Temporal and spatial variation in polychlorinated biphenyl chiral signatures of the Greenland shark (Somniosus microcephalus) and its arctic marine food web

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ABSTRACT

Polychlorinated biphenyls (PCBs) chiral signatures were measured in Greenland sharks (Somniosus microcephalus) and their potential prey in arctic marine food webs from Canada (Cumberland Sound) and Europe (Svalbard) to assess temporal and spatial variation in PCB contamination at the stereoisomer level. Marine mammals had species-specific enantiomer fractions (EFs), likely due to a combination of in vivo biotransformation and direct trophic transfer. Greenland sharks from Cumberland Sound in 2007–2008 had similar EFs to those sharks collected a decade ago in the same location (PCBs 91, 136 and 149) and also similar to their conspecics from Svalbard for some PCB congeners (PCBs 95, 136 and 149). However, other PCB EFs in the sharks varied temporally (PCB 91) or spatially (PCB 95), suggesting a possible spatiotemporal variation in their diets, since biotransformation capacity was unlikely to have varied within this species from region to region or over the time frame studied.

1. Introduction

Chiral molecules exist as non-superimposable mirror image forms with the same physical–chemical properties, except for optical rotation. Chirality is valuable for understanding the environmental effects and fates of persistent organic pollutants (POPs) because different enantiomers of a chiral compound usually have different biological and toxicological impacts (Wong and Warner, 2009). For example, chiral polychlorinated biphenyls (PCBs) can stereoselectively disrupt $\text{Ca}^{2+}$ ion signaling via sensitization of ryanodine receptors (Pessah et al., 2009), affect $\text{Ca}^{2+}$ uptake by adult rat cerebellum microsome and disturb protein kinase C (PKC) translocation (Lehmler et al., 2005), thereby causing stereoselectively linked neurotoxicity. In addition, stereoselective cytochrome P-450 isozyme (CYPs) induction by chiral PCBs 88, 139 and 197 has been observed in male Sprague–Dawley rat livers or chick embryo hepatocytes (Pütthmann et al., 1989; Rodman et al., 1991). Therefore, enantiomer-specific contaminant analysis is necessary to assess exposure and toxicity of PCBs to organisms accurately (Lehmler et al., 2010). Chirality can also be exploited as a marker to trace biological weathering processes (Lehmler et al., 2010), because changes in the enantiomer distributions of chiral chemicals in the environment are generally due only to biological processes (e.g., interactions with biological molecules, microbial degradation, metabolism or predation).

Although PCB production has been widely banned since the mid-1970s, PCBs are still ubiquitous in the environment. As with other legacy POPs, PCBs typically degrade very slowly. However, atropisomer analysis of 19 environmentally stable chiral PCB congeners has demonstrated that atropisomer- and congener- and species-specific biochemical weathering processes do occur for various PCBs in aquatic food webs (Wong et al., 2001, 2004; Warner et al., 2005; Dang et al., 2010). The different environmental fates of
chiral PCB atropisomers might be due to stereoselective biotransformation of chiral PCBs in vivo or uptake of non-racemic residues from prey or sediments.

Marked declines in concentrations of legacy POPs, including PCBs, have been observed in arctic biota after these pollutants were banned by the Stockholm Convention (Muir et al., 2013), but it is unclear how the enantiomer signatures of POPs change through time and space in food webs, particularly in the Arctic. A constant chiral signature of POPs in an organism can result from an equilibrium between uptake and elimination processes (Vetter et al., 2001). Therefore, changes in the enantiomer compositions of chiral POPs are potential indicators for disruption of such equilibrium in organisms, and also perhaps indicators of disturbances in relevant ecosystem processes (Vetter et al., 2001). Given the limited biotransformation capacity of some arctic species such as Greenland sharks (Somniosus microcephalus) towards POPs (Fisk et al., 2002; MacNeil et al., 2012), any shifts in the chiral signatures of POP residues might indicate a change in POP uptake from prey (i.e., changes in diet composition from prey with racemic signatures to those with non-racemic signatures). McKinney et al. (2012) recently found that increasing numbers of transient/sub-arctic animals might alter the food web dynamics of organochlorine contaminants in Cumberland Sound, Nunavut, Canada by affecting consumption patterns, and thus POP uptake. These changes might be related to recent climate-change induced shifts in arctic food webs. In the present study, we hypothesize that any observed spatial and temporal variation in the PCB chiral signatures of Greenland sharks is largely driven by differences or changes in feeding strategies (i.e., diet choices), which may be a consequence of a variety of ecological factors.

