been established.

The present study investigated concentrations of the same suite of CUPs analyzed in the terrestrial environment at

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3 distinct locations in Nunavut, Canada. Our goals were 1) to explore differences in concentrations of the CUPs between locations in seawater and in biota composing the polar bear and ringed seal food chains, 2) to assess the bioaccumulation and biomagnification processes occurring in water-respiring and air-breathing organisms and food chains, and 3) to compare these results with those from a previous investigation of an arctic terrestrial food chain [3].

MATERIALS AND METHODS

Analytes

The analyte suite for biota is the same as that screened in Morris et al. [3] and includes chlorpyrifos, chlorothalonil, dacthal, α-endosulfan, β-endosulfan, and endosulfan sulfate (α-endosulfan + β-endosulfan + endosulfan sulfate = Σendosulfan), and PCNB. Trifluralin and ethalfluralin were tentatively quantified in seawater; however, their respective qualification ion fragments were not detected, thus, these results were excluded. Properties and structures of all analytes are given in Supplemental Data, Table S1 and Figure S1.

Sampling locations and times

Three marine sampling locations in Nunavut were selected based on their unique characteristics and proximity to Inuit communities (Supplemental Data, Figure S2). Barrow Strait (Resolute Bay, Nunavut, Canada; N74°41′51″, W094°49′56″) is a well-characterized, high Arctic location where delivery of contaminants is largely atmospheric. Rae Strait (Gjoa Haven, Nunavut; N68°37′33″, W095°52′30″) is a lower-latitude location close to mainland Nunavut, influenced by inflows from the Back, Hayes, and Ellice Rivers as well as other smaller rivers nearby. Cumberland Sound (Pangnirtung, Nunavut; N66°08′52″, W065°41′58″), on the east coast of Baffin Island, is influenced by Greenland and North Atlantic Ocean currents and has large numbers of transient (range >1000 km) and resident species of fish and mammals compared with the other locations [19].

Sampling of seawater

High-volume (177–486 L) seawater samples were collected using portable pumps with coworkers from each community. Water samples were collected at Barrow Strait in June 2007, 2008, and 2010; at Rae Strait in June 2008; and at Cumberland Sound in August 2007 and 2008. Field, laboratory (resin) and procedural blanks were also employed at each location (samples that used the same resin batch had the same laboratory blank). Samples were drawn through fired (400 °C, 12–24 h) glass microfiber honeycomb filters (FulFlo Honeycomb Filter, pore size 0.5 μm; Parker Advanced Filtration). Samples were then drawn through tandem, stainless steel resin columns packed with approximately 70 g of Amberlite XAD-2® resin (Supelco Analytical). Resin columns were spiked with brominated diphenyl ether 71 (BDE71) as an internal recovery standard (resin and column preparation are detailed in the Supplemental Data). After sampling, resin columns were stored at 2 °C, and filters were frozen (–20 °C) until analyses (only filters from 2008–2010 were extracted). The results of XAD-2, spike-recovery experiments are provided in Supplemental Data, Table S2. Details of resin and column preparation, water sampling, and blank handling are given in the Supplemental Data, and locations and conditions are given in Supplemental Data, Table S3.

Processing of water samples

All samples of seawater and biota were processed in a clean-room laboratory (positive pressure, carbon, and high-efficiency particulate air [HEPA] filters) at Environment Canada (Burlington, ON). To maximize recoveries of the CUPs, XAD-2 resin was eluted per Meyer et al. [20], with some modification and minimal cleanup. We used a pressurized fluid extractor (ASE 300; Dionex) for extraction of the glass microfiber filters. One of the cells for each filter was spiked with BDE71 and [$^{13}C_8$]mirex for the recovery estimation of the CUPs under study. After extraction, the methods also followed those of Meyer et al. [20], from the back-extraction stage of the XAD-2 resin extraction forward (see Supplemental Data).

Sampling of biota

Samples of biota were collected with the help of Inuit subsistence hunters at each location. Samples from Barrow Strait included ice–algae ($n = 10$), plankton ($n = 18$), mixed amphipods ($n = 8$), Arctic cod (*Boreogadus saida*, $n = 23$), blubber of ringed seals ($n = 18$), and fat of polar bears ($n = 8$). At Rae Strait samples of plankton ($n = 4$), polar cod (*Arctogadus glacialis*, $n = 6$), blubber of ringed seals ($n = 6$), and fat of polar bears ($n = 7$) were successfully obtained. In Cumberland Sound, samples consisted of plankton ($n = 3$), capelin (*Mallotus villosus*, $n = 5$), Arctic char (*Salvelinus alpinus*, $n = 5$), blubber of ringed seals ($n = 8$), and fat of polar bears ($n = 8$). Polar bears [21,22], blubber of seals from Cumberland Sound [23], and the lower–trophic level biota from Cumberland Sound [19,24] were collected as parts of, or in cooperation with, other studies but were processed under the same conditions as the other samples. The cod will be referred to by their species names to avoid confusion because both Arctic cod and polar cod have been used interchangeably as common names for these species. Samples were handled minimally in the field and frozen at –20 °C as soon as possible after collection. Details of sample collection are available in the Supplemental Data, and morphometric data for seals, bears, and fishes are provided in Supplemental Data, Tables S4 through S6.

Extraction of biota

Extraction methods have been described previously [3], so only a brief summary is given in the Supplemental Data. Lipid fractions were determined gravimetrically by evaporation of the first fraction eluted during gel permeation chromatography [3], and lipid content was determined for normalization of the wet weight contaminant data.

Analyses, quantification, and quality assurance/quality control

Extracts were analyzed by gas chromatography, negative chemical ionization, low-resolution mass spectrometry (GC-NCI-MS). The GC-MS parameters, analyses, and quantification methods are identical to those previously reported [3] and are briefly outlined in the Supplemental Data. Mass to charge (m/z) ratios of ion fragments monitored for each compound are included in Supplemental Data, Table S2.

Concentrations of CUPs dissolved in seawater were blank-corrected using pooled blanks from sampling trips that used resin from the same batch. Samples of seawater were analyzed individually ($n = 2$–4/location/yr), and means were only calculated to assess the bioaccumulation factors of the contaminants. The fraction of the CUPs adsorbed to dissolved organic carbon was calculated [20]; however, because of their low -K_{OW} values, this correction had no effect on the

dissolved-phase concentrations (calculations given in Supplemental Data, results in Table S7). Filters were extracted together, so all of the blanks were pooled for blank corrections of particulate-phase samples.

Method blanks were extracted with each batch of 10 to 12 biota samples, along with standard reference materials (1588b or 1946; National Institute of Standards and Technology). Analyte recoveries from the standard reference materials were typically within acceptable ranges, including that of the analyte with properties closest to the CUPs (BDE28/33 recovery = 65–97%, log $K_{OW} = 5.9$, log $K_{OA} = 9.4$), as were CUP recoveries during spike-recovery experiments (given in the Supplemental Data and Supplemental Data, Table S2). Method blanks for biota were sorted into 6-mo blocks based on their time of extraction and averaged for blank correction and for calculation of the method detection limits (MDLs). Concentrations in blanks were mass-corrected for each sample type and subtracted from the wet weight concentrations of the samples. Biota samples were then recovery-corrected (relative to [$^{13}C_8$]mirex recoveries) and lipid-normalized for final presentation of the data. The lipid equivalent fraction (ϕ_{Leq}) was used for normalization of plankton and algae to incorporate other significant nonlipid organic matter (proteins, carbohydrates) into the estimates. Total organic carbon was measured in a subset of algae and plankton and applied along with total nitrogen content and the lipid content to estimate the ϕ_{Leq}. Methods for the lipid equivalent correction are given in the Supplemental Data and have been described previously [3,12]. The lipid equivalent fraction was assumed to be equal to the lipid fraction (ϕ_{Lipid}) for amphipods, fishes, blubber of seals, and fat of polar bears, similar the assumptions of previous studies [12,25].

Method detection limit concentrations were calculated as 3 times the standard deviation of the method blank concentrations (sorted as for blank correction), corrected to the average sample volume or mass. Instrument detection limits were used rather than MDLs when analytes were not detected in the blanks, which were calculated using the standard deviations of the responses of repeated injections ($n = 8$) of low-concentration running standards and simple t statistics as described in Wells et al. [26]. If an analyte's detection frequency was <20% in subsets of samples (Barrow Strait plankton, Rae Strait plankton, Cumberland Sound seal blubber, etc.), the analyte was considered a nondetect. Method detection limit/2 (or instrument detection limit/2) substituted concentrations were used in place of 0 values when detection frequencies were >20%, and these were lipid-normalized for each sample and included in geometric means, error terms, and statistics.

