Environ. Sci. Technol. **2008,** *42,* 1024–1031

Occurrence and Biomagnification of Polychlorinated Naphthalenes and Non- and Mono-*ortho* PCBs in Lake Ontario Sediment and Biota

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Received July 23, 2007. Revised manuscript received November 8, 2007. Accepted November 20, 2007.

Biota and surface sediments collected from Lake Ontario were analyzed for polychlorinated naphthalenes (PCNs) and non- and mono-*ortho*-substituted polychlorinated biphenyls (n/m-*o*-PCBs) to compare bioaccumulation behavior of these classes of dioxin-like chemicals in a food web from the Great Lakes. Mean ΣPCN concentrations (tri-octaCN) ranged from 14 ± 9 pg/g in plankton to 3500 ± 3200 pg/g (wet weight) in lake trout, while sediments contained from 21 to 38 ng/g (dry weight). Principal components analysis of PCN congener patterns indicated that chlorine substitution determined which congeners favored accumulation (e.g., CN-42, -52, -60, -66, -67, and -73), while others may be subject to metabolism. The bioaccumulative congeners exhibited similar trophic magnification factors (TMFs; 1.23–1.42) and biomagnification factors (BMFs; 5.5–8.6) to the n/m-*o*-PCBs for the trout/weighted diet relation, although BMFs for a benthic feeding relationship (slimy sculpin/Diporeia) indicated that the n/m-*o*-PCBs were more bioavailable through the benthic pathway. PCNs contribute significantly to the burden of dioxin-like compounds in Lake Ontario biota, contributing between 12 and 22% of total PCN + PCB TEQ in lake trout and up to 69% in benthic organisms.

Introduction

Polychlorinated naphthalenes (PCNs) are planar halogenated aromatic compounds, structurally similar to the polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and non- and mono-*ortho*-substituted polychlorinated biphenyls (n/m-*o*-PCBs). PCNs have been nominated for consideration as candidate persistent organic pollutants (POPs) under the United Nations, Economic Commission for Europe (UNECE), Long Range Transboundary Air Pollution (LRTAP) Convention, Aarhus Protocol on POPs, in which PCDD/Fs and PCBs are already listed. PCNs were used as dielectrics for flame resistance and insulation in capacitors and cables (*1*, *2*), are found in PCB mixtures (*3*), and are formed during combustion processes (*4*, *5*). They exhibit toxicity in the same manner as the PCDD/Fs and n/m-*o*-PCBs, with measured relative potencies (REPs) and proposed dioxin toxic equivalency factors (TEFs) of the same magnitude as many of the n/m-*o*-PCBs (*6–9*).

Bioaccumulation of chemicals is one key criterion under legislation and treaties such as the Aarhus protocol. Bioaccumulation of PCNs has been indicated in selected predator–prey relationships in the Baltic Sea region (*1*, *10*) and in benthic biota in riverine areas of Michigan (*11*). In the Great Lakes basin, binational programs are in effect to monitor and reduce inputs of PCDD/Fs and PCBs which, as a result of foodweb biomagnification, are responsible for lake-wide and localized sportfish consumption advisories (*12*). A better understanding of the significance of PCNs as a dioxin-like POP and its bioaccumulation behavior relative to the n/m-*o*-PCBs, the dominant compound class causing fish consumption advisories, is needed for risk assessors and resource managers to consider, especially if PCNs become listed as a POP under global and binational treaties.

This study reports PCN and n/m-*o*-PCB concentrations in sediments and biota of varying trophic levels from Lake Ontario. This is an ideal system for the study of PCNs because it is highly impacted by chemical contaminants such as PCBs and PCDD/Fs from upstream sources (*13*). Previous studies of Great Lakes biota (*11*, *14*, *15*) and sediments (*16–18*) have focused on relatively less-contaminated systems (Lakes Huron and Superior) or the highly contaminated Detroit River region (summarized in ref *19*). We systematically assess and compare bioaccumulation of individual PCN congeners, including separated pentaCNs-52 and -60 and hexaCNs-66 and -67, and we compare their behavior to the n/m-*o*-PCBs using trophic transfer (stable nitrogen isotope relations) and biomagnfication factor calculations as tools. This evaluation, as well as calculations estimating dioxin toxic equivalents (TEQs) for PCNs and the n/m-*o*-PCBs, illustrates that there are differences in the bioaccumulation behavior between these two compounds classes and highlights the relevance of PCNs as a contaminant class in this and other aquatic systems.

Experimental Section

Sample Collection, Extraction, Analysis, and Quality Control. Sampling and chemical analysis methodologies are briefly described below with details included as Supporting Information (SI). Quality control data, stable isotope analysis methods, and an expanded background of the contaminant trophodynamics data analysis are also included as SI.