Greenland sharks collected from Cumberland Sound (Canada) and Svalbard (Norway) were used to address these issues. The Greenland shark is a suitable organism for tracing spatial and temporal trends of POPs in arctic biota, because Greenland sharks are widely distributed in the Arctic, are thought to have a long life span (>50 years) and are top predators (Fisk et al., 2002; Leclerc et al., 2012; MacNeil et al., 2012). Concentrations and atropisomer compositions of chiral PCBs were also determined in potential prey species of Greenland sharks within the Cumberland Sound food web to assess whether trophic transfer influences the EFs of PCBs in these sharks. Temporal variation in the stereoisomer composition of chlordanes and PCBs in air (Bidleman et al., 2002; Jamshidi et al., 2007), PCBs in soil (Jamshidi et al., 2007), hexachlorocyclohexanes in water (Padma and Dickhut, 2002) and hexabromocyclododecanes in biological samples (Peck et al., 2008; Esslinger et al., 2011) have been previously investigated, providing important information about the source, behavior and fate of POPs in the environment. However, to our knowledge, the present study is the first study that compares temporal patterns (i.e., a decade apart) in EFs of chiral PCBs in an arctic species.

2. Materials and methods

2.1. Sample information

Biota samples were collected from various trophic levels of the Cumberland Sound food web (Fig. 1) in 2007–2008: mixed zooplankton (n = 6), scallop (Chlamys islandica, n = 7), herring (Clupea harengus, n = 1), capelin (Mallotus villosus, n = 5), Greenland halibut (Reinhardtius hippoglossoides, n = 8), Arctic skate (Amblyraja hyperborea, n = 5), sculpin (Myoxocephalus scorpius, n = 9), Arctic char (Salvelinus alpinus, n = 5), Greenland shark (n = 11), ringed seal (Phoca hispida, n = 5), harp seal (Pagophilus groenlandicus, n = 4), narwhal (Monodon monoceros, n = 7) and beluga whale (Delphinapterus leucas, n = 4) (see McKinney et al., 2012 for details). Greenland shark samples were also collected from Cumberland Sound from 1999 to 2000 (n = 15) and Svalbard (n = 44 for liver samples; n = 43 for plasma samples) (Fig. 1) from 2008 to 2009 (see Fisk et al., 2002; Leclerc et al., 2012; Molde et al., 2013 for details). Zooplankton, scallop, Greenland halibut, Arctic skate, sculpin, Arctic char, ringed seal and beluga whale were classified as resident species, while herring, capelin, harp seal, Greenland shark and narwhal were considered to be transient species (McKinney et al., 2012).

Total and some individual PCB concentration data were reported previously (Fisk et al., 2001, 2002; McKinney et al., 2012; Molde et al., 2013). However, concentrations of chiral congeners are reported for the first time in the present work for Greenland sharks and their prey. In addition, total PCB concentration data were not used previously to assess the temporal and spatial variation of PCB contamination in Greenland sharks and their prey. The trophic position classification is based on McKinney et al. (2012). PCBs were analyzed in the blubber of marine mammals and

Fig. 1. Location of sampling sites in Cumberland Sound, Nunavut, Canada and Svalbard, Norway.
muscle of fishes, in the liver, muscle or plasma of Greenland shark samples, and in whole organism homogenates of other species (see Supplemental materials for details). All data were normalized to lipid weight concentrations for comparisons with lipid-normalized concentrations in the literature, unless otherwise indicated.