Stable isotope analyses and calculation of trophic levels

Ratios of stable isotopes of carbon ($\delta^{13}C = {}^{13}C/{}^{12}C$) and nitrogen ($\delta^{15}N = {}^{15}N/{}^{14}N$) were measured in most of the reported biota (exceptions noted below) at the Environmental Isotope Laboratory (University of Waterloo, Waterloo, ON, Canada). Details of these analytical methods have been published [3,27]. Stable isotope data for the plankton and fish samples from Cumberland Sound were not available for the specific individuals that were analyzed for CUPs (tissue samples were limited in size). Isotopic ratios were randomly generated for these samples within the ranges provided in a large, previously reported data set consisting of samples collected concurrently with those reported in the present study [19,24]. Isotopic ratios in polar bears [21,22] and in seals from Cumberland Sound [23] have also been previously reported.

Stable isotope ratios were measured in muscle of mammals and fishes and in whole-organism subsamples of invertebrates. Subsamples were taken for isotopic analyses in the field and immediately frozen at –20 °C in sterile cryotubes. There were excess contaminant samples at Barrow Strait (3 algae, 2 plankton, and 3 cod), so random stable isotope values were assigned to the missing samples within the range of those measured for each type of organism (in the same year). Trophic levels were calculated for individual samples using the lowest individual $\delta^{15}N$ signal in each food chain (algae at Barrow Strait, plankton at the other locations) and by applying a trophic enrichment factor ($\Delta^{15}N$) of 3.8‰ [25,28] using previously reported equations [29].

Bioaccumulation and biomagnification

"Food chain" is used in the present study to refer to direct feeding relationships established at each location (e.g., Rae Strait food chain = plankton–*A. glacialis*–ringed seal–polar bear). "Food web" is used to refer to a larger subset of data (e.g., the marine mammal food web uses all data in all trophic levels at all locations; the marine poikilothermic food web uses all nonmammalian data from the 3 locations).

Bioaccumulation factors (log BAFs, liters per kilogram) were calculated only for water-respiring biota as the log of the ratio of the arithmetic mean concentrations of CUPs in the organism (micrograms per kilogram lipid wt) to those in the seawater at each location (micrograms per liter; all depths, duplicates, and years included in means) [30].

Biomagnification factors (BMFs) were calculated as the ratio of arithmetic mean concentrations of CUPs in the consumers to their diet. Trophic magnification factors (TMFs) were calculated as the anti logs of the slopes of linear regression analyses of log-transformed CUP concentrations (picograms per gram lipid wt) versus trophic level. Although BMF calculation methods have been presented elsewhere [3,31], the formulae are again provided in the Supplemental Data. Trophic magnification factors were calculated using 1) individual trophic levels and concentrations within each food chain; 2) trophic levels and concentrations for the composite, Arctic-wide marine mammal food web; and 3) only the poikilothermic portion of this marine food web (i.e., from algae to fish). Trophic magnification factors were only calculated for analytes when their raw detection frequencies were 50% or greater in the samples included for each regression.

Statistics

Data from seawater were reported as individual concentrations (picograms per liter) and assessed qualitatively between sites and depths due to small n values. Data for concentrations of contaminants in biota were typically log-normally distributed and are therefore expressed as geometric means (with their 95% confidence intervals); all statistical analyses for biota used log-transformed data. Significance for statistical tests was assessed relative to a type I error rate of $\alpha = 0.05$. Grubb's tests were used to determine outlying data points in the blanks prior to blank correction. Pair-wise comparisons were made using the Student t test or Mann-Whitney U test (when data did not satisfy the parametric assumptions of the t test). Multigroup comparisons were made using one-way analyses of variance (ANOVA) with Tukey's post hoc tests to identify significantly different groups or Kruskal-Wallis ANOVAs on ranks with Dunn's tests when data did not meet the assumptions of ANOVA.

All BAFs and BMFs are presented as means and their standard errors (SEs), calculated using previously reported

equations [3]. As in Morris et al. [3], BMFs were tested for significant differences from 1.0 using the Student *t* test. Trophic magnification factors, with their 95% confidence intervals, are reported only when their regressions had slopes significantly different from 0 ($p < 0.05$).

Pearson correlation analyses were used to establish relationships between log-transformed, lipid-normalized concentrations of the CUPs. The BAFs (logarithm), BMFs, and TMFs for CUPs were tested for correlations with their log K_{OW} and log K_{OA} values. The BMFs in Cumberland Sound seal blubber were not tested for these correlations (only β-endosulfan and endosulfan sulfate were detected).

RESULTS AND DISCUSSION

Concentrations of CUPs in seawater

The freely dissolved concentrations of CUPs differed temporally, spatially, and with depth in seawater; but the current-use pesticides were detectable at all 3 sampling locations (Figure 1; Supplemental Data, Table S9, blanks in Table S10). The greatest unbound, freely dissolved concentrations of chlorothalonil (2.0 pg L^{-1}; 2010, 10 m) and β-endosulfan (0.52 pg L^{-1}; 2010, 2 m) were found at Barrow Strait (Figure 1; Supplemental Data, Table S9), despite it being the most northern sampling location (Supplemental Data, Figure S2). Concentrations of PCNB (2.6 pg L^{-1}) and endosulfan sulfate (19 pg L^{-1}) in the dissolved phase were greatest at Rae Strait (2008, 2 m), whereas those of α-endosulfan (2.4 pg L^{-1}) and dacthal (15 pg L^{-1}) were greatest in the Cumberland Sound (2007, 10 m). Concentrations of Σendosulfan were also greater in both the Rae Strait (range = <17–<21 pg L^{-1}) and Cumberland Sound (3.0–9.6 pg L^{-1}; 2007 and 2008, 10 m) than in Barrow Strait (<0.29–<6.5 pg L^{-1}). The concentration of chlorpyrifos was unusually high in 1 Cumberland Sound sample (90 pg L^{-1}; 2008, 10 m); but it was not detected in the duplicate sample, and qualification ion ratios did not match those of the standards within acceptable ranges; thus, we excluded this data point. Chlorpyrifos was detected at a greater concentration in a single sample from Rae Strait (8.1 pg L^{-1}; 10 m) than the range of concentrations observed at Barrow Strait (0.61–0.77 pg L^{-1}, 2010; Figure 1; Supplemental Data, Table S9).

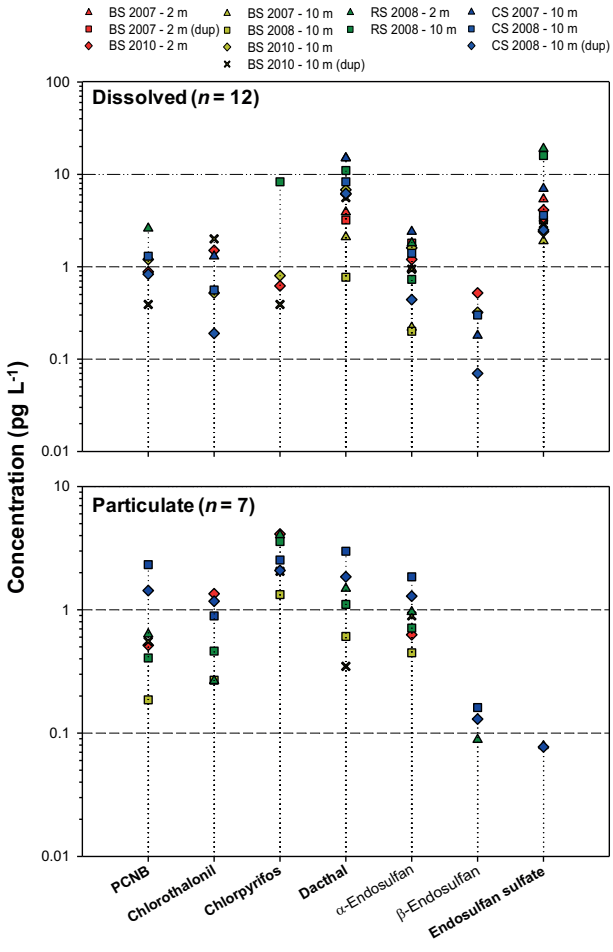

Figure 1. Concentrations of current-use pesticides in the unbound and dissolved phase (upper panel) and the particulate phase of seawater at 3 Arctic locations. Only concentrations that were greater than the method detection limit are shown. Sample points at the top indicated by "(dup)" are separate duplicate samples taken at the same depth, collected immediately after the first sample. BS = Barrow Strait; CS = Cumberland Sound; RS = Rae Strait; PCNB = pentachloronitrobenzene.

The greatest particle-bound concentrations for PCNB (2.3 pg L^{-1}), dacthal (3.0 pg L^{-1}), α-endosulfan (1.9 pg L^{-1}), β-endosulfan (0.16 pg L^{-1}), and Σendosulfan (2.0 pg L^{-1}) were observed in Cumberland Sound in 2008 (Figure 1; Supplemental Data, Table S11, blanks in Table S12). Endosulfan sulfate was again greatest in Rae Strait (0.079 pg L^{-1}; 2008, 2 m), whereas chlorothalonil (1.4 pg L^{-1}) and chlorpyrifos (4.1 pg L^{-1}) had their largest concentrations in Barrow Strait (2010, 2 m). The log K_{OW} and mean particle-bound concentrations (both before and after logarithmic transformations) were not correlated (Pearson correlations, $p > 0.05$, $n = 7$), largely because of the influence of outliers such as β-endosulfan, which had small concentrations but a relatively large K_{OW}, and because of the small number of current-use pesticides detected in the particulate phase (Figure 1; Supplemental Data, Table S11). The relationship improved but remained insignificant (Pearson $r^2 = 0.52$, $p = 0.11$, $n = 6$) after the exclusion of β-endosulfan.