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10.1021/es071819g CCC: $40.75

TABLE 1. Summary of Stable Isotope Data, PCN and n/m-*o*-PCB Concentrations, and Dioxin Toxic Equivalents (TEQ) (±Standard Deviation) in Foodweb Samples (Wet Weight; ww) and Surface Sediments (Dry Weight; dw) from Lake Ontario

					concentrations (ng/g ww or dw)			TEQ (pg/g ww or dw)	
	N	% lipid	δ^{15}N	δ^{13}C	ΣPCN[e]	Σm-*o*-PCB[f]	Σn-*o*-PCB[g]	PCN	PCB
net plankton	4[b]	0.7 ± 0.2	8.1 ± 0.6	−23.8 ± 0.4	0.014 ± 0.009	0.16 ± 0.12	0.01 ± 0.01	0.006 ± 0.004	0.03 ± 0.01
Diporeia hoyi	2[b]	3.3 ± 0.6	10.3 ± 0.1	−26.3 ± 0.2	1.4 ± 0.1	5.2 ± 0.1	0.32 ± 0.02	1.3 ± 0.0	0.59 ± 0.01
Mysis relicta	3[b]	4.3 ± 0.9	11.3 ± 1.1	−26.7 ± 1.5	0.3 ± 0.1	4.3 ± 1.0	0.17 ± 0.04	0.14 ± 0.05	0.42 ± 0.09
slimy sculpin	3[c]	3.2 ± 0.6	15.8 ± 0.4	−23.8 ± 0.2	1.1 ± 0.2	32 ± 9	0.36 ± 0.08	1.9 ± 0.3	2.0 ± 0.7
alewife	4[c]	4.6 ± 2.2	11.7 ± 0.5	−21.7 ± 0.8	0.14 ± 0.05	6.9 ± 2.6	0.18 ± 0.07	0.10 ± 0.04	0.84 ± 0.28
rainbow smelt	5[c]	1.8 ± 0.7	15.3 ± 0.7	−23.9 ± 1.2	0.4 ± 0.2	9.5 ± 3.7	0.26 ± 0.09	0.46 ± 0.29	0.88 ± 0.34
lake trout	5	13 ± 4	17.6 ± 0.7	−21.9 ± 0.4	3.5 ± 3.2	209 ± 211	4.0 ± 4.0	3.8 ± 3.5	22 ± 27
sediment[a]	5	3.6 ± 0.8[d]	NA	NA	28.9 ± 6.7	23 ± 5	2.7 ± 0.8	17 ± 4	3.1 ± 0.8

[a] Surface sediment. [b] Pooled samples; >100 organisms. [c] Pooled samples; 5–25 organisms. [d] % organic carbon. [e] Tri-octaCNs. [f] PCB-118, -105, -114, and 156. [g] PCB-81, -77, -126, and -169.

Forage fish (alewife [*Alosa pseudoharengus*], rainbow smelt [*Osmerus mordax*], slimy sculpin [*Cottus cognatus*]) and invertebrates (net plankton [mainly zooplankton; copepods and cladocerans], mysids [*Mysis relicta*], amphipods [*Diporeia hoyi*]) were collected from open waters in Lake Ontario off Niagara-on-the-Lake, Port Credit, Port Hope and in the eastern basin in September 2003, while lake trout (*Salvelinus namaycush*; 8–9 year olds) were collected in June and July of 2002 from the eastern basin using previously reported methods (*20, 21*). Surface sediments (top 3 cm) were collected from stations in the Niagara, Mississauga, and Rochester basins of Lake Ontario in 1998 (*13*). Biota (−80 °C) and sediment (−20 °C) samples were archived frozen until analysis.

Tissue and sediment samples were thawed, weighed, and fortified with recovery surrogate solutions of mass-labeled $^{13}C_{10}$-PCNs and $^{13}C_{12}$-PCBs, then extracted by accelerated solvent extraction with 1:1 dichloromethane (DCM)/hexane (biota) and by Soxhlet with DCM (sediments). Lipids (biota) were determined gravimetrically, followed by size exclusion chromatography. All biota and sediment extracts were then fractioned in a two-step process, first using silicic acid (SA) columns, eluting with hexane (F1; contained PCNs and PCBs), followed by fractionation of F1 on mini-carbon/SA columns, eluting with 30% DCM in cyclohexane (F1-1) and toluene (F1-2; contained PCNs and n/m-*o*-PCBs), as described previously (*22*). The PCNs and n/m-*o*-PCBs were quantified by gas chromatography (GC)−electron capture negative ion mass spectrometry, monitoring selected ions. Coeluting penta- and hexa-CNs were further resolved using a Rt-βDEXcst capillary GC column (*23*).

Chromatographic peaks were identified by retention times and quantified when the target/qualifier ion ratios were within ±20% of standard values. Procedural blanks and blank spikes using Halowax 1014 and native n/m-*o*-PCBs were included to monitor interferences and recoveries, while the ^{13}C-labeled surrogates accounted for recoveries in individual samples. Mean recoveries of native PCNs were 60–93% (relative standard deviations, RSDs, of 13–22%), and 90–120% when corrected for $^{13}C_{10}$-PCN recoveries. Mean $^{13}C_{10}$-PCN recoveries in samples ranged from 75 to 88% (RSDs of 10–17%). Native n/m-*o*-PCB recoveries averaged 86–98% (RSDs of 4–12%) and the $^{13}C_{12}$-PCB-77 and -126 recoveries were similar, while mean $^{13}C_{12}$-m-*o*-PCB-118 and -105 recoveries were lower (58 and 69%) and more varied (RSDs of 35 and 28%, respectively) (discussed in SI). Concentrations were blank and ^{13}C-recovery corrected and were reported if values exceeded the limit of detection (LOD), defined as the average individual congener amount in blanks +3 standard deviations. Detection limits (0.1–5 pg/g wet weight of tissue or dry weight of sediment) varied by congener and sample amount extracted.

