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Bioaccumulation and Trophic Magnification of Short- and Medium-Chain Chlorinated Paraffins in Food Webs from Lake Ontario and Lake Michigan

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Chlorinated paraffins (CPs) are complex mixtures of chlorinated alkanes used in a myriad of industrial applications as flame retardant plasticizers and additives. In this study, the distribution and bioaccumulation/biomagnification of short-chain CPs (C_{10}–C_{13}, SCCPs) and medium-chain CPs (C_{14}–C_{17}, MCCPs) were investigated in samples collected between 1999 and 2004 from Lake Ontario and northern Lake Michigan. Total (Σ) SCCPs and ΣMCCPs concentrations in water from Lake Ontario were 1190 pg/L and 0.9 pg/L (data from 2004 only), respectively. CPs were also detected in invertebrates and fish from both lakes. SCCP predominated in organisms from Lake Michigan with the highest mean concentrations found in lake trout [*Salvelinus namaycush*, 123 ± 35 ng/g wet weight (ww)]. In Lake Ontario, MCCPs predominated in most species with the highest levels detected in slimy sculpin (*Cottus cognatus*, 108 ng/g ww) and rainbow smelt (*Osmerus mordax*, 109 ng/g ww). Bioaccumulation and biomagnification of CPs was evaluated on an isomer basis (i.e., $C_{10}H_{17}Cl_5$, $C_{10}H_{16}Cl_6$, etc). Log bioaccumulation factors for lake trout (lipid based) ranged from 4.1 to 7.0 for SCCPs and 6.3 to 6.8 for MCCPs. SCCPs and MCCPs were found to biomagnify between prey and predators from both lakes with highest values observed for *Diporeia*-sculpin (Lake Ontario, $C_{15}Cl_9$ = 43; Lake Michigan, $C_{10}Cl_5$ = 26). Trophic magnification factors for the invertebrates–forage fish–lake trout food webs ranged from 0.41 to 2.4 for SCCPs and from 0.06 to 0.36 for MCCPs. Given the prominence of CPs, particularly in lake waters and in lower food web organisms, further investigation is needed to evaluate the magnitude of their distribution and accumulation/magnification in the Great Lakes environment.

Introduction

Chlorinated paraffins (CPs) are industrial chemicals used as flame retardants and additives in metal-working fluids, paints, and sealants as well as plasticizers in plastics such as polyvinyl chloride (PVC). The environmental release of CPs may occur during the production, storage, transportation, and use of CP-based products or during leaching, runoff, or volatilization from landfill, sewage sludge, waste disposal sites, and incineration (*1, 2*).

The chain length of CPs can reach 30 carbons with a chlorine content usually between 30 and 70%. CPs are classified into three categories based on the number of carbons: short-chain CPs (C_{10}–C_{13}, SCCPs), medium-chain CPs (C_{14}–C_{17}, MCCPs), and long-chain CPs (C_{18}–C_{30}). SCCPs have the highest potential for environmental release because of open use (e.g., metal working fluids) and have been shown to have the highest aquatic and mammalian toxicity of all CPs (*2, 3*). SCCPs have been placed on the United States EPA Toxics Release Inventory and are also classified as Priority Toxic Substances by the Canadian Environmental Protection Act (*4*). In the European Union, SCCPs have been listed as priority hazardous substances and uses have been reduced under Directive 2002/45/EC (*5*). SCCPs and MCCPs are high production volume chemicals (*6*) with North American production of about 8 and 18 kt/year, respectively, in the late 1990s (*4*). To date, SCCPs and MCCPs have been reported in air, water, sediment, biota (*2, 7–9*), and human milk (*10*). The presence of CPs in top predators such as seals and whales suggests that bioaccumulation and possibly biomagnification of some CPs is occurring in the environment. SCCPs and MCCPs are hydrophobic chemicals (Log K_{ow} of 5.9–8.1) (*4*) with bioaccumulation potentials that generally increase with chain-length and chlorine content based on experimental exposure of fish (*11*). Dietary bioaccumulation experiments with fish have also suggested that SCCPs and MCCPs with 4–6 chlorines have the greatest potential for biomagnification (*12*). There have been no detailed studies on biomagnification of SCCPs and MCCPs in natural aquatic food webs.

CPs have been detected in Great Lakes biota, water, and sediments (*3, 9, 13*), however, compared to other halogenated organics, the number of studies and the geographical coverage are very limited. In samples from open lake sites, concentrations of SCCPs have generally been found to be in the low ng/g (wet wt) range in lake trout and sediments and thus lower than polychlorinated biphenyls (PCBs) (*2, 6*). However, elevated concentrations of SCCPs have been observed in fish near industrial areas in the Great Lakes (*3, 4, 13, 14*).

The objectives of this study were to analyze a series of SCCPs and MCCPs in aquatic organisms from northern Lake Michigan and Lake Ontario, investigate the chain length and formula group isomer pattern of contamination, and evaluate the bioaccumulation and biomagnification in the benthic and pelagic food webs of the lakes.