Though the quantification ions of trifluralin (*m/z* 335) and ethalfluralin (*m/z* 333) were detected in both phases of seawater, the qualification ions for these compounds were not detected, leading to the exclusion of these data. The low relative abundance of the qualification compared with the quantification ion fragments (≈10% of the quantification ion abundance) reduces their likelihood of detection at already low picogram per liter concentrations.

Endosulfan sulfate and dacthal were the most consistently detected CUPs with the greatest seawater concentrations. They were also the most frequently detected CUPs in the Devon Island ice cap (Nunavut), along with chlorothalonil, trifluralin, PCNB, metribuzin, and the endosulfan isomers [6]. Approximately 30% of the technical mixture of endosulfan is β-endosulfan; and β-endosulfan was a prominent component of Σendosulfan in the Devon Island ice cap (greater than or equal to α-endosulfan in some layers of the ice cores) [6]. Conversely, as confirmed in the present study, β-endosulfan is a minor component of Σendosulfan in seawater (Figure 1 and Figure 2; Supplemental Data, Tables S9 and S11) [5,32]. This is likely the result of differential processes affecting the dissipation and transformation of the isomers in water versus those postdeposition to sea ice [4].

Both the dissolved-phase and particulate-phase concentrations of endosulfan are affected by its environmental chemistry in water. For example, the isomerization of β-endosulfan to α-endosulfan in aquatic conditions occurs at approximately 3 times the rate of the reverse reaction, which is the most likely reason for the small representation of β-endosulfan in both

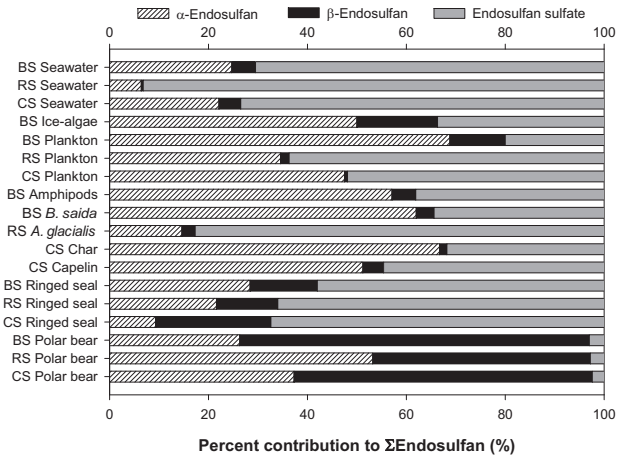

Figure 2. The percent contribution of the endosulfan isomers and endosulfan sulfate to Σendosulfan (α-endosulfan + β-endosulfan + endosulfan sulfate) of seawater and biota for the 3 locations investigated. *A. glacialis* = *Arctogadus glacialis*; *B. saida* = *Boreogadus saida*; BS = Barrow Strait; CS = Cumberland Sound; RS = Rae Strait.

phases of seawater [33–35]. Endosulfan sulfate is less volatile than the parent isomers, is equally as soluble in water as β-endosulfan, and is formed via the oxidation of both isomers [35], resulting in a prominent presence in the dissolved phase of seawater and the Devon Island ice cap [6]. Endosulfan sulfate has low sorption to particles in relation to its abundance in the dissolved phase because of its small log K_{OW} value (3.2; Supplemental Data, Table S2), which resulted in low detection frequencies and concentrations in the particle phase (Figure 1 and Supplemental Data, Table S11). The small proportion of endosulfan sulfate on particles also suggests that further oxidation of α-endosulfan and β-endosulfan to endosulfan sulfate may be limited once they are particle-bound in seawater.

In the majority of paired comparisons in both phases of seawater, CUPs concentrations were greater at depths of 2 m than 10 m (Figure 1; Supplemental Data, Tables S9 and S11). This is suggestive of flux from the sea ice, delivery of CUPs to both phases of seawater from sea-ice melt, or runoff from nearby shores/rivers. The differences between CUPs in the dissolved phase at 2 m and 10 m at Barrow Strait were less prominent in 2010 than in 2007 (Figure 1), perhaps because of the lesser sea-ice melt (qualitatively assessed; Supplemental Data, Table S3) during sampling that year.

These results, combined with other studies in Arctic seawater [5,7], ice caps [6], and air [36], confirm that dacthal, chlorothalonil, chlorpyrifos, and the endosulfans are consistently found in Arctic environmental media. Pentachloronitrobenzene has also been found throughout the Arctic but is detected less consistently than the other CUPs described in the present study [36]. Several of the contaminants investigated here were also recently reported in data from cruises of the Beaufort Sea and the central, high Arctic Archipelago [7]. Concentrations that were within reasonable range of the present study's results included (ranges from the present study are in parentheses) dacthal 4.6 pg L^{-1} to 13 pg L^{-1} (0.77–15 pg L^{-1}), chlorpyrifos 2.3 pg L^{-1} to 18 pg L^{-1} (0.39–8.3 pg L^{-1}), α-endosulfan 1.6 pg L^{-1} to 5.5 pg L^{-1} (0.20–2.4 pg L^{-1}), and endosulfan sulfate 0.28 pg L^{-1} to 26 pg L^{-1} (not detected to 19 pg L^{-1}). In contrast, chlorothalonil and β-endosulfan had greater concentrations than those observed in the present study, with ranges of 6.6 pg L^{-1} to 970 pg L^{-1} (not detected to 2.0 pg L^{-1}) and not detected to 3.7 pg L^{-1} (not detected to 0.52 pg L^{-1}), respectively [7]. Differences in sampling times and conditions as well as in sampling and analytical methodologies affect the comparability between studies and contribute to the deviations observed between the present study's results and those of previous investigators.

Prior to the inclusion and regulation of endosulfan under the Stockholm Convention [37], its use was voluntarily curtailed in North America and Europe [4]. Concentrations of α-endosulfan measured in the present study did show some decreases compared with those measured in 1993 and 1998. For example, the concentrations of α-endosulfan at Barrow strait in 1993 were approximately 2.6 pg L^{-1} (range 2.0–5.7 pg L^{-1}) [38] compared with a range of 0.94 pg L^{-1} to 1.6 pg L^{-1} (2010 samples) reported in the present study. Similarly, the concentration of α-endosulfan in seawater was 2.7 pg L^{-1} at Baffin Bay in 1998 (eastern shore of Baffin Island) [32] compared with a range of 0.44–1.4 pg L^{-1} (2008) reported in the present study at Cumberland Sound (Supplemental Data, Table S9) [38].

The particle-phase data in the present study are markedly different from concentrations reported in the Bering-Chukchi Sea, where all such concentrations were below MDLs [5]. The concentrations obtained from previous studies may not be appropriate for comparison with the data presented in the present study because of differences in sampling methodologies and conditions. Zhong et al. [5] used a seawater intake system on an icebreaker, operating in deep water, during summer conditions (open water). Likewise, samples taken by Jantunen et al. [7] were drawn through ship intakes. The present samples were taken under the sea ice (Barrow and Rae Straits) or from a stationary vessel in open-water or drift-ice conditions (Cumberland Sound), using portable pumps. Also, because the filters capture any particles >0.5 μm, the particulate-phase data include particulate organic carbon <0.5 μm, algae, plankton, and dissolved organic carbon.

Structure of the food web

Within the Barrow and Rae Strait food chains, the mean $\delta^{13}C$ and $\delta^{15}N$ signatures were significantly different between every classification of organism (e.g., algae, plankton, amphipods; ANOVAs and 2-tailed t tests, $p < 0.05$) except for the $\delta^{13}C$ signatures of amphipods and seals in the Barrow Strait ($\delta^{13}C = -18.7$ and -19.1, respectively; Supplemental Data, Tables S13–S15). At Cumberland Sound, the $\delta^{13}C$ of plankton ($\delta^{13}C = -20.3 \pm 0.0592‰$) was significantly ^{13}C-depleted relative to polar bears ($-16.6 \pm 0.590‰$). Conversely, $\delta^{15}N$ of polar bears ($19.6 \pm 0.961‰$) was significantly ^{15}N-enriched compared to plankton ($\delta^{15}N = 10.8 \pm 0.287‰$) and capelin ($13.6 \pm 0.247‰$), though no other isotopic ratios at Cumberland Sound were significantly different. Discussion regarding differences in isotopic ratios between locations is restricted to the Supplemental Data and Supplemental Data, Table S16. However, it should be noted that the ^{13}C-depleted $\delta^{13}C$ signatures of plankton ($-28.4 \pm 0.440‰$) and seals ($-24.0 \pm 0.890‰$) at Rae Strait (Supplemental Data, Table S16) confirm the results of Butt et al. [39] and indicate a strong influence of terrestrial carbon from the rivers that terminate nearby. The $\delta^{15}N$ signatures followed a consistent pattern of ^{15}N enrichment (Supplemental Data, Figure S3), resulting in logical trophic levels that are given with concentrations in Supplemental Data, Tables S13 to S15.