Data Analysis. A principle component analysis (PCA) was conducted to assess similarities and differences among PCN and PCB congener concentrations and patterns in this Lake Ontario food web (Statistica for Windows; Statsoft, Inc., Tulsa, OK). Congeners included in the PCA were detected in greater than 60% of the samples and lipid-adjusted concentrations were $\log_{10}$-transformed prior to analysis to optimize the normality of the data set (Kolmogorov–Smirnov, $p > 0.05$). For the PCA, nondetects were substituted with the detection limit value. Nondetects and disqualified values were otherwise excluded from means and summations.

Biomagnification of PCNs and the n/m-*o*-PCBs was assessed via two methods. The first considered contaminant trophodynamics in the invertebrate−forage fish−lake trout food web from Lake Ontario, as defined by stable nitrogen isotopes, following the approaches outlined in a recent review (*24*). We present contaminant trophodynamic data via both the approaches summarized in this review (further discussion and tables in SI) to facilitate comparisons, as both have been used in Great Lakes food web studies (*20, 21, 25, 26*). However, discussions in this paper are based on the log concentration (lipid-adjusted)−stable nitrogen isotopes ratio (δ^{15}N) relation (*25, 27*)

$$\log[\mathrm{conc_{lw}}] = b \times \delta^{15}N - a \tag{1}$$

The antilog of the slope of eq 1 gives what has been described as a trophic magnification factor (TMF) (*24, 25, 28*)

$$\mathrm{TMF} = 10^{b} \tag{2}$$

Equation 1, which represents the concentration increase per unit δ^{15}N, contains fewer assumptions than the approach based on trophic levels (discussed further in SI).

Second, biomagnification factors (BMFs) were determined on the basis of predator–prey relationships and defined as the lipid-adjusted analyte concentration in the predator divided by the concentration in its prey. Lake trout/prey BMFs presented are based on diet-weighted prey concentrations, assuming a diet of 90% alewife, 7% rainbow smelt, and 2% slimy sculpin, as was done previously (*26*). BMFs were calculated for the commonly detected congeners and nondetects were not included.

Results and Discussion

Occurrence in Lake Ontario Biota and Sediment. Mean concentrations of ΣPCN, the mono-*ortho*-substituted PCBs (Σm-*o*-PCBs), and the non-*ortho*-substituted PCBs (Σn-*o*-PCBs) exhibited increasing trends from net plankton to forage fish to the predator lake trout in Lake Ontario (Table 1). Benthic dwelling *Diporeia* and slimy sculpin concentrations were greater relative to other invertebrates and forage fish, respectively. Concentrations of PCNs and the non- and mono-

PCBs (n/m-*o*-PCBs) in Lake Ontario lake trout were greater than those found in the other Great Lakes, (*14*) and the PCNs were an order of magnitude greater than salmon from the Baltic Sea (*29*).

In sediment, ΣPCN concentrations ranged from 21 to 38 ng/g dry weight (dw) (Table 1), indicating a relatively uniform distribution in depositional basins across the open lake, and were considerably higher than sediment from Lake Michigan (*17*). However, sediments in contaminated areas of the Detroit river had greater concentrations (*16, 17*). Sediment Σn/m-*o*-PCB concentrations in this study were lower than in 1993 samples from locations in the north and central part of Lake Ontario (*30*) but were within the degree of spatial variation for PCBs in the lake (*13*).

Relative Toxicity. Contributions to dioxin-like toxicity were estimated using relative potencies (REPs) from enzyme activity assays to calculate dioxin toxic equivalents (TEQ) for PCNs (*6–8*) and the n/m-*o*-PCBs (*31*) (Table 1). PCNs contributed from 12 to 22% of total PCN + PCB TEQ in lake trout and from 49% (slimy sculpin) to 69% (*Diporeia*) in the benthic organisms. This latter observation indicates that sediments are an important source of the more toxic PCNs, and relatively lower PCN TEQ contributions in pelagic species suggests that the toxic PCNs may be less bioavailable or accumulate to a lesser extent than the n/m-*o*-PCBs in the pelagic food web. Similarly, PCN contributions to PCN + PCB TEQ were found to be greater in mussels than in fish (bass and gobies) in selected Michigan rivers (*11*). The mean PCN TEQ in Lake Ontario lake trout was more than an order of magnitude greater than that found in whole lake trout from Lake Superior (*14*), indicating there have been more source contributions of toxic PCN congeners to Lake Ontario than in the other Great Lakes studied. Although the n/m-*o*-PCBs are the dominant contributors of dioxin TEQs compared to PCDD/Fs in Lake Ontario fish, it is worth noting that for the first level of restrictions for fish consumption (2.7 pg/g TEQ ww (*12*)), PCNs alone would result in lake trout from this study having TEQ concentrations above this level when proposed PCN TEFs are used in calculations (*9*). While these proposed TEFs are not yet broadly accepted, and they have been applied to whole fish rather than fillets, the calculation illustrates the potential for PCNs to impact risk assessment and management.