2.2. Atropisomer analyses

Chiral PCB compositions were quantified using an Agilent 5890 gas chromatograph/5989 mass spectrometer (GC/MS) under electron impact ionization (70 eV) as described in Wong et al. (2002). A Chirasil-Dex column (25 m length × 0.25 mm internal diameter × 0.25 μm film thickness, Varian, Palo Alto, CA) was used for atropisomer analysis. The chiral PCBs monitored (and their ions) included: PCBs 91 and 95 (m/z 324, 326, 328), PCBs 136 and 149 (m/z 358, 360, 362), and PCBs 174 and 176 (m/z 392,394, 396).

2.3. Quality assurance/quality control

QA/QC for achiral PCB analysis were published previously (Fisk et al., 2001, 2002; McKinney et al., 2012; Molde et al., 2013). For enantioselective analysis, Standard Reference Material SRM 1945 (organics in whale blubber; triplicate measurements) was used to assess the accuracy of EF measurements (Wong et al., 2002). A solvent blank and a standard solution were analyzed as quality controls every five samples to check for interference and cross contamination. The detection frequencies of chiral PCBs in organisms are listed in Table S1.

2.4. Data analyses

Enantionomer fractions (EFs) (Harner et al., 2000) were used to describe atropisomer distributions, and are defined as the concentration ratio of the first-eluting atropisomer (E1) and the total concentration of both atropisomers (E1 + E2) (PCBs 91 and 95) or as the concentration ratio of the (+)-atropisomer and total concentration for which optical rotation is known (PCBs 136, 149, 174 and 176) (Haglund and Wiberg, 1996; Wong et al., 2002):

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EF = \frac{E1}{E1 + E2} \quad \text{or} \quad EF = \frac{(+)}{(+)} = \frac{(+)}{(+)}
\]  

(1)

PCB concentrations were determined using PeakFit v4.12 (Systat Software, San Jose, CA) to deconvolute chromatograms (Asher et al., 2009), Prism 5 (GraphPad Software, La Jolla, CA) was used for statistical analyses. The D’Agostino-Pearson omnibus normality test was used to examine whether the concentration and EF data followed normal distributions. Then, non-parametric (Mann–Whitney test or Kruskal–Wallis test with post-hoc Dunn’s multiple comparison test) or parametric (unpaired t-test with Welch’s correction or one-way ANOVA) test, as appropriate, was performed to evaluate differences among species, areas and sampling times. The statistical significance was set at α = 0.05. Data are reported as mean ± standard error unless otherwise indicated. Racemic standards (mixture of racemic PCBs 91, 95, 136, 149, 174 and 176) had EF values that ranged from 0.496 ± 0.002 to 0.503 ± 0.004. EFs were considered to be non-racemic if values deviated from racemic value beyond 0.032 (95% confidence interval; Le., < 0.468 or > 0.532) (Wong et al., 2004).

3. Results and discussion

3.1. Spatial and temporal trends of PCBs

3.1.1. Cumberland Sound food web

PCB concentrations in organisms of the Cumberland Sound food web (Fig. 2) generally fell within expected levels compared with other temperate and arctic ecosystems (Table S2). Similar to other areas, penta- and hexa-chlorinated PCBs were the predominate congeners in all species. These comparisons must be interpreted with some caution because these samples, and the PCB concentrations therein, were collected at different time points, and because methods of quantitation and the number of congeners making up the sum of PCBs may also differ. That having been said, the methods of PCB quantification were similar, and the number of congeners analyzed has little impact on the reported total PCB concentrations, as these methods analyze for the vast majority of congeners by weight that were present.