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Materials and Methods

Sample Collection. Water (4 m depth) was collected at sites in the western, central, and eastern basins of Lake Ontario in October 2000, June 2002, and July 2004 [Supporting Information (SI) Figure S1] from the Canadian Coast Guard ship Limnos. Water (100 L; prefiltered with 102 μm Nytex netting) was pumped through glass fiber filters (GFF; 0.7 μm) and then through an XAD-2 cartridge (70 g wet resin; 26 cm $\times$ 2.25 cm, Supelco) at 200 mL/min. Three techniques were evaluated: (a) pumping into an onboard holding tank and then through the XAD, (b) direct pumping into an XAD column using a submersible pump and on-board valving system (*15*), and (c) *in situ* collection using an Infiltrex (Axys Instruments, Sidney BC) placed in the water column for 24 h. Technique "a" had been used in previously reported results for Lake Ontario (*2*). XAD columns were prespiked with δ-HCH and PCB 166 to check recoveries. Primary and secondary columns were used for technique "b" to assess CP recovery efficiency. Primary columns were prespiked with PCB 204 (5 ng). Recovery results are provided in SI Table S1.

Net plankton (primarily zooplankton >110 μm), *Mysis* (*Mysis relicta*), slimy sculpin (*Cottus cognatus*), alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*), and lake trout (*Salvelinus namaycush*) were collected in northern Lake Michigan (near Charlevoix, MI) and in western Lake Ontario in July 2001 using the Canadian Coast Guard vessel Shark. Additional plankton samples were collected in Lake Ontario in July 2004 from the CCS Limnos using a 110 μm mesh net at sites for water samples (SI Figure S1). *Diporeia* were collected in northern Lake Michigan in 1999 (near Manistique, MI) and in Lake Ontario in July 2001 from surficial sediments using an epibenthic sled.

Extraction. Whole invertebrates and fish homogenates were analyzed for SCCPs and MCCPs and a subset were analyzed for PCBs. All forage fish were processed as composites of 5−10 similar-sized whole fish while lake trout were processed individually. Processing included recording of standard biological data, sample homogenization in a food grinder (Hobart Manufacturing Co., Troy, OH), and gravimetric determination of lipid content. Individual lake trout were aged using a combination of coded wire tags, fin clips, or scales. Subsamples of all biota were analyzed for nitrogen and carbon stable isotope ratios (δ^{15}N; δ^{13}C) by the Environment Canada, Stable Isotope Laboratory (Saskatoon, SK). All samples were stored at −80 C prior to analyses.

Internal recovery standards of 1,3,5-tribromobenzene, 1,2,4,5-tetra-bromobenzene, δ-HCH, PCB-30, and PCB-204 were added prior to extraction to monitor method performance. Homogenized tissue was mixed with precleaned sodium sulfate (450 C for 4 h) to form a dry powder and Soxhlet extracted for 6 h with dichloromethane (DCM). The DCM solution was reduced in volume to 2 mL and the extract was applied to the top of a gel permeation column (GPC; Biobeads SX3, Bio-Rad Laboratories, Hercules, CA) to remove lipids using hexane/DCM (1:1) as elution solvent. The lipid content was determined gravimetrically on the first 150 mL of GPC eluate by evaporating off the solvent.

For water samples, XAD-2 resin cartridges were eluted with methanol and DCM as described by Muir et al. (*16*). The extraction of the XAD columns was conducted in a dedicated clean-room laboratory (carbon and HEPA filters, positive pressure). Field and laboratory blanks consisting of XAD-2 resin cartridges for each sampling location were extracted and analyzed concurrently.

The GPC eluates and XAD extracts were reduced to a small volume, quantitatively exchanged into hexane, and chromatographed on activated silica gel (*16*). Silica columns were eluted with hexane (Fraction A) and hexane/DCM (1:1) (Fraction B) (*16*). CPs were quantitatively eluted in Fraction B and PCBs in Fraction A. PCBs (114 congeners including coeluters) were quantified by GC-ECD using external standard calibration while CPs were quantified by GC-high resolution (HR) mass spectrometry (MS).

Prior to instrumental analysis, extracts were reduced to an appropriate final volume under a gentle nitrogen stream and $^{13}C_8$-mirex was added as an internal standard. All food web samples were analyzed for both SCCPs and MCCPs by GC-HRMS (electron capture negative ion mode; ECNI) (*17*). Specific m/z values corresponding to the molecular formulas of $[M - Cl]^-$ ions of all major C_{10}−C_{13} and C_{14}−C_{17} formula groups were monitored concurrently. Corrections were made for the fractional abundance of specific m/z value and number of Cl atoms. Quantitation was performed by comparing the response for specific m/z values in the sample to that of an external standard. The external standard was a mixture of two commercial mixtures (Dover Chemical Corp., Dover, OH): C_{10}−C_{13} with 60% Cl and C_{14}−C_{17} with 53% Cl.