PCN Homologue and Congener Patterns. The average PCN homologue profile in Lake Ontario lake trout at the top of the food web was dominated by the penta- and hexa-CN homologues, shifting from a profile which includes greater contributions from the tri- and tetra-CNs in lower trophic organisms such as plankton, *M. relicta*, and alewife (Figure SI-1). Such a shift was observed in Baltic Sea biota (*10, 32*) and biota at varying trophic levels and locations in the Great Lakes basin (*11, 14, 15, 19*). In the benthic *Diporeia* and slimy sculpin, the penta- and hexa-CNs were also prevalent.

In Lake Ontario sediments, the hexa- (20%), hepta- (22%), and octa-CN (28%) homologues were most prevalent (Figure SI-1), varying from profiles reported in Lake Michigan (*17*) and Detroit River sediments (*17, 18*), which had lower contributions of octa-CN. In upper Detroit River sediments, the tetra- to hexa-CNs were the primary contributors, indicating that use and emissions of Halowax mixtures were the primary PCN sources (*17*). The greater contribution of octa-CN to Lake Ontario sediments indicates that sources having impacted the lake may differ from other areas of the Great Lakes, possibly from historic inputs from the chemical industry in the Niagara River area. Indications of contributing PCN sources to Lake Ontario are discussed further in the SI, although we recommend more targeted monitoring to address source apportionment in detail.

The PCN homologue shift in biota coincided with variation of the PCN congener profile by species. In both the benthic (Figure 1a) and pelagic (Figure 1b) components of the food web, the number of congeners contributing to the profile decreased with increasing trophic position, resulting in a few more prevalent congeners in species such as the slimy sculpin and lake trout. Ensuing discussions consider the benthic and pelagic components of the food web as they have been defined previously (e.g., ref *20*). However, the Lake Ontario food web has and is undergoing considerable change with several invasive species (e.g., Dreissenid mussels, round gobies, etc.) (*33*) potentially changing energy and material flow (defined in part by δ^{13}C) and trophic positions (δ^{15}N). Inferences in future accumulation assessments may be modified as a result, and a detailed assessment of the current Lake Ontario food web is certainly of merit.

At the base of the benthic component of the food web, the sediment profile contained numerous tetra- and penta-CN congeners, but four congeners were present in the greatest proportions (12–28%): CNs-66, -67, -73, and -75 (Figure 1a). The profile in the detritus-feeder, *Diporeia*, was nearly identical to the sediment profile, reflecting sediment exposure, except for octa-CN (<1%) and the hepta-CN (CN-73; 10%), which were not as efficiently accumulated within *Diporeia*. In *M. relicta* (Figure 1b), tetra-CNs-42 and -33/34/37 and penta-CN-60 were more abundant, and hexa-CNs-66 and -67 were less so than in *Diporeia*, reflecting the more pelagic feeding habits of *M. relicta* (*34*). In the slimy sculpin, which tends to feed on *Diporeia* (*20*), the hexa-CNs-66 (18%) and -67 (13%) dominated the profile, followed by penta-CN-60 (7%), while other congener contributions were minor, generally <1% (Figure 1a). The lower accumulation of these other congeners in sculpin compared with *Diporeia* could result from the interaction of several uptake or loss processes (*35*), and possibly a shifting diet. However, we hypothesize that the sculpin profile reflects its ability to metabolize certain PCN congeners. For example, penta-CN-50 diminishes in relative importance compared with *Diporeia*, whereas hexa-CN-66 becomes more dominant. Hexa-CN-66 is less likely to be metabolized compared with penta-CN-50 and is thus favored to accumulate (*1*), although their physical-chemical properties are similar (*36*). The ability of sculpin to metabolize organohalogen chemicals was noted for PCBs in the deepwater sculpin (*Myoxocephalus thompsoni*) from Lake Michigan (*37*), and PCN congener profiles in amphipods from the Baltic Sea reflected sediment exposure, while profiles in fourhorned sculpin were modified (*10*).

In the pelagic food web components, the PCN distribution in net plankton contained considerable contributions from tri-CN-24, tetra-CNs-42, -33/34/37, -28/43, and -38, and penta-CN-60, hexa-CNs-66 and -67 (4–11%; Figure 1b). The tri- and tetra-CN contributions are consistent with exposures from the Lake Ontario water column, where these homologues are most prevalent (*38*). The profile observed in plankton varied from higher trophic level species such as the rainbow smelt and lake trout, which had more congeners with minor contributions. Lake trout profiles were dominated by tetra-CN-42, penta-CNs-52, -60, -61, and hexa-CNs-66 and -67 (3–13%; Figure 1b). The profile for rainbow smelt was similar to lake trout but with a greater contribution from hepta-CN-73 (8%), possibly because of benthic feeding as *Diporeia* can form a portion of the smelt diet (*20*). In the comparison of lake trout profiles from other Great Lakes, penta-CNs-52/60 contributed a much higher percentage, while hexa-CNs-64/68, -69, and -71/72 were similar in magnitude to hexa-CNs-66/67 in Lake Superior lake trout, and penta-CNs-52/60 were also most prevalent in trout fillets from Lakes Huron and Michigan (*14*). The sediment and trout patterns indicate that Lake Ontario lake trout receive greater exposures to the more toxic hexa-CN-66 and -67 congeners than trout from other areas of the Great Lakes,