Total PCB concentrations in Cumberland Sound zooplankton (~5 ng/g wet wt.) were lower than values observed for zooplankton in temperate freshwater lakes (Lake Superior, ~370 ng/g wet wt., collected in 1998) (Wong et al., 2004), but higher than in zooplankton from the Bering-Beaufort–Chukchi Seas (collected in 1997–1998; Hoekstra et al., 2002). Scallop...
in 2001 in Outer Dvina Bay and Onega Bay, in the White Sea of Russia (Muir et al., 2003); however, it must be noted that this Russian location is likely to be heavily polluted. Concentrations in Cumberland Sound ringed seals were also lower than in conspecifics from Hudson Strait (Canadian Arctic, collected between 1999 and 2003) (Kelly et al., 2008) and East Greenland (collected in 2004; Rigét et al., 2006), but similar to ringed seals from nearby West Greenland (collected in 2006; Vorkamp et al., 2008). In Cumberland Sound ringed seals collected in 1993 (Fisk et al., 2002), had ΣPCBs that was about 1.8 times higher than in samples collected in 2007–2008. A similar temporal pattern has been observed in ringed seals from Svalbard (Wolkers et al., 2008). Subadult ringed seals sampled in 2004 in Svalbard had about a three-fold lower ΣPCB concentrations compared to similarly aged animals collected in 1996 (Wolkers et al., 2008). ΣPCB concentrations in harp seals from the White Sea (collected between 1998 and 2001; Muir et al., 2003) were about 2 times higher than those in harp seals in the present study. The ΣPCB concentrations in Cumberland Sound beluga were similar to those in Alaskan beluga (collected between 1989 and 2006; Huguet et al., 2013) and in female beluga from Hudson Strait (collected between 1998 and 2003; Kelly et al., 2008), but were lower than those measured in male belugas from Hudson Strait (collected between 1995 and 1997; Andersen et al., 2001) or male belugas from Hudson Strait (collected between 1998 and 2003; Kelly et al., 2008). ΣPCB concentrations in Cumberland Sound narwhal were lower than that in narwhal from Svalbard in 2001 (Wolkers et al., 2005), but similar to levels measured in conspecifics in West Greenland (collected in 1993; Dietz et al., 2004).

3.1.2. Greenland sharks

ΣPCB concentrations in Greenland sharks from Cumberland Sound did not change (p = 0.68, unpaired two tailed test) between 1999 (3400 ± 700 ng/g in liver) (Fisk et al., 2002) and 2008 (3100 ± 400 ng/g in muscle) (Fig. 2B). The levels of ΣPCBs in the Svalbard Greenland sharks (5340 ± 750 ng/g in liver, 4810 ± 1000 ng/g in plasma) in 2008 were higher than those of Greenland sharks from Cumberland Sound (Fig. 2B), but were not statistically different (p = 0.18, Kruskal–Wallis test). High organochlorine contaminant concentrations have been reported from Svalbard and East Greenland biota previously (Letcher et al., 2010; Sonne, 2010). The concentrations of 17 PCB congeners in Greenland sharks from Iceland in 2001–2003 were about 4100 (muscle)-4400 (liver) ng/g (Strid et al., 2007), which are higher than in sharks from Cumberland Sound, but similar to Svalbard.

Chiral PCB concentrations in Greenland sharks from Cumberland Sound were not different (p = 0.95, 0.08, 0.72, 0.79, 0.92 for PCBs 91, 95, 136, 149 and 174, respectively) between 1999 and 2008 (Fig. 3). However, higher levels of PCB 149 were measured in Svalbard sharks compared with Cumberland Sound sharks during the 2007 and 2008 sampling interval (p = 0.005), indicating some geographic differences in chiral PCB contamination (Fig. 3). Data for other chiral PCBs are not available for Svalbard Greenland sharks. Thus, PCB levels in Greenland sharks from Cumberland Sound were similar in 1999 compared with 2008, and generally lower than those found in the European Arctic.

3.2. Atropisomer enrichment of chiral PCBs in the Cumberland Sound food web

PCBs 95 and 149 were the dominant chiral PCB congeners in Cumberland Sound organisms, while PCBs 91, 136, 174 and 176 were only detected in a few high trophic level species (Table S1, Fig. 4 and Fig. S1), consistent with results from the Northwater Polynya (NOW), north of Cumberland Sound, in 1998 (Warner et al., 2005). Transient species had higher chiral PCB concentrations than resident species (Figs. S1 and S2), consistent with the higher occurrence of penta-, hexa- and hepta-chlorinated PCBs in transient species (McKinney et al., 2012). However, there was no significant difference in the trophodynamics between the two atropisomers of any of the detected chiral PCBs (Fig. S2), implying no clear trend of EFs with trophic level (Fig. S3). Instead, species-specific EF patterns were observed in the Cumberland Sound food web, but in this case no obvious differences in EF patterns were observed between transient and resident species (Fig. 4 and Fig. S3). This result indicates that the atropisomer compositions of chiral PCBs in these organisms were not dependent on their tissue contamination levels (Vetter et al., 2001), but more likely they are linked to in vivo biotransformation activities and EFs in their prey (see below).