Concentrations of current-use pesticides in biota

The majority of the lipid-normalized, geometric mean concentrations of the CUPs were greatest in lower–trophic level biota. β-endosulfan concentrations were the exception

among the CUPs, being greatest in ringed seals and polar bears (Supplemental Data, Table S13–S15). Concentrations of the contaminants in bears and ringed seals varied across a small range and were rarely significantly different between these species (ANOVAs or Kruskal-Wallis ANOVAs on ranks, $p > 0.05$). The smallest concentrations in biota were found for PCNB, chlorpyrifos, dacthal, and endosulfan sulfate in polar bear fat, ranging from less than the MDL to 0.032 ng g^{-1} lipid weight.

The greatest concentrations of PCNB were in plankton at Rae Strait (0.50 [0.13–1.9] ng g^{-1} lipid wt), capelin at Cumberland Sound (0.49 [0.063–3.9] ng g^{-1} lipid wt), and *B. saida* at Barrow Strait (0.35 [0.21–0.58] ng g^{-1} lipid wt; means are given with their 95% confidence intervals in brackets). The highest concentrations of chlorothalonil were in capelin from Cumberland Sound (1.4 [0.81–2.3] ng g^{-1} lipid wt), ice-algae from Barrow Strait (1.1 [0.65–2.0] ng g^{-1} lipid wt), and *A. glacialis* from Rae Strait (0.40 [0.27–0.60] ng g^{-1} lipid wt). Dacthal was also highest in capelin (2.1 [1.3–3.5] ng g^{-1} lipid wt), followed by plankton from Rae Strait (1.7 [1.0–2.9] ng g^{-1} lipid wt) and Arctic char from Cumberland Sound (0.49 [0.15–1.6] ng g^{-1} lipid wt). Chlorpyrifos was greatest in plankton at all locations, with the greatest concentrations measured at Cumberland Sound (1.1 [0.010–131] ng g^{-1} lipid wt) > Barrow Strait (0.41 [0.33–0.51] ng g^{-1} lipid wt) > Rae Strait (0.33 [0.11–0.95] ng g^{-1} lipid wt). Lastly, Σendosulfan concentrations and those of most of the individual endosulfans were greatest in plankton at both Rae Strait (<11 [5.3–24] ng g^{-1} lipid wt) and Cumberland Sound (<8.7 [3.1–25] ng g^{-1} lipid wt), as well as in amphipods at Barrow Strait (<2.9 [1.9–4.4] ng g^{-1} lipid wt;(individual concentrations of the isomers and endosulfan sulfate are provided in Supplemental Data, Tables S13–S15).

The majority of the CUP concentrations were significantly correlated with other CUPs concentrations throughout the individual food chains and the marine food web (Pearson correlations of logged values, $p < 0.05$; Supplemental Data, Table S17). Rae Strait had the fewest significant correlations, likely because of several factors, including the multiple sources of contaminants to this area (atmospheric deposition, runoff, riverine inputs) and because *A. glacialis* are more closely linked to the benthic rather than the pelagic food web, unlike the rest of the organisms in the present study [40]. In general, these correlations suggest similar patterns of delivery, uptake, and bioaccumulation of the CUPs throughout these areas, which is logical given their similar patterns of usage globally and their physicochemical properties [2,4,41,42].

Spatial variation of concentrations in biota

There were some significant differences in concentrations of CUPs between the 3 locations (only 2008 data were compared when possible to reduce temporal variability; polar bears from Barrow and Rae Straits and seals from Cumberland Sound were exceptions; see Supplemental Data, Tables S4 and S5 for capture data). The variation in concentrations was larger in poikilothermic organisms than in mammals, which prevented some significant differences from being detected, even when geometric mean concentrations were dissimilar (e.g., see dacthal geometric means and 95% confidence intervals in Supplemental Data, Table S18). When concentrations of CUPs were significantly different between locations, they tended to be greater at Rae Strait and Cumberland Sound than at Barrow Strait (ANOVAs or Kruskal-Wallis ANOVAs on ranks, $p < 0.05$; Figure 3; Supplemental Data, Table S18). Plankton from Rae Strait and Cumberland Sound had greater concentrations of α-endosulfan, endosulfan sulfate, and Σendosulfan than those from Barrow Strait, with Σendosulfan concentrations of 11 (5.3–24) ng g^{-1} lipid weight and 8.7 (3.1–25) ng g^{-1} lipid weight (Rae Strait and Cumberland Sound, respectively) and 1.7 (1.0–2.8) ng g^{-1} lipid weight (Barrow Strait; Figure 3; Supplemental Data, Table S18).

Among the fishes, capelin had the greatest concentrations of chlorothalonil (1.4 [0.81–2.3] ng g^{-1} lipid wt), chlorpyrifos (0.31 [0.017–5.5] ng g^{-1} lipid wt), dacthal (2.1 [1.3–2.5] ng g^{-1} lipid wt), endosulfan sulfate (0.94 [0.062–14] ng g^{-1} lipid wt), and Σendosulfan (<5.1 (2.2–12) ng g^{-1} lipid wt; Supplemental Data, Table S18). Arctic char had the highest concentrations of α-endosulfan (1.5 [0.70–3.2] ng g^{-1} lipid wt), whereas *B. saida* had the greatest concentrations of PCNB (0.77 [0.26–2.2] ng g^{-1} lipid wt) and β-endosulfan (0.11 [0.043–0.28] ng g^{-1} lipid wt; Figure 3). The greater concentrations of Σendosulfan and related compounds in capelin are probably the result of different exposure pathways and concentrations during migrations into temperate regions [19,43], whereas concentrations in char are likely affected by their anadromous life cycle [44], though whether this would increase or decrease concentrations is unclear. Capelin are 1 of several transient species in Cumberland Sound and have been shown to have elevated concentrations of legacy organochlorine pesticides compared with other Arctic fishes of comparable trophic position [19]. Though the number of CUPs is small, the present study's results support the hypothesis that transient species such as capelin can act as biovectors for select organic contaminants, delivering them to the Arctic from regions closer to agricultural and urban areas in North America and Europe [19].

Mammalian concentrations of CUPs had little spatial variation between the 3 locations. Concentrations were very low in seal blubber (≤0.22 ng g^{-1} lipid wt), and none were significantly different between the Barrow and Rae Strait (few CUPs were detected in blubber from Rae Strait; Figure 3). Concentrations of β-endosulfan (0.051 [0.036–0.066] ng g^{-1} lipid wt), endosulfan sulfate (0.14 [0.086–0.21] ng g^{-1} lipid wt), and Σendosulfan (0.22 [0.15–0.28] ng g^{-1} lipid wt) were significantly higher (t tests or ANOVAs, $p < 0.05$) in the blubber of seals from Cumberland Sound than in Barrow Strait animals. Seals from the Barrow Strait yielded the only detectable concentrations of α-endosulfan in their blubber between the 3 locations (0.016 [0.0068–0.038] ng g^{-1} lipid wt (Supplemental Data, Table S13). Concentrations of the CUPs in the fat of polar bears had no significant spatial variation between the 3 locations and were of approximately the same scale as concentrations in the blubber of seals (≤0.27 ng g^{-1} lipid wt; Figure 3; Supplemental Data, Table S18).

Poikilothermic organisms (from algae to fish) from the Rae Strait and Cumberland Sound tended to have greater concentrations of the CUPs than those from Barrow Strait (with exceptions, see Figure 3). Because both Rae Strait and Cumberland Sound are at lower latitudes than Barrow Strait, they are more likely to have a broader range of semivolatile contaminants deposited to them than would high Arctic locations [45], which is the simplest explanation for the elevated concentrations in these areas. The uniformity of concentrations in mammals between the 3 locations, as well as the low concentrations of CUPs in general, are further evidence that seals and polar bears have a high capacity to biotransform and/or eliminate these contaminants, as they do some organochlorine pesticides [46]. Rapid metabolism and depuration would theoretically negate differences in exposures to these CUPs in mammals between locations, resulting in few