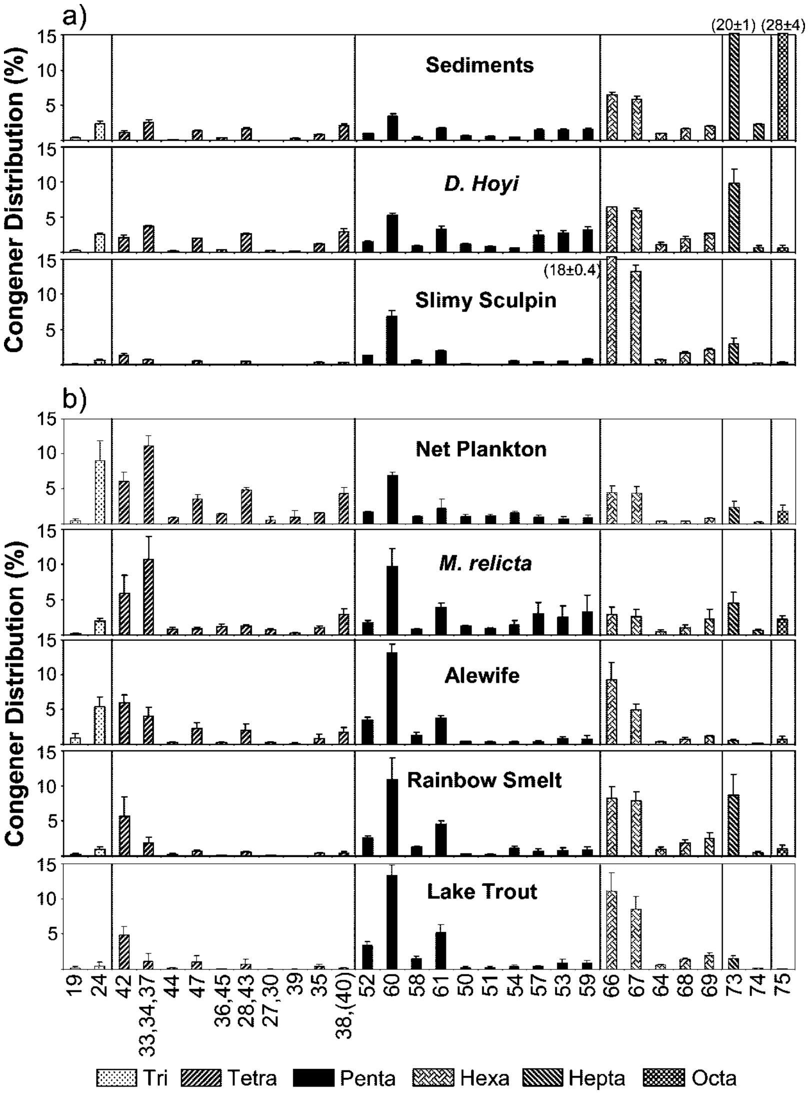

FIGURE 1. Mean (+ standard deviation) polychlorinated naphthalene (PCN) congener profiles in (a) benthic and (b) pelagic components of the Lake Ontario food web. Congeners detected in >70% of samples were included in calculations.

which in part account for their greater estimated TEQ concentrations.

There was little variation in the homologue (tetra-hexa-CB) and congener distributions of PCBs since only the n/m-*o*-PCBs congeners were included here. CB-118 was the dominant m-*o*-PCB in all species and the sediments, followed by CB-105 then CB-156. Similarly, CB-77 was the most abundant n-*o*-PCB, followed by CB-126 then CB-81. These distributions are consistent with those reported previously in fish (*39*).

PCA provided further insight into PCN and PCB congener bioaccumulation patterns. For PCNs, three principal components were retained based on the Scree Test, accounting for 97% of the model variance. The PCN scores distribution on principal components PC1 and PC2 shows low trophic level samples grouped from the lower right and progressively moving to the upper left with increasing trophic level (Figure 2a). Sediments and *Diporeia* were grouped to the upper right of the score plot, away from other species.

Analysis of the loadings (Figure 2b) indicated that chlorine substitution contributes to the observed congener distributions. Falandysz (1998) observed in Baltic Sea biota that PCN congeners without adjacent (or vicinal) carbons unsubstituted with chlorine (NVC-Cl) were resistant to metabolism and more likely to bioaccumulate (*1*). In contrast, congeners having two (DVC-Cl), three (TVC-Cl), or two pairs (DDVC-Cl) of adjacent (vicinal) unsubstituted carbons can be more readily metabolized or excreted by vertebrates (*1*) because of both hydroxylation via arene oxide intermediates and hydroxylation−dechlorination (*40*).