3.2.1. Zooplankton and benthic invertebrates

Mixed zooplankton had racemic EF values averaging 0.500 ± 0.007, 0.472 (single measurement) and 0.487 ± 0.008 for PCBs 95, 136 and 149 (Fig. 4), respectively, similar to those observed in plankton from Lake Superior in Canada (Wong et al., 2004) and the NOW (Warner et al., 2005). These values are also consistent with racemic chiral signatures of other POPs in arctic zooplankton, indicating that these species likely have poor biotransformation capabilities and do not stereoselectively bioaccumulate POPs (Hoekstra et al., 2003).

The EFs of PCBs 95 and 149 in Cumberland Sound scallops were 0.498 ± 0.015 and 0.504 ± 0.010, respectively (Fig. 4). Since scallops feed mainly on plankton, these racemic atropisomer compositions indicate that scallops do not stereoselectively accumulate nor biotransform these PCBs. Similarly, near-racemic PCB 149 was observed in blue mussels (Mytilus edulis) in the German Bight (Hühnerfuss et al., 1995), consistent with the generally poor capacities to biodegrade PCBs shown by many invertebrate species.

3.2.2. Pelagic fishes

The racemic signatures for both herring and capelin (Fig. 4) also suggest limited biotransformation abilities towards PCBs in these species and in their prey, although it is important to note that only a single measurement exists for herring. As with invertebrates, many freshwater pelagic fishes have more non-racemic PCB residues, and higher biotransformation capacities, than similar marine species. For example, atropisomer enrichment of chiral PCBs in cisco (Coregonus artedii) was detected in Lake Superior (Wong et al., 2004); in vivo metabolism or uptake from prey were identified as two reasons responsible for the non-racemic signatures of PCBs in this species (Wong et al., 2004).

3.2.3. Benthic fishes

Short-horned sculpin, Greenland halibut and Arctic skate in Cumberland Sound did not exhibit atropisomer enrichment for most PCB congeners (Fig. 4). The only exception was for PCB 176 in Greenland halibut (EF = 0.433 ± 0.023). Significant atropisomer enrichments of PCBs 91, 95, 136 and 149 have previously been observed in freshwater sculpins (Cottus cognatus) compared to their food sources, indicating stereoselective biotransformation of these pollutants in that freshwater species (Wong et al., 2004). While congener-specific stereoselective biotransformation of PCB 176 or take up of non-racemic PCB 176 from scavenging on dead marine mammals that fall to the bottom (Jeremiah Young, personal observation) may explain the observed enrichment in Greenland halibut, these reasons do not fully explain the racemic atropisomer composition of other, more easily biodegradable congeners (e.g., PCBs 91 and 95).
3.2.4. Arctic char

Arctic char from Cumberland Sound showed significant PCB atropisomer enrichment, with EFs of PCBs 95 and 176 of 0.423 ± 0.026 and 0.459 (one measurement), respectively (Fig. 4). Arctic char exposed intraperitoneally in the laboratory had racemic proportions of PCB 95, that suggested no stereoselective biotransformation capacity of this congener in this species (Wiberg et al., 2006). Thus, the non-racemic chiral PCBs in wild char likely came from stereoselective bioaccumulation from Cumberland Sound or from sediment, which were not measured in the present study. Alternatively, different exposure pathways (oral versus intraperitoneal injection) of chiral PCBs may result in different atropisomer signatures in organisms (Kania-Korwel et al., 2007). Thus, comparison of chiral PCB EFs in wild char with previous laboratory exposures (Wiberg et al., 2006) must be considered cautiously, especially since similar atropisomer enrichment patterns (i.e., with the same enantiomer enrichment) were observed previously in lake trout (Salvelinus namaycush; EF of PCB 95 and 176 were about 0.36 and 0.34 respectively), a salmonid species which apparently does biotransform PCBs (Wong et al., 2004).