Samples of water and zooplankton collected in 2004 were analyzed by GC-HRMS with metastable atom bombardment (MAB) ionization (*18*) using the same SCCP and MCCP standards used for the analysis by ECNI-MS. The two most intense ions in the [M – HCl]+ cluster were monitored. A quality assurance section can be found in the Supporting Information.

Biomagnification and Bioaccumulation Factor Calculations. Trophic magnification factors (TMFs) were determined based on the relationship between δ^{15}N and contaminant concentration (*19*). The bioaccumulation factor (BAF) and the biomagnification factor (BMF) were also determined as BAF = ([predator]/[water (filtered)]) and BMF = ([predator]/[prey]) where the concentrations in predators and preys are on a lipid basis.

Results and Discussion

Chlorinated Paraffins in Water. Despite different sampling techniques, different years, and different analytical methods used for the detection of CPs, total SCCP concentrations were in a similar range (606−1935 pg/L) (SI Table S1). SCCPs containing 12 carbons were the predominant chain length groups detected in water samples from Lake Ontario with concentrations averaging (±SD) 740 ± 364 pg/L in 2004. SCCPs were found at much higher concentrations (ΣSCCPs = 1080 ± 500 pg/L) compared to MCCPs (ΣMCCPs = 0.9 ± 1.2 pg/L) in 2004 samples. The only exception is one result for the west Lake Ontario site in 2002 which had ΣMCCP = 47 pg/L. This value is an outlier compared to all other results for MCCPs in water and is possibly related to the first use of the tank system during the cruise. This effect was not noticed using the direct pumping or Infiltrex "in situ" pump methods but it does illustrate the potential for field contamination. Over the 3 sampling periods October 2000, June 2002, and July 2004 concentrations of ΣSCCPs ranged from 1039 to 1935 pg/L at the West Lake Ontario sites and from 606 to 1488 pg/L in the central basin site. The higher ΣSCCP concentrations in western Lake Ontario probably reflect closer proximity to urban areas, e.g., greater Toronto area (population ~5 M) compared to the central basin. The ΣSCCP concentrations detected in this study are lower than levels reported for water samples collected in the St. Lawrence river (3.5−21.1 ng/L) (*18*) and rivers near Barcelona, Spain (SCCPs <20–1100 ng/L) (*20*). High concentrations of SCCPs and MCCPs have also been reported for industrialized areas of the UK (<0.1–1.7 μg/L) (*21*). PCB concentrations in the Lake Ontario water samples averaged 119 ± 31 pg/L in the 2004 samples. Thus, on average, ΣSCCPs were about 8-fold higher than PCBs in western and central Lake Ontario (SI Table S1).

Chlorinated Paraffins in Whole Organisms. In Lake Michigan, all samples analyzed for C_{10} to C_{17} had higher levels of ΣSCCPs compared to MCCPs (Figure 1; Table 1). The lowest mean concentration of the ΣSCCPs (7.5 ± 3.9 ng/g ww) was

FIGURE 1. Total SCCP and MCCP concentrations in whole organisms from Lake Michigan and Lake Ontario. MCCPs were not detected in plankton, *Diporeia*, *Mysis*, and rainbow smelt from Lake Michigan, and plankton and *Mysis* samples from Lake Ontario.

detected in *Mysis* and the highest SCCP levels were found in lake trout homogenates (123 ± 35 ng/g ww). ΣMCCP concentrations were the highest in alewife and lake trout (5.6 ng/g ww and 5.6 ± 4.8 ng/g ww, respectively). No correlations were found between the weight and length of lake trout and ΣSCCP or ΣMCCP.

The pattern of CP contamination in organisms from Lake Ontario was somewhat different from that in Lake Michigan. Concentrations of ΣSCCPs were higher in plankton, *Mysis*, and lake trout compared to ΣMCCPs (Figure 1; Table 1). However, ΣMCCPs predominated in alewife, sculpin, and rainbow smelt compared to ΣSCCPs. The lowest and highest ΣSCCP concentrations were detected in *Mysis* (2.8 ± 2.3 ng/g ww) and lake trout (34 ± 37 ng/g ww), respectively. As for MCCPs, concentrations were nondetectable for plankton and *Mysis*; average concentrations of 108 and 109 ng/g ww were found in homogenates of sculpin and rainbow smelt, respectively.

The range of ΣSCCPs (2.8−123 ng/g ww or 172−1030 ng/g lw) and ΣMCCPs (nd−109 ng/g ww or nd−2218 ng/g lw) concentrations reported here for whole fish from Lake Michigan and Lake Ontario overlap the concentrations reported for liver of several species of fish from the Baltic and North Seas (SCCPs: 19−286 ng/g ww; MCCPs: <10−260 ng/g ww) (*7*) and muscle of whitefish, Arctic char, and herring from Sweden (range of 570–1600 ng/g lw) (*22*). The concentrations are, however, lower in whole fish from this study compared to SCCPs in muscle of yellow perch (1200 ng/g ww) and carp (300 ng/g ww) from the Detroit River, Michigan (*14*) as well as whole carp from Hamilton Harbour, Ontario, Canada (2630 ± 2560 ng/g ww) (*3*). CP concentrations reported for freshwater fish (tissue not specified) from industrial areas of the UK (<100–5200 ng/g ww) are among the highest reported in the literature (*21*). Mean concentrations of ΣSCCPs in lake trout (34 ± 37 ng/g ww) were slightly lower than our previous measurements for whole lake trout collected at two different sites from western Lake Ontario (59 ± 51 and 73 ± 47 ng/g ww) (*3*).