This PCA analysis provides a statistical foundation supporting Falandysz's (1998) observations. All NVC-Cl PCNs, except CNs-73, -74, and −75, loaded high onto PC2 and low onto PC1, grouping together because of their ability to biomagnify in this food web, while the nonbioaccumulative DDVC-Cl congeners (tri-CN-24; tetra-CNs-38, -27/30, and -36/45) separated out from the other PCNs, loading high onto PC1 and low onto PC2 (Figure 2b). The DVC-Cl and TVC-Cl congener loadings overlapped, intermediate to the NVC-Cl and DDVC-Cl congeners, consistent with the suggestion that susceptibility to metabolic degradation of PCNs increases with the number of unsubstituted adjacent carbons (*1*). In contrast to the other NVC-Cl PCNs, hepta-CNs-73, -74, and octa-CN grouped with the DVC-Cl and TVC-Cl congeners. Hepta-CN-73 loaded closest to the other NVC-Cls, but octaCN was close to the DDVC-Cls. These PCNs are larger molecules with high octanol–water partition coefficients (*36*), which may result in lower gill and dietary uptake and assimilation efficiency (*41, 42*). Furthermore, congeners substituted in the 1,8- and 4,5-positions are more susceptible to photodegradation, likely because of steric interactions of the chlorines in these positions (*43, 44*). With this reduced

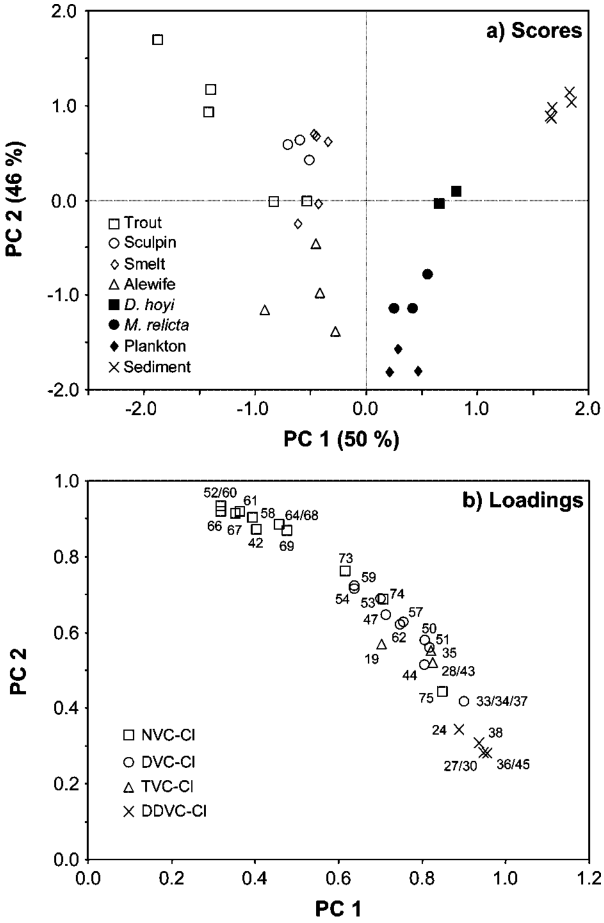

FIGURE 2. (a) Score and (b) loadings plots from the principal components analysis separating species and indicating PCN congener groupings by substitution pattern. Loading groupings include no adjacent (or vicinal) carbon substituted with chlorine (NVC-Cl), two (DVC-Cl), three (TVC-Cl), and two pairs (DDVC-Cl) unsubstituted with chlorines. Coeluting congeners were categorized by the congener with the most adjacent unsubstituted carbons if numbers differed.

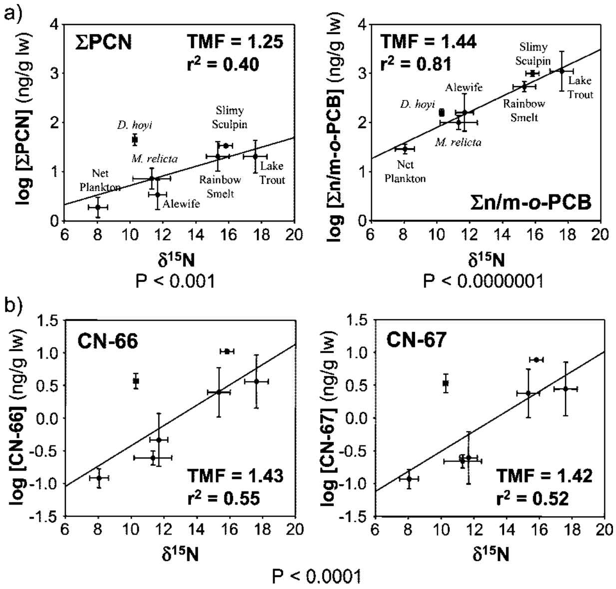

FIGURE 3. Plots of log mean concentration (±standard deviation) versus the mean stable isotope ratio for nitrogen (‰; ± standard deviation) for (a) ΣPCNs and Σn/m-*o*-PCBs and (b) the separated hexa-CN-66 and -67 congeners. Regressions are based on all individual data points.

stability, CN-74 and -75, substituted with chlorines in both the 1,8- and 4,5-positions, and CN-73, substituted in one 1,8-position (Figure SI-2; SI), may be more susceptible to biotic transformation or degradation.

