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Current status of short- and medium chain polychlorinated n-alkanes in top predatory fish across Canada

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HIGHLIGHTS

- Short and medium chain PCAs were measured in fish from nine water bodies in Canada.
- Highest sPCAs levels were measured in sites where atmospheric transport is suspected.
- Highest mPCAs levels were found in the highly industrialized/urbanized Great Lakes.
- sPCAs decreased 6.6-fold in Lake Ontario lake trout in the last ten years.
- Homologue groups patterns in fish aids in the identification of PCAs sources.

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ABSTRACT

Short and medium chain polychlorinated n-alkanes (sPCAs and mPCAs) were measured in top predatory fish from nine freshwater bodies across Canada in 2010–2011. Maximum sPCA concentrations were measured in brook trout from Kejimikujik Lake in Nova Scotia (10 ± 8 ng g^{-1} wet weight) while the lowest concentrations were found in lake trout from Kusawa Lake in the Yukon (2 ± 3 ng g^{-1} wet weight). The presence of sPCAs in fish from these sites is strongly suggestive of long range atmospheric transport, given the absence of known point sources. The highest mPCA concentrations (11–12 ng g^{-1} wet weight) were found in lake trout from Lakes Huron, Erie and Ontario. These results showed that fish from sites impacted mostly by atmospheric sources contained higher concentrations of sPCAs than mPCAs while the opposite was observed in sites impacted by industrialization. $C_{12}H_{20}Cl_6$, $C_{12}H_{19}Cl_7$, $C_{14}H_{24}Cl_6$ and $C_{14}H_{23}Cl_7$ were the most abundant homologue groups observed. Lake trout from Lake Huron showed a markedly different sPCA homologue profile, characterized by higher abundances of $C_{11}H_{15}Cl_9$ and $C_{12}H_{17}Cl_9$, indicating local sources. Principal components analysis of sPCA homologues abundances showed that $C_{12}H_{20}Cl_6$, $C_{12}H_{19}Cl_7$, $C_{11}H_{18}Cl_6$, $C_{11}H_{17}Cl_7$ were associated with lakes influenced by atmospheric sources while $C_{11}H_{16}Cl_8$, $C_{12}H_{18}Cl_8$, $C_{11}H_{15}Cl_9$, $C_{12}H_{17}Cl_9$ were associated with sites influenced by urban/industrial sources. Finally, concentrations of sPCAs in Lake Ontario lake trout collected in 2011 decreased 6.6-fold compared to 2001, however no significant differences were observed for mPCAs.

1. Introduction

Polychlorinated n-alkanes (PCAs), also referred to as chlorinated paraffins, are complex synthetic mixtures used as additives in lubricants and metal cutting fluids. PCAs are also used as flame retardants and as additives in paints and plastics. These chemicals are classified according to the length of the alkane chain into: short chain PCAs (sPCAs, 10–13 carbons), medium chain PCAs (mPCAs, 14–17 carbons) and long chain PCAs (lPCAs, 18–30 carbons). PCAs are hydrophobic chemicals which have a high octanol–water partition coefficient (K_{ow}) thus they tend to bioaccumulate in lipid tissues of living organisms (Feo et al., 2009). PCAs are toxic and have been detected in all environmental compartments, humans and indoor environments (Bayen et al., 2006; Friden et al., 2011).

In Canada, sPCAs and mPCAs were found to bioaccumulate and biomagnify in Lake Ontario food webs (Houde et al., 2008). sPCAs have been found in sediments and wild life from remote locations such as the Canadian Arctic, hence there is potential for their long-range atmospheric transport (Tomy et al., 1999; Tomy et al., 2000). PCAs are persistent, bioaccumulative and toxic chemicals with similar properties as other Persistent Organic Pollutants (POPs)

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such as polychlorinated biphenyls (PCBs), toxaphene and organochlorine pesticides (Feo et al., 2009). Consequently, sPCAs are currently under consideration to be included in the list of chemicals under the Stockholm convention (Stockholm Convention, 2008). sPCAs have been included in the Toxic Substances Control Act (TSCA) by the U.S.A. Environmental Protection Agency (USEPA, 2013). In Canada, sPCAs and mPCAs have been proposed for virtual elimination under the Canadian Environmental Protection Act (CEPA) (Environment Canada, 2013).

There is little information regarding sPCAs and mPCAs concentrations in fish, limited to a handful of studies in Canada (Houde et al., 2008; Ismail et al., 2009), one study in the North and Baltic seas (Reth et al., 2005) and a recent survey in the Norwegian Arctic (Harju et al., 2013). The most recent studies of PCAs in the Canadian aquatic environment were conducted with samples collected in 2001 (Houde et al., 2008) and by Ismail et al. with samples from 1998 to 2004 (Ismail et al., 2009). Houde et al. conducted a detailed study on biomagnification which provided concentrations and group patterns of sPCAs and mPCAs in Lake Ontario and Lake Michigan food webs; however, information was limited to the Great Lakes region. Ismail et al. studied temporal trends of sPCAs and mPCAs in lake trout from Lake Ontario collected during 1998–2004, but the study was limited as well to Lake Ontario. Spatial and temporal changes in homologue group patterns (same chain length but different chlorine number i.e., $C_{10}H_{17}Cl_5$, $C_{10}H_{16}Cl_6$, etc.) and chain length group patterns (same chain length but varying chlorine number i.e., C10, C11, etc.) of PCAs can provide valuable insights into potential sources of PCAs and long-range atmospheric transport (Muir, 2010). However, there is no clear trend to more volatile homologs in fish from remote areas (Muir, 2010) and the previous studies conducted in Canada were limited to study homologue group patterns, mostly in Lake Ontario.