The relatively high concentrations of SCCPs and MCCPs detected in deepwater and slimy sculpin from Lake Michigan and Ontario, respectively, suggest that sediment may be a source of contamination for these bottom-dwelling fish.

TABLE 1. Sample Size, Percentage (%) of Lipid, δ^{15}N and SCCP and MCCP Concentration (ng/g ww) in Whole Organisms and Water (pg/L) Collected from Western Lake Ontario and Northern Lake Michigan

species	*n*	% lipid	δ^{15}N (‰)	total C_{10}	total C_{11}	total C_{12}	total C_{13}	ΣSCCPs	total C_{14}	total C_{15}	total C_{16}	total C_{17}	ΣMCCPs
Lake Michigan													
plankton	3	1.5 ± 0.073	7.3 ± 0.22	4.9 ± 3.5	8.6 ± 5.9	8.3 ± 5.7	1.3 ± 0.86	23 ± 16	nd[a]	nd	nd	nd	nd
Diporeia	3	4.0 ± 0.66	7.8	12 ± 9.6	5.5 ± 4.6	5.7 ± 4.7	0.26 ± 0.23	24 ± 19	nd	nd	nd	nd	nd
Mysis	3	3.7 ± 0.70	9.3 ± 0.72	2.9 ± 1.5	2.4 ± 1.2	2.1 ± 1.1	0.20 ± 0.08	7.5 ± 3.9	nd	nd	nd	nd	nd
alewife	2	3.7	9.9	9.7	12	15	0.62	37	5.1	0.50	nd	nd	5.6
rainbow smelt	2	4.7	11	5.4	5.6	5.2	0.36	17	nd	nd	nd	nd	nd
sculpin	2	9.9	13	24	23	21	1.1	69	2.4	0.46	nd	nd	2.9
lake trout	7	20 ± 3.4	14 ± 0.53	51 ± 15	30 ± 8.7	40 ± 11	1.6 ± 0.45	123 ± 35	4.6 ± 3.9	1.02 ± 0.82	nd	nd	5.6 ± 4.8
Lake Ontario													
water[b]	10	–	–	110 ± 70	380 ± 200	660 ± 300	41 ± 34	1190 ± 430	0.80 ± 1.0	0.10 ± 0.20	nd	nd	0.90 ± 1.2
plankton	3	1.1 ± 0.21	8.5 ± 0.17	0.21 ± 0.05	0.42 ± 0.13	0.34 ± 0.13	0.05 ± 0.02	1.02 ± 0.33	nd	nd	nd	nd	nd
Diporeia	3	2.9 ± 0.90	11 ± 0.40	0.99 ± 0.87	2.3 ± 2.1	2.3 ± 2.2	0.31 ± 0.29	5.9 ± 5.5	2.8 ± 4.8	1.2 ± 1.9	0.22 ± 0.30	nd	4.2 ± 7
Mysis	3	9.2 ± 1.5	13 ± 0.88	0.40 ± 0.52	0.93 ± 1.3	0.91 ± 1.31	0.12 ± 0.17	2.4 ± 3.3	nd	nd	nd	nd	nd
alewife	2	2.7	13	0.90	1.7	1.9	0.17	4.6	8	20	6.0	0.3	35
rainbow smelt	2	5.5	15	3.0	8.4	7.03	0.68	19	24	64	19	1.6	109
sculpin	2	4.8	16	3.8	11	8.6	1.04	25	38	54	14	1.1	108
lake trout	7	16 ± 2.8	18 ± 0.81	3.4 ± 3.7	13 ± 14	16 ± 18	1.9 ± 2	34 ± 37	17 ± 19	6.2 ± 6.9	0.48 ± 0.54	nd	24 ± 26

[a] nd = <MDL = 0.1 ng/g ww for most organisms and <1 pg/L for water. [b] Average for MCCP based on 2004 only. See SI Table S1 for the full water data set.