3.2.5. Marine mammals

Marine mammals in this study had species- and congener-specific PCB atropisomer signatures similar to those documented previously in many aquatic species (Hoekstra et al., 2002; Warner et al., 2005; Ross et al., 2011) (Fig. 4). This is the first report of stereoselective PCB enrichment in harp seals, narwhals and beluga whales. The EFs of PCB 95 in harp seals and ringed seals were 0.581 ± 0.013 and 0.751 ± 0.076, respectively. No significant atropisomer enrichment was observed for PCB 149 in these species. Atropisomer signatures of these two congeners in Cumberland Sound ringed seals were consistent with those measured in ringed seals captured a decade ago in the NOW (0.849 ± 0.072 for PCB 95, 0.478 ± 0.045 for PCB 149, mean ± standard deviation; Warner et al., 2005). The racemic atropisomer distributions of chiral PCBs in their potential prey such as herring, capelin (from the present study).
study) and Arctic cod (Warner et al., 2005) indicate that biotransformation is likely the major reason for non-racemic chiral signatures in the seals. Indeed, CYP2B-like enzymes, which biotransform chiral PCBs stereoselectively (Warner et al., 2009; Lu and Wong, 2011), were suggested to be involved in biotransformation processes of xenobiotics in harp and ringed seals (Wolkers et al., 1998, 1999; Routti et al., 2008).

The EFs of PCBs 91, 136, 149 and 174 in beluga whales were $0.409 \pm 0.010$, $0.423 \pm 0.011$, $0.420 \pm 0.009$ and $0.552 \pm 0.004$, respectively, with no significant atropisomer enrichment observed for PCBs 95 ($0.497 \pm 0.012$) and 176 ($0.486$) (Fig. 4). In narwhals, significant non-racemic atropisomer distributions were detected for PCBs 91 ($0.375 \pm 0.010$), 95 ($0.464 \pm 0.004$) and 149 ($0.467 \pm 0.006$). Bowhead whales (Balaena mysticetus) in the Bering–Chukchi–Beaufort Sea showed similar EF patterns for PCBs 91 ($0.456 \pm 0.021$) in blubber compared with beluga whales and narwhals in the present study (Hoekstra et al., 2002). However, no significant atropisomer enrichments were observed for PCBs 95, 136, 149 and 174 in those bowhead whales (Hoekstra et al., 2002). This is consistent with the fact that bowhead whales are baleen whales that filter-feed on plankton, which usually contain racemic chiral PCBs. Therefore, diet, combined with poor biotransformation activity, probably explains the EFs of bowhead whales (Hoekstra et al., 2002). In contrast, belugas and narwhals are toothed whales and mainly feed on fish. Thus, different diet compositions, and possibly also different biotransformation abilities, among these whales may explain the different EFs of chiral PCBs in their tissues.

The enrichment of (−)-PCB 149 in belugas and narwhals from Cumberland Sound was in agreement with values measured for dolphins and larger whales collected in the Mediterranean Sea (Reich et al., 1999). Although the expression of CYP2B-like activity is low in belugas (McKinney et al., 2004), in vitro metabolism of certain PCBs (McKinney et al., 2006a) and formation of hydroxylated–PCB (OH–PCB) and methylsulfonyl–PCB (MeSO$_2$–PCB) metabolites have been observed in beluga liver subcellular fractions (McKinney et al., 2006b), indicating that stereoselective biotransformation could be the source of non-racemic chiral PCBs EFs observed in this species.