Given the limited information regarding current levels and geographical coverage of PCAs in Canada, the main goal of this study was to provide a current spatial status of sPCAs and mPCAs in Canadian aquatic environments. Lake trout was selected as a biomonitor to study the levels and spatial distribution of sPCAs and mPCAs in nine freshwater bodies across Canada during 2010–2011. Locations from industrialized/urban areas as well as remote areas were included. Lake trout are a top predatory fish which are found in many large lakes in Canada and they accumulate pollutants due to their high lipid contents and long life span. Other suitable top predators, walleye or brook trout, were selected for those locations where lake trout were not present or abundant. Since PCAs homologue groups and chain length group patterns can provide important clues regarding PCAs sources and long-range atmospheric transport, an examination of both homologue groups and chain length group patterns in fish from various locations in Canada was included.

2. Experimental section

2.1. Fish collection

Fish were collected from nine freshwater systems across Canada (Fig. 1. See also Table S1, Supplementary data). These water bodies are routinely monitored as part of Environment Canada's National – Fish Contaminants Monitoring and Surveillance Program. Fish were collected in 2010 and 2011 following the protocols used by the National Aquatic Biological Specimen Bank (NABSB) (McGoldrick et al., 2010).

2.2. Analytical methodology

Samples (10 g wet weight) were mixed with Na_2SO_4 and Soxhlet extracted with DCM. The DCM extract was concentrated and lipids were removed using gel permeation chromatography. Lipid-free extracts (1 mL) were applied to a column packed with acidic silica gel (22% H_2SO_4). The column was first eluted with 15 mL of hexane (F1.1) and then with 65 mL of hexane:DCM (1:1, v/v) (F1.2). Fraction 1.2 was concentrated (1 mL) and then applied to a column containing SiO_2 3%. The sample was first eluted with 50 mL of hexane (F2.1) and then with 40 mL of hexane:DCM (1:1, v/v) (F2.2). Fraction F2.2 was solvent exchanged to isooctane before mass spectrometric analyses.

Chromatographic separations were conducted using an Agilent 7290A gas chromatograph equipped with a split/splitless injector and an Agilent DB-5MS fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The GC system was coupled to a Thermo Scientific double focusing sector high resolution mass spectrometer (Thermo Fisher Scientific Inc., Bremen, Germany). The mass spectrometer was operated in the negative ion chemical ionization (NICI) mode with Argon as the reagent gas. Homologue group profiles and quantitation were obtained by monitoring the two most abundant isotopic ions of $[M\text{-}Cl]^-$ for sPCAs and mPCAs in the SIM mode (Tomy et al., 1997; Tomy and Stern 1999). See Supplementary data for details.

2.3. Data analyses

Results are presented as the mean ± standard deviation. In some instances, concentrations are presented as the mean ± standard error of the mean (SEM) for comparison purposes with other studies. Concentrations were blank subtracted and are expressed in ng g^{-1} wet weight (ng g^{-1} ww) and ng g^{-1} lipid. If needed, log transformations were applied to obtain normal distributions. Student's *t*-test was used to evaluate two groups of data. Analysis of variance (ANOVA) was used for multiple group comparisons employing the Holm-Sidak method for post hoc tests. All statistics analyses were performed using SigmaPlot (SigmaPlot, version 12.5, Stystat Software Inc., CA, USA), except principal components analysis (PCA), which used SPSS (SPSS, version 20.0, SPSS Inc. Chicago, IL, USA).

2.4. Quality assurance

Samples corresponding to a given waterbody were processed and analyzed as a batch. Each batch was composed of 9–10 fish samples, one procedural blank, one Na_2SO_4 blank spiked with sPCAs (sPACs 63% Cl, 5 μg) and another one spiked with mPCAs (mPCAs 57% Cl, 5 μg). Recoveries were 82.5 ± 22.9% (n = 7) for sPCAs.

sPCAs and mPCAs were present in our procedural blanks (ΣsPCAs = 0.9 ± 0.5 ng g^{-1} ww, n = 8; ΣmPCAs = 0.6 ± 0.3 ng g^{-1} ww, n = 9), most likely originating from solvents and the laboratory environment despite the precautions taken. sPCAs are known to be ubiquitous and can be present at relatively high concentrations in indoor air and dust (Friden et al., 2011). Concentrations of sPCAs and mPCAs in the blanks were significantly lower than sample concentrations (Fig. S2); thus we blank subtracted our data and included the procedural blanks in our discussion.

3. Results and discussion

3.1. Concentrations of PCAs in top predatory fish across Canada during 2010–2011

3.1.1. sPCAs

sPCAs were detected in fish from all locations (Table 1). The lowest concentrations (ng g^{-1} ww) of sPCAs were observed in lake trout from Kusawa Lake (2 ± 3 ng g^{-1}) in the Yukon followed closely by Lake Erie (3 ± 2 ng g^{-1}), Lake Superior (3 ± 3 ng g^{-1}) and