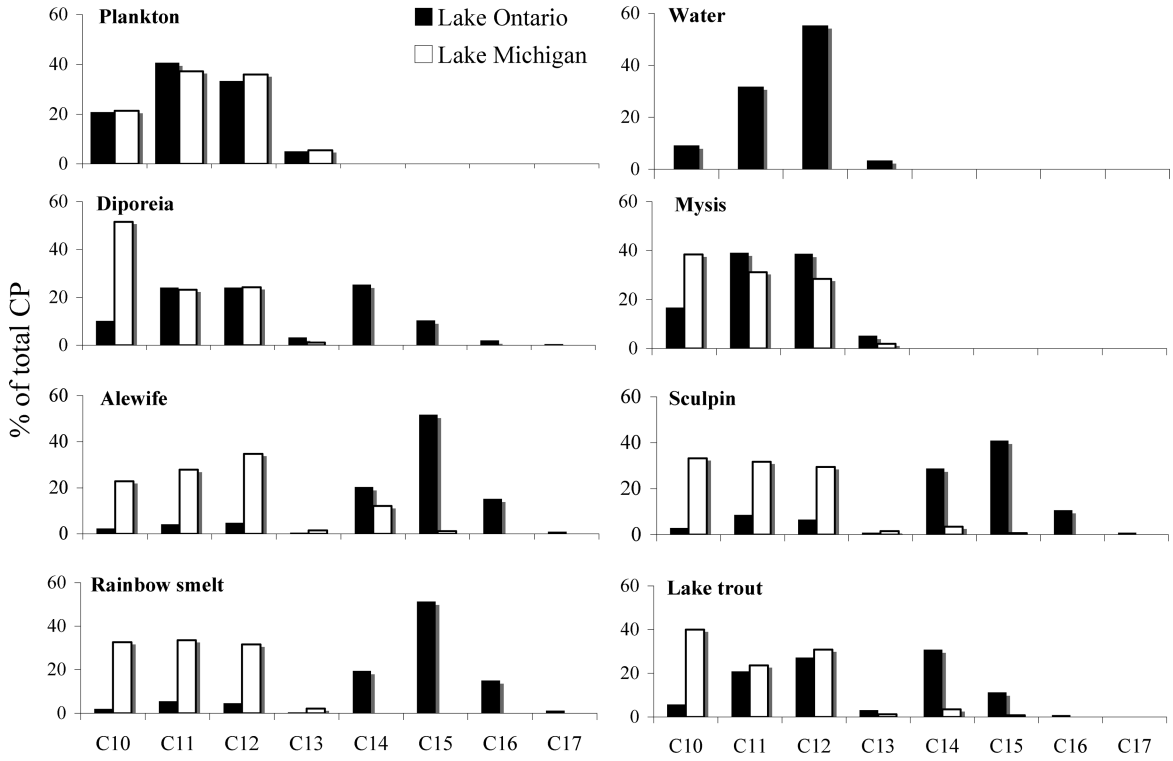

FIGURE 2. Percentage (%) of CP chain length groups in water (2004), plankton, *Mysis*, *Diporeia*, alewife, rainbow smelt, slimy sculpin, and lake trout from northern Lake Michigan and western Lake Ontario. See Figures S2 and S3 for proportions of specific compounds included in each chain length group.

SCCPs have been previously detected in sediment from Lake Ontario (*9*). The relative contribution of carbon chain groups to total of SCCPs in sculpin (ΣC_{10} = 16%, ΣC_{11} = 45%, ΣC_{12} = 35%, ΣC_{13} = 4) is very similar in proportion to results reported for sediment samples collected in Lake Ontario [ΣC_{10} = 24%, ΣC_{11} = 35%, ΣC_{12} = 34%, ΣC_{13} = 6.6% (*9*)] supporting the hypothesis that sediment is a source of CP contamination in sculpin.

Compared to other persistent organic pollutants, concentrations of SCCPs and MCCPs in plankton, *Diporeia*, and *Mysis* from Lake Ontario and *Diporeia* and *Mysis* from Lake Michigan were much lower than ΣPCB and ΣDDT levels in the same samples (SI Table S2). Previous studies have shown that ΣPCB and ΣDDT in lake trout homogenates from Lake Ontario were higher than SCCPs in the same samples (*3*). These results are consistent with the observation that the half-lives of short-chain and highly chlorinated CPs in fish are generally shorter than those for PCBs when studied under identical conditions (*12*).

Chain Length Group Pattern. SCCPs with 10 to 12 carbon atoms were dominant at both locations with proportions varying between 20 and 50% of the ΣSCCP concentrations; proportions of C_{13} were <6% of the ΣSCCPs in all species (Figure 2). MCCPs with 14 and 15 carbons were frequently observed in organisms from Lake Ontario, i.e., the C_{14} group was predominant in *Diporeia* and lake trout and C_{15} was the most abundant MCCP group in alewife, sculpin, and rainbow smelt from this location. The pattern of CP contamination in fish from lakes Michigan and Ontario is similar to the general observations made in fish livers from the Baltic and North Seas where C_{11} and C_{12} have been found to be abundant (*7*). Tomy et al. reported high proportions of C_{11} and C_{12} SCCPs in Detroit River fish with smaller quantities of C_{10} and C_{13} compounds (*14*). Coelhan et al. have reported a dominance of C_{10} in 5 out of the 8 fish species from the market examined for SCCPs (*8*). The profile of MCCPs reported in lake trout from Lake Ontario in this study is very similar to the contamination pattern detected in fish from the Detroit River where a predominance of C_{14} compounds was observed as well as very low concentrations of C_{16}–C_{17} MCCPs (*17*).