### 3.3. Temporal and spatial trends of PCB chiral signatures in Greenland sharks

Non-racemic chiral signatures of PCBs were found in Greenland sharks, but varied based on sampling time, tissues examined and locations of collections (Figs. 4 and 5). A significant decrease was observed for PCB 91 in Cumberland Sound Greenland sharks between 1999 and 2008, with EFs changing from $0.447 \pm 0.024$ to $0.298 \pm 0.015$ ($p = 0.007$) (Fig. 5A). The EFs of PCB 91 were similar in the sharks sampled from Cumberland Sound and Svalbard in 2008 (Fig. 5A). Similar to PCB 91, for PCB 95, no significant changes of EFs...
in Cumberland Sound Greenland sharks were observed between the two time periods (Fig. 5B). However, a different enrichment pattern of PCB 95 was detected in the liver of Greenland sharks from Svalbard compared to the samples from Cumberland Sound (Fig. 5B). There was no significant temporal or spatial shift in EFs of PCBs 136 and 149 in Greenland sharks (Fig. 5C and D), suggesting that the chiral signatures of some PCB congeners did not change significantly in Greenland sharks between 1998 and 2008 in Cumberland Sound; this is similar to the situation seen in Cumberland Sound ringed seals (Vetter et al., 2001).

A review of contaminants in Greenland sharks suggested that they have very limited biotransformation capacities for organochlorine contaminants (MacNeil et al., 2012). Thus, chiral signatures of contaminants in Greenland sharks are likely driven by values in their prey. Greenland sharks are apex predators in both pelagic and benthic food webs where they exist, that opportunistically consume invertebrates, fish and marine mammals (MacNeil et al., 2012). Since invertebrates (Fig. 4) and forage fishes (e.g., herring, capelin and Arctic cod) (Warner et al., 2005) in the Arctic usually contain racemic atropisomers, marine mammals are likely the major source of non-racemic chiral PCBs for Greenland sharks. Indeed, ringed seals and whales (e.g., minke whale, Balaenoptera acutorostrata, beluga and narwhal) have been found in the stomachs and gastrointestinal tracts of Greenland sharks, indicating consumption of these mammals by the sharks either by scavenging or active feeding (Leclerc et al., 2011, 2012; MacNeil et al., 2012). The chiral signatures of PCB 91 in Greenland shark were consistent with the patterns in ringed seal (Warner et al., 2005), beluga and narwhal (Fig. 4), indicating the possible influence of atropisomer signatures of these prey on the shark signatures.

One possible explanation for temporal variation in the chiral signatures of Greenland sharks might be related to changes in their feeding ecology towards consumption of more marine mammals, which may be driven by changes in prey species abundance, distribution or accessibility as a consequence of environmental changes (e.g., climate change). The increased consumption of marine mammals could affect the sharks’ overall contamination levels (McKinney et al., 2012; Molde et al., 2013) and perhaps chiral signatures of some pollutants in Greenland sharks. Climate change-related temperature increases, sea ice declines and other concomitant habitat changes are having important impacts on arctic marine mammals (Kovacs and Lydersen, 2008). For example, decreases in sea ice reduce available habitat for lair construction and haulout places for ringed seals, resulting in less protection against predators as well as them being forced to spend more time in the water (Kovacs and Lydersen, 2008; Kovacs et al., 2011). Ice-associated whales, such as belugas and narwhals, also use sea ice to avoid predators (e.g., killer whales Orca orcinus etc.) (Kovacs and Lydersen, 2008), though fish predators such as Greenland sharks are not likely to be deterred by ice cover. Bite wounds attributed to Greenland sharks have been observed recently, suggesting that sharks actively prey on live whales (MacNeil et al., 2012). Greenland shark feeding on dead narwhals has also been observed in the Canadian Arctic (MacNeil et al., 2012). Temporal changes in the consumption of marine mammals by Greenland sharks is also supported by the observation that the percentage of marine mammal tissues in Cumberland Sound Greenland sharks’ stomachs increased from 14% to 33% during the period from 1999 to 2008 (Fisk et al., 2002; McMeans et al., 2012). The temporal shift of PCB 91 chiral signatures in Cumberland Sound Greenland sharks was consistent with this increased consumption of marine mammals.