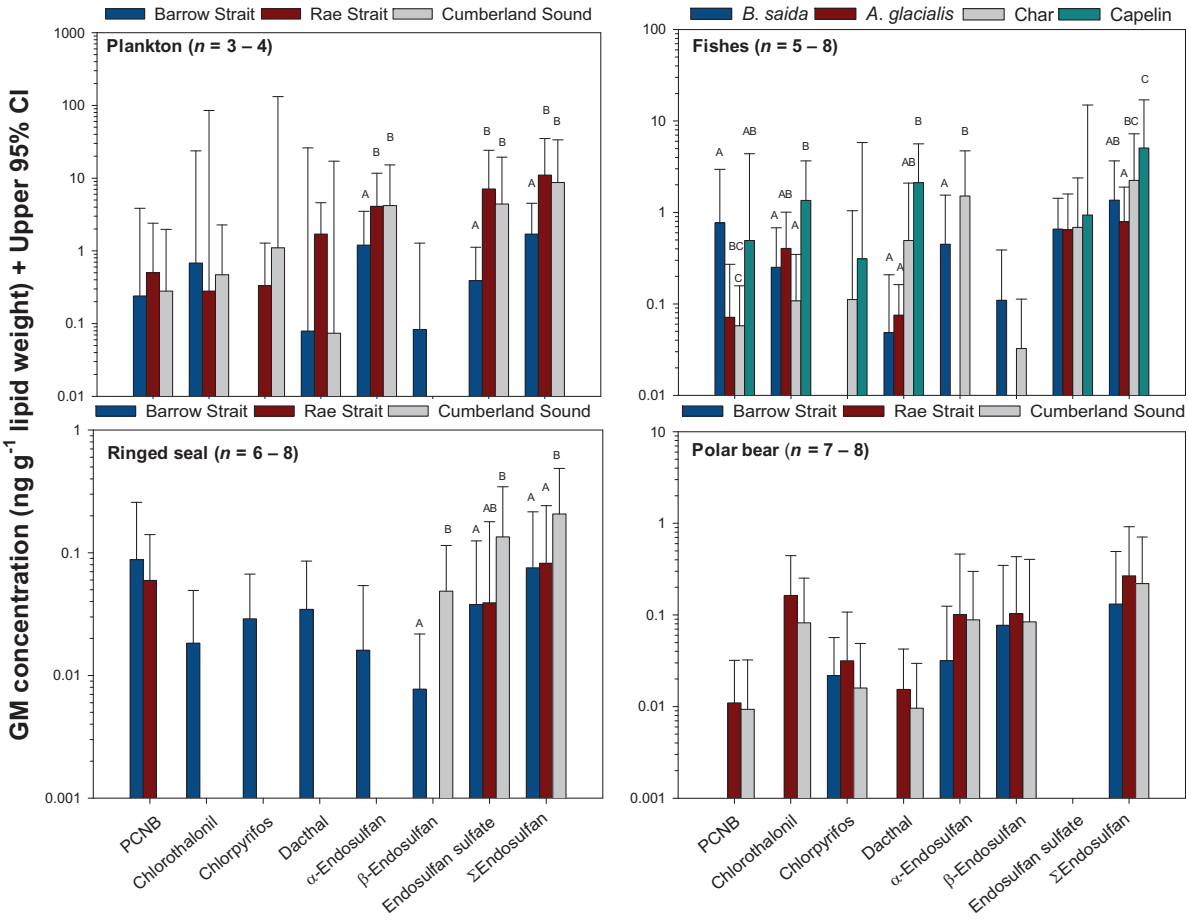

Figure 3. Spatial comparisons of geometric mean concentrations of current-use pesticides in biota from 3 locations in the Canadian Arctic + Upper 95% confidence interval. *A. glacialis* = *Arctogadus glacialis*; *B. saida* = *Boreogadus saida*; CI = confidence interval; GM = geometric mean; PCNB = pentachloronitrobenzene. Bars that share letters in common, or are not marked with any letters, are not significantly different ($p > 0.05$).

significantly different concentrations, as observed in the present study.

Previous work has also found elevated concentrations of perfluorinated alkyl substances (as well as the aforementioned ^{13}C-depleted δ^{13}C isotope signatures) in seals from Rae Strait relative to those from Barrow Strait, supporting some of the data in the present study [39]. Runoff from the catchments of rivers that terminate near the Rae Strait has been hypothesized to increase delivery of perfluorinated alkyl substances to the strait [39]. This could also increase the delivery of the CUPs and other organic contaminants present in the terrestrial environment to marine biota [3], though likely to a lesser degree than perfluorinated alkyl substances, as the CUPs are less water soluble. The abundance of transient species as well as the influence of different air and ocean currents at the Cumberland Sound result in differences in the delivery of organic contaminants to predators from this region [19].

Though there are few data to compare with, the concentrations in primary producers and consumers in the marine food chains are within range of those in the vegetation–caribou–wolf food chain in the Bathurst Region (Northwest Territories and Nunavut) for biota at comparable trophic positions [3]. Of interest is that polar bears sampled more recently from the Hudson Bay Region (2013), had nondetectable concentrations of endosulfan [47]. This could be caused by several factors, but the most likely reason for these deviations from the present study's results are reduced exposures of Arctic biota to endosulfan (from increased restrictions on its use and emissions) [4,37] coupled with rapid depuration of residues from the tissues of mammals [13]. Simple spatial differences in exposure as well as differences in processing and analyses of the CUPs also likely play a role in these deviations.

The concentrations of Σendosulfan reported in the present study were approximately an order of magnitude less than those in comparable Greenland biota, even considering that the Σendosulfan from Greenland only included α-endosulfan and β-endosulfan [8]. For example, capelin and ringed seal (blubber) from western Greenland had concentrations of 50 ng g^{-1} lipid weight and 3.4 ng g^{-1} lipid weight, respectively [8], whereas concentrations in the same organisms from the Cumberland Sound were <5.1 (2.2–12) ng g^{-1} lipid weight and <0.22 (0.14–0.27) ng g^{-1} lipid weight, respectively (Supplemental Data, Table S15). Concentrations of Σendosulfan in *B. saida* (<1.8 (1.4–2.4) ng g^{-1} lipid weight) and ringed seal (<0.070 (0.054–0.092) ng g^{-1} lipid weight) at the high Arctic Barrow Strait were even smaller when compared with these same Greenland organisms. Previous investigations into chlorinated persistent organic pollutant concentrations throughout the Arctic did show a greater degree of contamination in polar bears from Greenland than in those from the Canadian Arctic Archipelago [22], differences which are related to food chain structure and contaminant delivery in these regions. However, it should be noted that differences from the data from Greenland collected in 1999 to 2000 could be the result of declining concentrations as

well as analytical methodology (GC-electron capture detection vs GC-NCI-MS in the present study).

Proportions of endosulfan in biota

The composition profiles for endosulfan (percentage contribution of α-endosulfan, β-endosulfan, and endosulfan sulfate to Σendosulfan based on arithmetic means) in biota differed from those in seawater at their respective locations, with increased proportions of α-endosulfan and β-endosulfan in biota. All of the Σendosulfan profiles in seawater had very little β-endosulfan (<5%; Figure 2). The profiles at Barrow Strait and Cumberland Sound were very similar when expressed as percentages of Σendosulfan (≈20–25%:5.0%:70–75% for α-endosulfan:β-endosulfan:endosulfan sulfate), whereas endosulfan in seawater from Rae Strait was present mostly as endosulfan sulfate (93%), with 0.40% β-endosulfan and 6.6% α-endosulfan. The greater concentrations and contributions of the more water-soluble endosulfan sulfate compared to Σendosulfan at Rae Strait are most likely explained by runoff and delivery from large fluvial sources terminating close to the Rae Strait (Supplemental Data, Figure S2) [39]. Significant modification of Σendosulfan from source medium (seawater) to apex predator was evident as well because endosulfan sulfate was <3% of Σendosulfan in polar bears (all concentrations less than MDL), despite its dominant presence in seawater. Also contrasting with seawater, β-endosulfan was the greatest contributor to Σendosulfan in all bears, ranging from 44% to 71% of Σendosulfan (compared with 0.40–5.0% in seawater; Figure 2).

Like seawater, biota at Rae Strait (with the exception of polar bears) had greater contributions from endosulfan sulfate to Σendosulfan than analogous organisms at similar positions in the food web at the other locations (Figure 2). For example, the Σendosulfan profiles in plankton from Barrow and Rae Strait were 69%:11%:20% and 34%:2.0%:64% (for α-endosulfan:β-endosulfan:endosulfan sulfate). The Σendosulfan profiles of lower–trophic level organisms differed from seawater, which contrasts with previous results in the terrestrial environment. There, lichens (*Cladonia* sp. and *Flavocetraria* sp.) and moss (*Rhytidium rugosum*), which are rootless, atmospherically dependent primary producers, had Σendosulfan profiles that were nearly identical to air [3]. The differences in proportions of Σendosulfan in plankton between locations did however reflect the differences in water, with uptake and accumulation in plankton and algae apparently in proportion to endosulfan availability in seawater at each location (Figure 2).

Pelagic fish (*B. saida*, capelin, Arctic char) and amphipods had profiles of Σendosulfan that were similar to each other and to plankton at their respective locations (as well as algae for Barrow Strait organisms), which is reflective of their trophic interactions via the pelagic food web. In contrast, Σendosulfan profiles in *A. glacialis* were dissimilar to those in plankton from Rae Strait, due to *A. glacialis* primarily feeding on benthos and not being tightly linked to the pelagic food web (Figure 2) [40].