However, in contrast to the results from Tomy et al. (*17*), C_{15} MCCPs were detected in higher concentrations in organisms from this study.

Formula Group Isomer Patterns. Short-chain formula group isomers were dominant in *Diporeia* ($C_{10}Cl_7$: 20% of the total CPs), sculpin ($C_{10}Cl_6$: 15%), lake trout ($C_{10}Cl_7$: 15%), rainbow smelt ($C_{10}Cl_6$: 17%), and alewife ($C_{12}Cl_6$: 15%) from Lake Michigan (SI Figure S2). In organisms from Lake Ontario, longer-chain CPs constituted the majority of compounds detected with some isomers representing up to 29% of the total concentrations of CPs (*Diporeia*, $C_{14}Cl_8$: 8%; alewife and rainbow smelt, $C_{15}Cl_8$: 29%; sculpin, $C_{15}Cl_8$: 22%; lake trout, $C_{14}Cl_8$: 10%) (SI Figure S3). While alewife, sculpin and rainbow smelt had similar CP formula group isomer patterns, *Diporeia* showed greater similarity to the combined analytical stan-

TABLE 2. Lipid-Normalized Bioaccumulation Factors (BAFs) on a Log Basis for SCCP/MCCPs in Lake Ontario (See Table S3 for Formula Group Specific BAFs)

	log bioaccumulation factors (BAFs)[a]				
Lake Ontario	water[b]–plankton	water–alewife	water–sculpin	water–rainbow smelt	water–lake trout
C_{10}	5.7	6.4	7.0	6.7	6.4
C_{11}	5.2	5.6	6.4	6.2	6.0
C_{12}	4.7	5.0	5.4	5.2	5.2
C_{13}	5.4	5.6	5.8	5.8	5.4
C_{14}	6.2	7.0	7.4	7.4	6.8
C_{15}	6.6	6.8	7.2	7.1	6.5
ΣSCCPs	5.4	6.0	6.6	6.3	6.1
ΣMCCPs	6.5	6.9	7.3	7.2	6.6

[a] BAFs calculated based on the 2002 and 2004 water data. BAFs for C_{16} and C_{17} could not be calculated due to nondetectable values. [b] Based on concentrations expressed in pg/L.

TABLE 3a. Lipid Normalized Biomagnification Factors (BMFs) for SCCP/MCCPs in the Lake Ontario and Lake Michigan Food Webs (See Table S3 for Formula Group Specific BMFs)

	Lake Ontario				Lake Michigan			
	lake trout−alewife	lake trout−rainbow smelt	lake trout−sculpin	sculpin−*Diporeia*[a]	lake trout−alewife	lake trout−rainbow smelt	lake trout−sculpin	sculpin−*Diporeia*
C_{10}[b]	1.3 ± 1.1	0.63 ± 0.30	0.50 ± 0.39	2.8 ± 2.5	0.98 ± 0.53	3.3 ± 2.7	1.3 ± 0.96	6.6 ± 11
C_{11}	1.6 ± 2.7	0.84 ± 0.74	0.44 ± 0.16	4.7 ± 5.9	0.60 ± 0.34	2.4 ± 1.8	0.80 ± 0.40	2.8 ± 1.8
C_{12}	4.3 ± 11	1.5 ± 6.7	0.66 ± 5.6	4.9 ± 5.5	0.60 ± 0.15	2.2 ± 0.5	1.0 ± 0.16	2.5 ± 1.1
C_{13}	3.5 ± 4.0	1.5 ± 1.6	0.58 ± 0.65	1.8 ± 0.55	0.47 ± 0.020	1.1 ± 0.064	0.70 ± 0.03	1.4 ± 0.61
ΣSCCPs	2.5 ± 2.7	1.04 ± 0.81	0.54 ± 0.24	3.6 ± 4.2	0.68 ± 0.37	2.4 ± 1.8	0.97 ± 0.55	3.6 ± 5.9
C_{14}	0.52 ± 0.24	0.31 ± 0.087	0.21 ± 0.10	2.7 ± 1.7	0.17 ± 0.028	-[c]	0.9 ± 0.20	1.0 ± 0.7
C_{15}	0.21 ± 0.21	0.11 ± 0.15	0.098 ± 0.095	10 ± 8.6	0.38[d]	-	1.0[d]	0.56[d]
C_{16}	0.048 ± 0.098	0.010 ± 0.018	0.031 ± 0.063	14 ± 8.9	-	-	-	-
ΣMCCPs	0.25 ± 0.26	0.14 ± 0.16	0.11 ± 0.11	8.7 ± 7.7	0.22 ± 0.10	-	0.94 ± 0.17	0.88 ± 0.71

[a] The BMF calculations for MCCPs in *Diporeia* from lake Ontario were based on the detectable concentrations of one sample. [b] Mean for each chain length group. [c] BMF could not be calculated because of nondetected values. [d] Only two isomers included in the mean value.

dards (SI Figure S4). The pattern of CP contamination in lake trout from Lake Ontario differed from that of forage fish with much lower proportions of C_{15} and C_{16} MCCPs.