The different atropisomer distribution of PCB 95 in Greenland sharks between Cumberland Sound and Svalbard may be due to different feeding regimes in these two areas (Fisk et al., 2002; Leclerc et al., 2011, 2012; McMeans et al., 2013; Molde et al., 2013). The chiral signature of PCB 95 in Cumberland Sound Greenland sharks was consistent with the signature in harp seals and ringed seals (Fig. 4). The concentrations and atropisomer
compositions of chiral PCBs in the marine mammals from Svalbard were not explored due to lack of samples. However, dietary composition differences of Greenland sharks from Cumberland Sound and Svalbard have been documented. Greenland sharks from both Svalbard (42.3%, sampled in 2008, Leclerc et al., 2012) and Cumberland Sound (14%, sampled in 1999, Fisk et al., 2002; 33%, sampled in 2008, McMeans et al., 2012) can have a high percentage of marine mammal tissues in their stomachs, and fatty acid data suggested a higher consumption of both seals and gadoid fishes by Greenland shark from Svalbard (sampled in June 2008, 2009) compared to Cumberland Sound (sampled in April 2008, McMeans et al., 2013). Based on the high diversity of known prey items (Fisk et al., 2002; Leclerc et al., 2012) and the opportunistic nature of Greenland shark feeding behavior (MacNeil et al., 2012), the precise makeup of this species’ diet (e.g., extent of marine mammal consumption) is likely variable in space and time. The observation that PCB 95 was consistent through time (in Cumberland Sound) but different between habitats, while PCB 91 exhibited the opposite trend, further suggests that the diet composition of Greenland sharks varies both spatially and temporally. Unfortunately, it would be difficult to provide more conclusive evidence of this variation using existing carbon and nitrogen stable isotope data, because the data were calculated and based on different baselines in different locations and from different tissues.

Another factor that undoubtedly affects the feeding ecology of Greenland sharks is human activities. Greenland sharks scavenge floating minke whale blubber left as a by-product of whaling activities near Svalbard (Leclerc et al., 2011). According to the International Whaling Commission, the number of minke whales harvested for commercial purposes increased from 218 in 1995 to 639 in 2005 and is now stable around 500–600 per year (International Whaling Commission, 2013). Marine mammal harvests do also occur in Cumberland Sound, although on a subsistence scale, not a commercial scale. However, these hunts could also provide Greenland sharks with scavenging opportunities, although in subsistence hunting the blubber is usually not discarded, only the entrails. Differences in opportunities to scavenge marine mammals could contribute to altered contaminant levels and chiral signatures in Greenland sharks among Arctic areas. Our results suggest that the enantiomer signatures of chiral contaminants might be a useful tool to trace changes in feeding ecology as a consequence of anthropogenic influences, such as climate changes and whaling. More investigations are needed to fully test these hypotheses. It is alternatively possible that EFs have changed in the food sources of Greenland sharks, resulting in the spatial and temporal EF patterns observed in the sharks. However, our current data do not support this explanation. We cannot fully distinguish among these potential reasons with the current data.

4. Conclusions

Levels of PCB contamination in Cumberland Sound organisms were generally lower than in similar species from other locations in the Arctic. Racemic compositions of chiral PCBs were detected in mixed zooplankton, invertebrates, benthic fishes and pelagic forage fishes, indicating low biotransformation capacities towards PCBs in these organisms (and in their prey). Non-racemic atropisomer enrichment of PCBs in Arctic char might suggest stereoselective bioaccumulation of chiral PCBs in piscivorous fishes. Marine mammals showed species-specific EFs, likely due to a combination of in vivo biotransformation and trophic transfer. The chiral signatures of PCBs 136 and 149 in Greenland sharks did not vary temporally over the period of a decade at one location or spatially across the North Atlantic Arctic. In contrast, the spatiotemporal variation in the atropisomer signatures of PCBs 91 and 95 might indicate differences in the feeding ecology of Greenland sharks over time and between different areas.

Acknowledgments

Funding was provided by the Natural Sciences and Engineering Research Council of Canada (Discovery Grants to CSW and ATF); the Canada Research Chairs Program (to CSW and ATF); Government of Canada Program for International Polar Year 2007/2008 (to ATF, grant IPY C144); the Research Council of Norway (Grant number 184644) and the Norwegian Polar Institute (to KMK, CL and ATF); and a Chinese Government Award for Outstanding Self-Financed Students Abroad from the China Scholarship Council (to ZL). We acknowledge Goldie S. Silva for providing some EF data from Greenland halibut and Arctic char, and thank Jennifer Low for helpful technical assistance.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.12.005.

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