Profiles of Σendosulfan in seal blubber did not differ substantially between Barrow (28%:14%:58%) and Rae Straits (22%:12%:66%; for α-endosulfan:β-endosulfan:endosulfan sulfate; Figure 2). Seals from Cumberland Sound had more β-endosulfan, less α-endosulfan, but approximately equal proportions of endosulfan sulfate (9%:23%:68%) compared with seals from the other locations (Figure 2). Consistent, relatively high proportions of endosulfan sulfate are indicative of oxidative metabolism of the endosulfan isomers in seals [4], as was observed for Arctic wolves and caribou [3]. In contrast, polar bears had minimal contributions of endosulfan sulfate to Σendosulfan at all locations (all concentrations were below the MDL; Figure 2). This is almost certainly the result of further biotransformation of endosulfan sulfate to endosulfan diol, ether, and other polar products [4] in polar bears over seals and other biota. Polar bears have been shown to very effectively metabolize and biotransform a broad range of organohalogen contaminants [46], which is supportive of the present results. The degree of metabolic isomerization of α-endosulfan and β-endosulfan in mammals is unknown; therefore, the effects of biotransformation versus differential bioaccumulation on the proportions of the endosulfan isomers in bears and seals are unfortunately impossible to ascertain. In addition to oxidation to endosulfan sulfate, differences in uptake and bioaccumulation, interconversion of the isomers by biotransformation [48–50], further metabolism of endosulfan sulfate to polar metabolites, and clearance of the individual endosulfan isomers [4,51], or most likely a combination of these factors, all affect the proportions of endosulfan between the mammals at each location.

The present study's results for Σendosulfan in lower–trophic level organisms are comparable to those of Σhexachlorocyclohexanes in the arctic marine food web (i.e., little modification of the respective profiles between invertebrates and fishes) [52]. However, unlike hexachlorocyclohexane [52], for which the accumulation patterns in 2 pinniped species were also very similar to their prey, we observed substantial modification of the Σendosulfan profiles between seals, polar bears, and their respective diets of fish and amphipods or seal blubber (Figure 2). These differences are likely also a result of biotransformation in the mammals, which is a species-specific, contaminant-specific, and condition-specific process [46].

Bioaccumulation and biomagnification of CUPs

The log BAFs of the CUPs in lower–trophic level, water-respiring organisms (algae to fishes, calculated relative to seawater concentrations) ranged from $3.8 \pm 2.7\,L\,kg^{-1}$ lipid weight (mean ± standard error) for dacthal in *A. glacialis* to a maximum of $7.4 \pm 7.1\,L\,kg^{-1}$ lipid weight for chlorothalonil in Rae Strait plankton (Table 1). The greatest BAFs were of the order (from greatest to smallest) chlorothalonil (Rae Strait plankton, $7.4 \pm 7.1\,L\,kg^{-1}$ lipid wt) > chlorpyrifos (Cumberland Sound plankton, $6.9 \pm 6.7\,L\,kg^{-1}$ lipid wt) > α-endosulfan (Cumberland Sound plankton, $6.5 \pm 6.0\,L\,kg^{-1}$ lipid wt) > β-endosulfan (Barrow Strait plankton, $6.0 \pm 5.3\,L\,kg^{-1}$ lipid wt) > endosulfan sulfate (Cumberland Sound plankton, $6.0 \pm 5.5\,L\,kg^{-1}$ lipid wt) > dacthal (capelin, $5.4 \pm 4.7\,L\,kg^{-1}$ lipid wt) > PCNB (*B. saida*, $6.3 \pm 5.9\,L\,kg^{-1}$ lipid wt; Table 1). Conversely, the smallest BAFs were typically calculated in *A. glacialis* (PCNB, dacthal, endosulfan sulfate; range 3.8–$4.9\,L\,kg^{-1}$ lipid wt) and Arctic char (PCNB, chlorothalonil, β-endosulfan, range 4.9–$5.3\,L\,kg^{-1}$ lipid wt). Despite the differences between species, these BAFs do indicate that the majority of the CUPs enter the food chain efficiently through the organisms at the base of the food web (algae and plankton), exposing higher–trophic level organisms including amphipods and fish to these contaminants (Table 1). Amphipods and fishes also retain and bioaccumulate the current-use pesticides to a substantial degree, though this varied by CUP, across species and location.

Marine mammals did not biomagnify the majority of the CUPs significantly (BMFs insignificantly different from 1), though there was some biomagnification of chlorothalonil and the endosulfan isomers (but not endosulfan sulfate) from ringed seal blubber to polar bear fat (Table 2). The BMFs for

Table 1. Bioaccumulation factors for water-respiring biota at the 3 sampling locations in Nunavut, Canada[a,b]

		Log BAF ± SE (L kg−1 lipid wt)						
	n[c]	PCNB	Chlorothalonil	Chlorpyrifos	Dacthal	α-Endosulfan	β-Endosulfan	Endosulfan sulfate
Barrow Strait								
Algae:water	17	6.1 ± 5.8	6.3 ± 5.8	—	5.1 ± 4.6[d]	5.7 ± 5.1	5.9 ± 5.3	5.0 ± 4.4
Plankton:water	25	6.1 ± 5.7	6.3 ± 5.7[d]	6.0 ± 5.1	4.8 ± 4.0	6.0 ± 5.3	6.0 ± 5.3	5.1 ± 4.3
Amphipods:water	15	5.8 ± 5.4	—	5.7 ± 5.0[d]	4.7 ± 4.0	6.3 ± 5.7	5.9 ± 5.4[d]	5.6 ± 4.9
Boreogadus saida:water	30	6.3 ± 5.9	5.4 ± 4.9	5.5 ± 4.7[d]	4.7 ± 4.0	6.2 ± 5.7	5.7 ± 5.3[d]	5.5 ± 4.6
Rae Strait								
Plankton:water	6	5.7 ± 5.5	7.4 ± 7.1	5.0 ± 4.8	5.1 ± 4.4	6.5 ± 6.0	—	5.6 ± 5.0
Arctogadus glacialis:water	8	4.9 ± 4.7	6.6 ± 5.7	—	3.8 ± 2.7	—	—	4.6 ± 3.6
Cumberland Sound								
Plankton:water	6	5.6 ± 5.3	5.9 ± 5.5	6.9 ± 6.7	4.3 ± 3.9	6.5 ± 6.0	—	6.0 ± 5.5
Char:water	8	4.9 ± 4.5	5.3 ± 4.9	5.8 ± 5.2	4.8 ± 4.4	6.1 ± 5.6	5.3 ± 4.9	5.3 ± 4.8
Capelin:water	8	6.2 ± 5.9	6.3 ± 5.8	6.7 ± 6.4	5.4 ± 4.7	—	—	5.8 ± 5.4

[a]Log BAFs were calculated using mean concentrations in biota (micrograms per kilogram lipid wt) compared to the mean concentration in water (micrograms per liter).
[b]Bioaccumulation factors were not calculated when current-use pesticide had 0% detection frequencies above the method detection limit (indicated by "—").
[c]$n = n_{Biota} + n_{Media}$.
[d]Detection frequency <20%.
BAF = bioaccumulation factor; PCNB = pentachloronitrobenzene; SE = standard error.

chlorothalonil and Σendosulfan were significantly >1 for $bear_{Fat}$:$seal_{Blubber}$ at Rae Strait (BMFs = 3.7 ± 0.63 and 3.8 ± 1.1 respectively). In this trophic relationship β-endosulfan only underwent significant biomagnification at Barrow Strait (BMF = 16 ± 4.9) and α-endosulfan solely at Rae Strait (BMF = 9.3 ± 2.8; Table 2).

In contrast, the BMFs for the CUPs in the blubber of seals were all <1 (or not significantly different from it, $p < 0.05$), regardless of the dietary comparison (Table 2). The BMFs in seals from Rae Strait should be interpreted with caution because of the dietary source utilized for the calculation—*A. glacialis* are consumed by seals (G. Konana, Gjoa Haven Hunters and Trappers Association, Gjoa Haven, Nunavut, personal communication) but are unlikely to compose a majority of the seal diet [28]. However, the concentrations of the CUPs in pelagic fish from other locations were generally of the same order of magnitude or greater than those in *A. glacialis* (Supplemental Data, Table S18), so the biomagnification estimates would, if anything, be smaller than those determined using *A. glacialis* as the divisor in the BMF equation.

At Barrow Strait, the BMFs for α-endosulfan and Σendosulfan in both the plankton:algae and amphipod:algae comparisons significantly exceeded 1 (BMF range 1.7 ± 0.30 to 3.9 ± 1.1; Table 2). Only endosulfan sulfate biomagnified significantly from plankton to *B. saida* (BMF = 2.6 ± 0.26), though both endosulfan sulfate and Σendosulfan also biomagnified from plankton to amphipods (BMFs = 3.8 ± 0.51 and 2.0 ± 0.31, respectively). PCNB also biomagnified in the *B. saida*:amphipod trophic relationship at Barrow Strait but did not significantly exceed 1 when comparing *B. saida* to plankton (BMFs = 3.4 ± 1.2 and 1.4 ± 0.49, respectively). This comparison demonstrates the importance of diet selection on potential biomagnification in the fish and in differences that can be generated depending on how the investigator chooses to calculate the BMF. No biomagnification was observed in *A. glacialis*:plankton trophic interactions, though these results must be interpreted with some caution because plankton are not a primary food source for *A. glacialis* [40]. The greatest BMF observed among the lower–trophic level biota was found for dacthal, calculated in the transient capelin relative to plankton at Cumberland Sound (BMF = 13 ± 5.0). Chlorothalonil also biomagnified significantly in this trophic relationship (BMF = 2.7 ± 0.70), but no other CUPs did (note that limited detections restricted the BMFs that could be appropriately calculated; Table 2).