Bioaccumulation Factors (BAFs). Bioaccumulation factors were calculated in Lake Ontario for SCCP/MCCP isomers that were detected in water and organism samples. The calculation was based on the 2002 and 2004 water data from Lake Ontario for which detailed isomeric results were available (See Table S1 for sampling method and analytical technique). BAFs in lake trout from Lake Ontario varied between (on a log basis) 4.6 and 7.0 for C_{10}, 4.1 and 6.5 for C_{11}, and 5.0 to 5.4 for C_{12} formula group isomers (see Table 2 for mean concentration by formula groups and SI Table S3A for Log BAFs of specific isomers). The BAF could be calculated for one C_{13} isomer ($C_{13}Cl_7$, Log BAF = 5.4), one C_{14} isomer ($C_{14}Cl_6$, Log BAF = 6.8), and two C_{15} (namely $C_{15}Cl_5$ and $C_{15}Cl_6$, Log BAF = 6.6 and 6.3, respectively) (Table 2, SI Table S3A). Similar results were observed for other fish species. The results indicated a general increase in BAFs with chlorination for C_{10} and C_{11} compounds. The highest BAFs for C_{10}−C_{15} SCCP/MCCPs were found in sculpin (up to 7.5 for $C_{10}Cl_8$) which may reflect their exposure to SCCP/MCCPs in sediment via consumption of *Diporeia* and other benthic organisms. Plankton had Log BAFs ranging from 4.5 for $C_{10}Cl_5$ to 6.8 for $C_{15}Cl_5$. The Log BAF values for the C_{14}−C_{17} MCCPs were generally higher than the log K_{ow} values for these chain length groups (*4*) (SI Table S4) which suggests that SCCPs in plankton are not at equilibrium with water. This disequilibrium may be due to our collection of a mixed group of planktonic organisms including some phytoplankton with a 110 um net, rapid growth rates, and overestimation of the dissolved phase (*23*).

The observed BAFs for lake trout were compared with predictions for salmonids using the Gobas food web model which is based on the Lake Ontario aquatic food web (*24*). Water concentrations (average for 2004) of individual C_{10}−C_{17}-CPs were used as inputs to the model along with sediment concentrations for SCCPs from Marvin et al. (*9*) and estimated log K_{ow} values (*4*). Because sediment concentrations of MCCPs were not available, we initially used lake-wide averages for each chain length group from Marvin et al. (*9*) and then adjusted iteratively. Further details are provided in SI Table S4. The model tended to overestimate concentrations of SCCP/MCCPs in fish, particularly in lake trout (SI Figure S5). Closest agreement between the model predictions and observations was obtained for C_{14} and C_{15} MCCP isomers. Overall model performance was reasonably good for invertebrates and forage fish considering that default values were used including the assumption of no biotransformation of CPs.

TABLE 3b. Lipid Normalized Trophic Magnification Factors (TMFs) for SCCP/MCCPs in the Lake Ontario and Lake Michigan Food Webs (See Table S3 for Formula Group Specific TMFs)

	Lake Ontario	Lake Michigan
C_{10}[a]	0.97 ± 0.39	1.3 ± 0.27
C_{11}	0.90 ± 0.44	1.3 ± 0.75
C_{12}	1.0 ± 0.20	1.3 ± 0.35
C_{13}	1.1 ± 0.27	0.63 ± 0.23
ΣSCCPs	0.97 ± 0.33	1.2 ± 0.51
C_{14}	0.29 ± 0.05	-[b]
C_{15}	0.18 ± 0.09	-
C_{16}	0.14[c]	-
ΣMCCPs	0.22 ± 0.10	-

[a] Mean for each chain length group. [b] TMF could not be calculated due to nondetected values in numerous species. [c] Two isomers detected.

Biomagnification and Trophic Magnification Factors (BMFs and TMFs). The evaluation of BMFs species for several SCCP isomers containing 10−13 carbons showed biomagnification of up to 10-fold from alewife to lake trout ($C_{12}Cl_9$), up to 3-fold from rainbow smelt to lake trout ($C_{12}Cl_9$), and up to 23 times from *Diporeia* to sculpin ($C_{12}Cl_8$) in Lake Ontario (Table 3a, SI Table S3B). SCCP concentrations also biomagnified between the same species in Lake Michigan with the highest BMFs reported for Sculpin−*Diporeia* ($C_{10}Cl_5$ = 26.4). The BMFs for a great majority of SCCPs and MCCPs studied were above 1 between *Diporeia* and sculpin in both lakes; MCCP results for other species were generally below 1 except for $C_{14}Cl_7$, $C_{14}Cl_9$, and $C_{15}Cl_5$ from sculpin to lake trout in Lake Michigan (SI Table S3B). Some BMFs could not be calculated due to nondetect values. The BMFs reported in this study corroborate the dietary bioaccumulation of CPs previously reported in juvenile rainbow trout; however, the association between BMFs and carbon-chain length observed in these experimental studies was not clearly observed here (*11, 12*).