The invertebrate species (plankton, *Diporeia*, and *M. relicta*) scored positively on PC1 (Figure 2a), in part because of exposure and uptake related to partitioning properties from sediments and the water column and because of their low metabolic capacity for chemical contaminants, resulting from their poorly developed mixed function oxygenase system relative to vertebrates (*45*). In contrast, the fish scored negatively on PC1. Pelagic species were separated along PC2 as scores increased with trophic position with plankton, mysids, and alewife scoring negatively, while smelt and lake trout had positive scores. For benthic samples, sculpin grouped with the smelt and trout, perhaps because of their apparent ability to metabolize PCNs. Sediments scored high on both PC1 and PC2 because they contain considerable contributions of both bioaccumulative and nonbioaccumulative PCNs, and *Diporeia* scored closest to sediment reflecting their exposure as detritus-feeders.

The loading of bioaccumulative and nonbioaccumulative PCNs on PC2 and PC1, respectively, also appears to be influenced by congener hydrophobicity (expressed via octanol–water partition coefficients, K_{OW}), with the more hydrophobic congeners loading high onto PC2 and the less hydrophobic congeners onto PC1 (Figure 2b). However, this may be an artifact. PCN congeners having lower K_{OW} values tend to be less chlorinated, leading to a greater number of unsubstituted carbons and increasing their probability of having DVC-Cl, TVC-Cl, or DDVC-Cl substitution patterns. This is illustrated by comparing congeners with similar log K_{OW} values but differing chlorine substitution. For example, tetra-CNs-42 and -33/34/37 have log K_{ow} values of approximately 6 (*36*), but tetra-CN-42, a NVC-Cl congener, loads strongly onto PC2, whereas tetra-CNs-33/34/37, which are DVC-Cl compounds, load strongly onto PC1. A similar but less pronounced trend occurs for penta-CNs (e.g., penta-CNs-52/60, -58, and -61 versus penta-CNs-50, -51, -54, and -57). This is consistent with the hypothesis that some PCN congeners are metabolized in the food web.

PCA was also conducted for the n/m-*o*-PCBs for comparison purposes, where the sample groups were separated primarily based on trophic position, reflecting the bioaccumulative properties of these compounds. In contrast to the PCNs, the results of this PCA did not appear to be affected by metabolic biotransformation, which is not surprising since PCB metabolism is generally assumed insignificant in fish and invertebrates (*35*). Further details of n/m-*o*-PCB PCA is presented in the SI.

Biomagnification. Stable nitrogen and carbon isotope results are expressed as $\delta^{15}N$ and $\delta^{13}C$ (Table 1). As discussed previously, the Lake Ontario food web has undergone considerable change over the last two decades (*33*), and as such, these data do not represent an in-depth analysis of the current trophic relationships. However, the $\delta^{15}N$ analysis provides a useful means of comparing bioaccumulation behavior of PCNs with the n/m-*o*-PCBs.

Congener-specific TMFs were calculated for the commonly detected PCNs and the n/m-*o*-PCBs (Table SI-1; SI) and selected log concentration (lw) versus $\delta^{15}N$ plots are presented (Figure 3). The PCN congeners having the highest TMFs within each homologue class and exhibiting the most significant concentration−$\delta^{15}N$ regressions were those having structures favoring accumulation (NVC-Cl) including tetra-CN-42, penta-CNs-52, -60, -58, and -61, hexa-CNs-66, -67, -64, -68, and -69, and hepta-CN-73, consistent with the profiles observed in higher trophic level species such as the lake trout, rainbow smelt, and slimy sculpin. The TMFs of

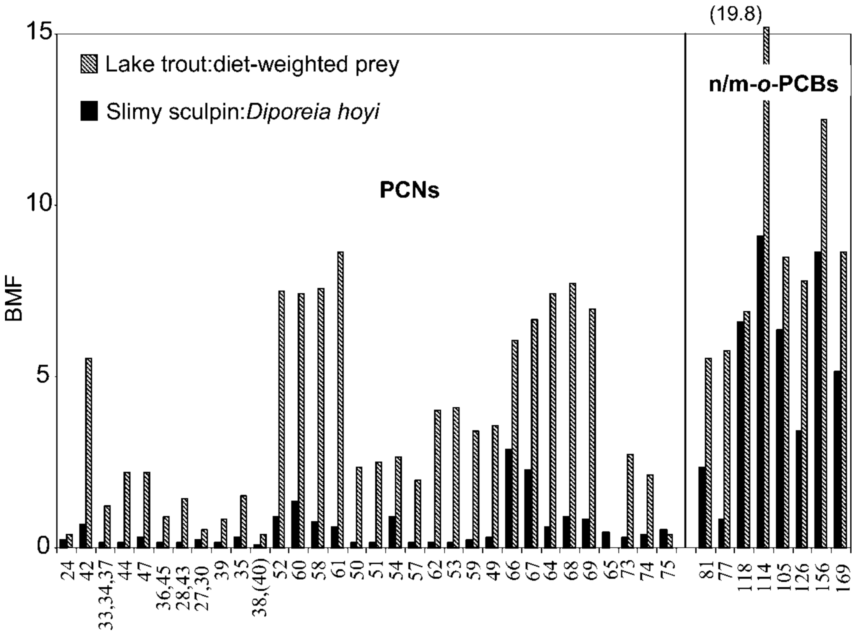

FIGURE 4. Biomagnification factors (BMFs; lipid-adjusted) for PCNs and n/m-*o*-PCBs in the lake trout/diet-weighted prey and slimy sculpin/*Diporeia* feeding relationships.