No comprehensive, field-based assessments of aquatic food chain biomagnification in the Canadian Arctic (or in any system to our knowledge) exist for PCNB, chlorothalonil, chlorpyrifos, or dacthal. Endosulfan has been shown to be bioaccumulative in aquatic and terrestrial food chains; however, evidence for its biomagnification has been conflicting [3,4]. Endosulfan did not biomagnify significantly in freshwater planktonic (USA) [53], arctic terrestrial (Canada) [3], or arctic marine (Greenland) [8] mammal food chains but did biomagnify in some freshwater piscivorous (Canada) [54], arctic piscivorous (marine fish), and seabird (both from Greenland) [8] food chains. The present study's results again demonstrate and support this previously observed variability in the biomagnification potential of endosulfan because biomagnification of the isomers and endosulfan sulfate was trophic level–specific, food chain–specific, and location-specific. However, it does seem, based on the available evidence, that endosulfan is more likely to biomagnify in poikilothermic/piscivorous comparisons than in those containing marine mammals (Table 2).

Like mammals in the present study, the majority of the tissue-specific BMFs of CUPs in muscle and liver of caribou and wolves in the Arctic terrestrial food chain did not significantly exceed 1 [3]. Only 2 CUPs biomagnified in caribou tissues: chlorothalonil ($caribou_{Muscle}$:diet BMF = 2.2 ± 0.61) and endosulfan sulfate ($caribou_{Liver}$:diet BMF = 2.1 ± 0.35), and only PCNB biomagnified significantly between caribou and wolves (in muscle, BMF = 2.5 ± 0.69). The BMFs for the CUPs in caribou and wolves were within range of most of the BMFs reported in the present study; however, there was further magnification of the endosulfan isomers in polar bears over wolves. The BMFs for β-endosulfan in $bear_{Fat}$:$seal_{Blubber}$ at Barrow Strait (16 ± 4.9; Table 2) was smaller, but was within range of previously reported BMFs for this CUP in cetaceans consuming fish in the Hudson Bay Region (BMF = 22) [12].

Trophic magnification analyses demonstrated that the CUPs underwent trophic dilution throughout the individual marine

Table 2. Biomagnification factors for biota in Barrow Strait, Rae Strait, and Cumberland Sound, Nunavut, Canada[a]

Trophic relationship	n[b]	Biomagnification factor ± SE							
		PCNB	Chlorothalonil	Chlorpyrifos	Dacthal	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	ΣEndosulfan
Barrow Strait									
Plankton:algae	28	1.1 ± 0.44	0.86 ± 0.20[f]	—	0.45 ± 0.11[c,e]	—	—	1.0 ± 0.16	1.7 ± 0.30[d]
Amphipods:algae	18	0.47 ± 0.20[c]	—	—	0.36 ± 0.11[c,e]	3.9 ± 1.1[d]	—	3.9 ± 0.69[d]	3.5 ± 0.67[d]
Amphipods:plankton	26	0.42 ± 0.14[c]	—	0.56 ± 0.092[c,f]	0.80 ± 0.16	1.6 ± 0.35	—	3.8 ± 0.51[d]	2.0 ± 0.31[d]
Boreogadus saida: plankton	41	1.4 ± 0.49	0.13 ± 0.032[c,e]	0.29 ± 0.046[c,f]	0.88 ± 0.16	1.4 ± 0.39	—	2.6 ± 0.26[d]	1.5 ± 0.29
B. saida:amphipods	31	3.4 ± 1.2[d]	—	0.52 ± 0.098[c,e,f]	1.1 ± 0.22	0.83 ± 0.27[c]	—	0.69 ± 0.068[c]	0.75 ± 0.16[c]
$Seal_{Blubber}$:*B. saida*	41	0.067 ± 0.023[c]	0.18 ± 0.040[c,f]	0.15 ± 0.025[c,e,f]	0.11 ± 0.020[c]	0.015 ± 0.0050[c,f]	—	0.056 ± 0.0074[c]	0.034 ± 0.0063[c]
$Seal_{Blubber}$:amphipods	26	0.22 ± 0.072[c]	0.051 ± 0.0080[c]	0.079 ± 0.013[c]	0.12 ± 0.022[c]	0.013 ± 0.0037[c]	—	0.039 ± 0.0068[c]	0.025 ± 0.0036[c]
$Bear_{Fat}$:$seal_{Blubber}$	26	—	—	1.3 ± 0.22[e]	0.42 ± 0.065[c,f]	2.9 ± 1.0	16 ± 4.9[d]	—	3.1 ± 0.92[d]
Rae Strait									
Arctogadus glacialis:plankton	10	0.18 ± 0.069[c]	0.17 ± 0.075[c,f]	0.095 ± 0.026[c]	0.042 ± 0.0050[c]	0.028 ± 0.0070[c]	0.10 ± 0.047[c]	0.086 ± 0.017[c]	0.068 ± 0.013[c]
$Seal_{Blubber}$:*A. glacialis*	12	0.56 ± 0.19[c]	0.12 ± 0.017[c,f]	—	—	—	—	0.094 ± 0.028[c]	0.12 ± 0.025[c]
$Bear_{Fat}$: $seal_{Blubber}$	13	0.22 ± 0.045[c]	3.7 ± 0.63[d,e]	0.90 ± 0.27	1.7 ± 0.34	9.3 ± 2.8[d]	—	—	3.8 ± 1.1[d]
Cumberland Sound									
Char:plankton	8	0.19 ± 0.056[c]	0.25 ± 0.10[c]	0.067 ± 0.035[c]	3.8 ± 1.8	0.41 ± 0.11[c]	—	0.18 ± 0.058[c]	0.29 ± 0.080[c]
Capelin:plankton	8	3.3 ± 1.5	2.7 ± 0.70[d]	0.53 ± 0.36	13 ± 5.0[d]	—	—	0.56 ± 0.23	0.66 ± 0.19
Char:capelin	10	0.057 ± 0.022[c]	0.093 ± 0.030[c]	0.13 ± 0.060[c]	0.30 ± 0.090[c]	—	—	0.32 ± 0.14[c]	0.44 ± 0.13[c]
$Seal_{Blubber}$:char	13	NM	NM	NM	NM	—	1.3 ± 0.31	0.17 ± 0.044[c]	0.085 ± 0.017[c]
$Seal_{Blubber}$:capelin	13	NM	NM	NM	NM	—	—	0.056 ± 0.018[c]	0.038 ± 0.0080[c]
$Bear_{Fat}$:$seal_{Blubber}$	16	—	—	—	—	—	4.0 ± 1.5	—	1.5 ± 0.45

[a]Biomagnification factors were not calculated when detection frequencies were 0% in either the consumer or the diet (indicated by "—").
[b]$n = n_{consumer} + n_{diet}$ (calculations are given in the Supplemental Data).
[c]Biomagnification factors are significantly <1 (2-tailed t tests, $p < 0.05$).
[d]Biomagnification factors are significantly >1 (2-tailed t tests, $p < 0.05$).
[e]Biomagnification factors with <20% detection frequencies that exceeded the method detection limit in the dietary item.
[f]Biomagnification factors with <20% detection frequencies that exceeded the method detection limit in the consumer.
NM = not measured; PCNB = pentachloronitrobenzene; SE = standard error.

mammal food chains at each location as well as in the composite marine mammal food web assembled from all contaminant data (TMFs < 1; Table 3; Supplemental Data, regression data in Table S19 and Figure S4). These results are consistent with our recent observations of trophic dilution of the same suite of CUPs in the terrestrial vegetation–caribou–wolf food chain [3]. Despite trophic dilution in the marine mammal food web, endosulfan sulfate underwent trophic magnification through the poikilothermic portion of the food web (TMF = 1.4 [95% confidence interval 1.1–1.9]; Table 3). This was likely driven by both the more efficient respiratory uptake of endosulfan sulfate from the surrounding water in the poikilotherms (compared with uptake across the lungs in mammals, which is essentially nil), and stronger retention of endosulfan sulfate in the fish after formation compared with the mammals, which seem to either excrete the endosulfan sulfate or metabolize it further (though residues of endosulfan sulfate did remain in seal blubber) [4]. Previous studies have also found different TMFs for organochlorine pesticides when calculated for whole food webs containing marine mammals or solely for poikilothermic food webs [12,29].