These results suggest that SCCP/MCCP concentrations in biota could increase through multiple trophic levels in aquatic food webs. To investigate this hypothesis, TMFs were evaluated based on the regressions between log concentrations of CP (on a lipid weight basis) and trophic levels of the organisms (derived from $\delta^{15}N$ (*19*)). TMFs ranged between 0.47 and 1.5 for SCCPs (17 isomers analyzed individually) and 0.06 and 0.36 for MCCPs (14 isomers) in the food web from Lake Ontario (Table 3b; SI Table S3C). In Lake Michigan, TMFs for SCCPs ranged from 0.41 to 2.4, while results for TMFs could not be evaluated for MCCPs due to the large

number of nondetectable values. Statistically significant relationships between trophic level of organisms and log CP concentrations (TMF >1) were observed at both locations for $C_{11}Cl_9$, $C_{12}Cl_8$, and $C_{12}Cl_9$ (SI Table S3C). A TMF above 1 indicates that certain SCCP isomers have the potential to biomagnify in aquatic food webs.

A major feature of the analysis of TMF is that lake trout have lower SCCP and MCCP concentrations than some of their prey on a lipid basis. Given that SCCPs in lake trout were overestimated by the food web model (where we assumed no biodegradation) the results suggest that lake trout are metabolizing SCCPs. The reduced proportions of SCCPs in lake trout compared to their prey also imply biotransformation. TMFs calculated without lake trout were generally higher in the Lake Ontario food web: C_{10} = 2.4 (with lake trout values = 0.97), C_{11} = 1.9 (0.90), C_{12} = 2.5 (1.0), C_{13} = 1.5 (1.1), C_{14} = 1.9 (0.29), C_{15} = 4.5 (0.18), C_{16} = 4.8 (0.14). This was not the case for the Lake Michigan food web where TMF for SCCP calculated without lake trout generally yielded lower TMFs.

TMFs reported in this study for SCCPs were lower than TMFs reported for perfluorooctane sulfonate (PFOS; TMF = 5.9) (*25*) and hexabromocyclododecane (TMF = 6.3) (*26*) evaluated in the same food web organisms from Lake Ontario. TMFs for SCCPs were also lower than for PCBs and *p,p′*-DDE based on the data of Kiriluk et al. (*27*) which were estimated as 5.7 for PCBs and 6.1 for *p,p′*-DDE (*25*).

TMFs for SCCPs were in the same range of biomagnification reported for toxaphene in Lake Superior (TMF = 1.3) (*16*). The lack of biomagnification potential (TMF ≤1) for some CP chain lengths, especially C_{14}−C_{16} MCCPs (Table 3b, SI Table S3C) suggest some similarity to the trophic dilution observed for high molecular weight phthalate esters in a marine food web from Western Canada (*28*).

This food web study of SCCPs and MCCPs in Lake Ontario and Lake Michigan has shown that these flame retardant chemicals are widely distributed in water and biota samples. However, the proportion of MCCPs differed greatly between the two lakes with MCCPs much more prominent in Lake Ontario. This difference may simply reflect the sources of CPs at these sampling locations. Previous studies showed profundal sediments in Western Lake Ontario had higher SCCP concentrations than the lake as a whole (*9*) and sediments from near urban areas along the western basin of Lake Ontario had elevated SCCP concentrations (*3*). The northern Lake Michigan sites sampled here may not be representative of the lake as a whole. Atmospheric concentrations of PCBs in northern Lake Michigan, in the Charlevoix, MI sampling area, were 4–10-times lower on average than near Chicago−Milwaukee (*29*). Unfortunately, no measurements of SCCP/MCCPs are available for southern Lake Michigan biota or for anywhere in or near the lake for abiotic samples. Sources and pathways of SCCP/MCCPs may differ from PCBs due to much different industrial and consumer use, particularly for MCCPs, which are incorporated as flame retardant plasticizers into many products. MCCPs, which are more hydrophobic and less volatile than SCCPs, may show more distinct gradients from urban source areas. Given the prominence of CPs, particularly in lake waters and in lower food web organisms, further investigation is needed to evaluate the magnitude of the distribution and accumulation/magnification of SCCP/MCCPs.

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Supporting Information Available

Quality assurance section, the concentration of SCCPs in surface water from Lake Ontario, the concentrations of PCBs and organochlorine pesticides in invertebrates from Lake Ontario, the formula group isomer profile of CP in organisms from Lake Michigan and Ontario and an analytical standard, the BAFs, BMFs, and TMFs of SCCPs and MCCPs in aquatic food webs, the predicted concentrations of CPs based on the Gobas food chain model, the observed versus predicted concentrations of SCCP chain length groups, and a map of the study area. This material is available free of charge via the Internet at http://pubs.acs.org.

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