these bioaccumulating PCNs were comparable in magnitude to n/m-*o*-PCB TMFs for congeners of the same degree of chlorination, indicating similar bioaccumulation behavior in the Lake Ontario food web. However, TMF plots for ΣPCN (TMF = 1.25) and Σn/m-*o*-PCB (TMF = 1.44) indicate that ΣPCN accumulation through the food web was significantly lower ($p < 0.05$; Student's *t* test on difference of slopes) than for the n/m-*o*-PCBs, likely because of the influence of nonaccumulating or metabolized PCN congeners (Figure 3a). The ΣPCN TMF is similar to that calculated for total PCBs (TMF = 1.23) from the data of Kiriluk et al. (1995) (*20*).

The bioaccumulation behavior of penta-CNs-52 and -60, hexa-CNs-66 and -67, and hexa-CNs-64 and -68 was assessed individually following analytical separation, and is beneficial as these congeners have varying REPs for dioxin toxic activity (*6–8*). Figure 3b depicts regressions of hexa-CN-66 and -67 concentrations versus δ^{15}N and the corresponding TMFs. No difference in trophodynamics was observed for CNs-66 and -67, hexa-CNs-64 and -68, and penta-CNs-52 and -60 (Table SI-1). Although relative contributions of each congener to the pair varied by species (Figure 1), no systematic pattern favoring accumulation of a particular congener was apparent.

Diporeia demonstrated markedly different behavior in the trophodynamic regressions between PCNs and n/m-*o*-PCBs, lying considerably further from the regression line for ΣPCNs than for Σn/m-*o*-PCBs. However, they could not be excluded as outliers (Cook's distance) and the ΣPCN slope did not vary significantly ($p > 0.05$) when *Diporeia* were excluded. Similarly, Martin et al. observed this for *Diporeia* and slimy sculpin studying perfluorooctane sulfonate (PFOS) in Lake Ontario biota, prompting the authors to exclude these species from TMF calculations (*26*). This indicates that exposure to PCNs through sediment is much higher for *Diporeia* relative to PCBs when compared to other species. This analysis also suggests that PCNs biomagnify to a lesser extent in the benthic pathway (smaller increase from *Diporeia* to slimy sculpin) than in the pelagic foodweb (Figure 3).

Biomagnification of PCNs is also indicated through BMF calculations for several feeding relationships (Table SI-2; SI), such as those for the lake trout/diet-weighted prey and the slimy sculpin:*Diporeia* relationships (Figure 4). Consistent with the TMF analysis and PCA, the congeners most resistant to degradation (NVC-Cl) had the highest BMFs. In the lake trout/diet-weighted prey relationship, BMFs for the bioaccumulating PCNs ranged from 5 to 10, and the n/m-*o*-PCB BMFs were generally in the same range (Figure 4). These BMFs and those for lake trout:alewife are similar to observed BMFs in the Baltic Sea biota (*1*). In other predator–prey scenarios, PCN BMFs tended to be lower (range of 0.1−2) than the n/m-*o*-PCB BMFs as is particularly the case for the slimy sculpin/*Diporeia* interaction (Figure 4; Table SI-2), indicating that differences exist in bioavailability, uptake, or accumulation behavior between PCNs and n/m-*o*-PCBs. PCN BMFs for sculpin/*Diporeia* were similar to other benthic interactions in the Baltic Sea area (*10*) and in the St. Clair River area in the Great Lakes region (*11*). Individual BMFs for penta-CN-52 and -60, hexa-CN-66 and -67, and hexa-CN-64 and -68 congeners were similar within each pair, confirming that for each case their bioaccumulation behavior is similar.

In conclusion, the more bioaccumulative and toxic PCNs accumulate within the Lake Ontario food web, resulting in estimated concentrations of dioxin TEQ in a range meriting consideration for risk management purposes. Sediment concentrations of PCNs result in higher exposures to toxic PCN congeners for benthic organisms relative to the n/m-*o*-PCBs, but the latter appear to be more bioavailable than PCNs, reducing the relative PCN contributions to TEQ in lake trout.

Acknowledgments

We thank M. J. Keir (Fisheries & Oceans) and the crew of the CCGS *Shark* for biota collection and preparation, the crew and technical staff aboard the CCGS *Limnos* for sediment collection, and T. Harner and M. Shoeib (Environment Canada) for laboratory time for sediment analyses. The suggestions of three anonymous reviewers and S. Bhavsar (Ontario Ministry of the Environment) improved the manuscript. This study was initiated while P.A.H. was a visiting fellow with Fisheries & Oceans (Winnipeg, MB).

Supporting Information Available

Detailed methods information, background on the contaminant trophodynamics in the food web analysis, and a discussion of source indications are included. The PCN homologue distribution and results of the PCB PCA are included as figures, as well as the TMF and BMF data as tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES071819G