Previous investigations have shown that the organochlorine pesticides with the greatest TMFs and BMFs in Arctic food webs were either the most recalcitrant compounds, such as *trans*-nonachlor (TMF = 10.4, BMF = 111) and PCB153 (TMF = 26.3, BMF = 325), or biotransformation products such as oxychlordane (TMF = 17.5, BMF = 141) and *p*,*p*′-dichlorodiphenyldichloroethane (DDE; TMF = 31.8, BMF = 250) [52]. Important to note is that the biotransformation products in the previous example had greater BMFs than *trans*-nonachlor (a known recalcitrant contaminant), and they also had greater TMFs in marine mammal food webs than in poikilothermic food webs [52]. This could be the result of more rapid metabolism of some xenobiotics in mammals over fishes, and of reduced elimination of low to intermediate K_{OW} and high K_{OA} organohalogens in air-breathing animals [11,12,46,55].

The present study's results, particularly those relating to the metabolite endosulfan sulfate ($\log K_{OW} = 3.2$, $\log K_{OA} = 9.7$), did not corroborate the previous results for organochlorine pesticide metabolites [52]. Given the rapid depuration of endosulfans from mammals in laboratory studies [13], it is likely that further metabolism of endosulfan sulfate to more polar metabolites, followed by excretion [4], hinders extensive biomagnification of this CUP in polar bears and seals. Given the small K_{OW} of endosulfan sulfate and the relatively larger K_{OW} values for oxychlordane ($\log K_{OW} = 5.5$) and DDE ($\log K_{OW} = 6.5$), it is logical to assume that those metabolites would be retained to a larger degree than endosulfan sulfate (K_{OW} estimates from the US Environmental Protection Agency's Estimation Programs Interface Suite, Ver 4.10).

When relationships can be established between the BAFs, BMFs, or TMFs and the log K_{OW} or log K_{OA}, the octanol partition coefficients can be used for quick assessments of the general bioaccumulation potential of organic contaminants when their metabolism is limited (e.g., Kelly and Gobas [18]). However, none of the BAFs and only a few BMFs and TMFs were significantly correlated with the log K_{OA} or log K_{OW} (Pearson correlations; Supplemental Data, Figure S5). None of the BMFs at any location were significantly correlated with the log K_{OW}, and only the $bear_{Fat}$:$seal_{Blubber}$ BMFs at Barrow Strait were significantly positively correlated with the log K_{OA} ($r^2 = 0.98$, $p = 0.0098$, $n = 4$; Supplemental Data, Figure S5).

Only the TMFs calculated at Rae Strait were significantly positively correlated with the log K_{OW} ($r^2 = 0.80$, $p = 0.039$, $n = 5$), and no TMFs were correlated with the log K_{OA}. Because relationships of the BAFs, BMFs, and TMFs with the log K_{OA} and log K_{OW} were very limited, the octanol partition coefficients are not suitable for use as predictive measures of bioaccumulation or biomagnification potential for CUPs in the marine food web. Also note the *n* values ($n = 4$–7) used for these tests were small and that, in some cases, there are few data points in the high-K_{OA} end of the figure, which skewed the results of the correlations (Supplemental Data, Figure S5).

The BMFs were also independent of relationships with the log K_{OW} and log K_{OA} in caribou and wolves, though the

Table 3. Trophic magnification factors[a] of current-use pesticides for the marine mammal and poikilothermic food webs using data from all locations[b] as well as for the individual food chains at Barrow Strait,[c] Rae Strait,[d] and Cumberland Sound[e]

	Trophic magnification factors with 95% confidence intervals							
	PCNB	Chlorothalonil	Chlorpyrifos	Dacthal	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	ΣEndosulfan
Marine mammal food web[f] ($n = 129$–137)	0.44 (0.29–0.44)	0.57 (0.38–0.57)	0.38 (0.27–0.38)	0.49 (0.32–0.49)	0.49 (0.30–0.49)	0.88 (0.61–0.88)	0.40 (0.26–0.40)	0.56 (0.38–0.56)
Poikilothermic food web ($n = 82$)	—	0.47 (0.32–0.71)	0.25 (0.18–0.35)	—	—	0.54 (0.40–0.72)	1.4 (1.1–1.9)	—
Barrow Strait food chain ($n = 85$)	0.36 (0.27–0.50)	0.34 (0.27–0.42)	0.27 (0.22–0.32)	0.43 (0.34–0.54)	0.38 (0.28–0.51)	0.60 (0.48–0.75)	0.43 (0.34–0.56)	0.49 (0.39–0.63)
Rae Strait food chain ($n = 23$)	0.34 (0.27–0.43)	—	0.57 (0.42–0.78)	0.27 (0.19–0.38)	0.41 (0.22–0.74)	—	0.15 (0.10–0.21)	0.34 (0.22–0.53)
Cumberland Sound food chain ($n = 21$–29)[f]	0.17 (0.090–0.34)	0.39 (0.22–0.70)	0.18 (0.076–0.42)	0.16 (0.058–0.43)	0.17 (0.060–0.46)	—	0.060 (0.034–0.11)	0.18 (0.10–0.33)

[a]Trophic magnification factors were not calculated when regressions did not yield significant *p* values and are indicated by "—." Regression coefficients are provided in Supplemental Data, Table S19. Trophic magnification factors are shown above their 95% confidence intervals (in parentheses).
[b]The marine mammal food web includes contaminant data from all 3 locations; food chain structure was algae–plankton–amphipods–fishes–ringed seal blubber–polar bear fat. The poikilothermic food web included all data but those for marine mammals.
[c]Food chain structure at Barrow Strait was algae–plankton–amphipods–*Boreogadus saida*–ringed seal blubber–polar bear fat.
[d]Food chain structure at Rae Strait was plankton–*Arctogadus glacialis*–ringed seal blubber–polar bear fat.
[e]Food chain structure at Cumberland Sound was plankton–capelin–arctic char–ringed seal blubber–polar bear fat (seal blubber data were not available for dacthal, chlorothalonil, chlorpyrifos, and PCNB).
[f]Sample numbers (*n*) were variable as only endosulfan data were available for ringed seals at Cumberland Sound—endosulfans have the greater *n* values in these rows, whereas all other current-use pesticides have the lower *n* values.
PCNB = pentachloronitrobenzene.

logarithms of the volumetric bioconcentration factors of CUPs were significantly correlated with the log K_{OA} in vegetation [3]. In contrast, the BAFs in algae were not significantly related to the log K_{OW}, which may be indicative of more complicated factors affecting bioaccumulation of CUPs in marine systems, even in relatively simplistic organisms like algae. This could be related to a number of differences, particularly reactions in seawater versus air during transport and differences in deposition and uptake between algae and terrestrial plants. The cuticle of terrestrial plants tends to effectively sorb contaminants from the gas phase and/or from deposition [56], resulting in greater prominence on the surfaces of vegetation, providing stronger relationships that directly relate to the K_{OA}. The small number of CUPs detected in the algae ($n = 6$) may also affect the correlations because highly significant relationships must be present to be detected at small values of n (which is likely an important factor for all of the correlation analyses). In addition, previous assessments have found that a lack of correlation of BMFs or BAFs with the partition coefficients in terrestrial mammals was related to the inclusion of nonrecalcitrant contaminants in the correlation analyses [11,12,18]. This is very likely the case in the present study because most of the CUPs are relatively environmentally and metabolically labile compared with legacy organochlorine pesticides used in previous analyses.

Our data do support the bioaccumulation of these current-use pesticides into the polar bear–ringed seal food chain in locations in the eastern, central, and high Arctic; however, there were few points of significant biomagnification in these systems. The greatest BMFs were observed for endosulfans in marine mammals and dacthal in capelin. The CUPs displayed trophic dilution throughout the mammalian food chains and webs, which indicates a limited risk of harmful biomagnification to top predators. However, endosulfan sulfate did biomagnify to a small degree through the poikilothermic portion of the food web (TMF = 1.4), which is interesting but not likely significant (because of the small magnitude of trophic magnification), particularly given the cessation of use of endosulfan under the Stockholm Convention [37]. Both K_{OW} or K_{OA} were unreliable predictors of the bioaccumulation, biomagnification, and trophic magnification potential of the suite of CUPs in the marine organisms and food chains/webs described in the present study.

The majority of the BMFs and TMFs of these CUPs in the marine systems measured were not substantially different from those measured recently in the vegetation–caribou–wolf food chain [3]. In the present study, β-endosulfan did biomagnify to a greater extent in polar bears than in the wolves [3]. These results seemingly contrast with previous hypotheses predicting that the biomagnification and trophic magnification of low K_{OW}, high K_{OA} contaminants ($10^2 < K_{OW} < 10^{10}$ and $K_{OA} \geq 10^6$) such as the CUPs would be greater in terrestrial organisms and food webs than in marine food webs [11,12]. Biotransformation of these CUPs in mammals is the most probable cause of deviations from the modeled results in both systems, as the original models assumed negligible metabolism of the contaminants, which is not the case with the CUPs. If food web models can be updated to include more accurate estimates of biotransformation, they would be more applicable to current-use contaminants of interest like the CUPs.

When the present study's data are combined with results from the Arctic terrestrial environment [3], it is apparent that there are limited risks of extensive biomagnification of these CUPs to concentrations that would be of concern to the top predators in either system, despite some limited biomagnification between various consumers and their diets.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3427.

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