

Session: POPs in Sediments and Aquatic Environments (Invited)**NEW AND EMERGING PERSISTENT ORGANIC POLLUTANTS IN
SEDIMENTS OF THE GREAT LAKES AND ASSOCIATED AREAS OF
CONCERN**

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Introduction

Recent surveys have been conducted throughout the Great Lakes to assess spatial and temporal trends in sediment and suspended sediment contamination by POPs. These surveys were designed to evaluate sediment quality, and to assist in the tracing of potential sources and vectors of contaminants. In addition to conventional POPs such as PCBs and organochlorine pesticides, we have developed and applied GC-HRMS and LC-MS methods for the determination of POPs of new and emerging concern including dioxin-like PCBs (DLPCBs), C₁₀ – C₁₃ short-chain chlorinated paraffins (SCCPs), polychlorinated naphthalenes (PCNs) and brominated flame retardants (BFRs), including hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBP-a). In this paper, we present our most recent findings on the occurrence of these POPs in bottom sediments of Lake Ontario, and suspended sediments of the Detroit River.

Methods and Materials

Analysis of Short-Chain Chlorinated Paraffins. This method has been described in detail by Tomy et al. (1997)¹. Samples were freeze-dried and extracted in dichloromethane using ASE. Extracts were evaporated, exchanged into hexane, and separated into three fractions of increasing polarity on Florisil (8 g; 1.2 % w/v water deactivated). The first fraction (F1) was eluted with hexane and contained PCBs, some OCs, and a small portion of the toxaphene congeners. Subsequent fractions (F2 and F3) were eluted with hexane/dichloromethane. F1 was subjected to an additional alumina column fractionation during which SCCPs were separated from PCBs by eluting the column with 1% diethyl ether/hexane followed by 50% diethyl ether hexane. SCCPs were quantified using high-resolution gas chromatography/electron capture negative ionization/high-resolution mass spectrometry (HRGC-ECNI-HRMS). Analyses were performed on a 5890 Series II gas chromatograph (Hewlett-Packard Instruments), fitted with a DB-5ms fused silica column (30 m x 0.25 mm i.d., 0.25 um film thickness), connected to a Kratos Concept MS (EBE geometry, Kratos). Analyses were performed in SIM mode at ~12 000 RP, with a cycle time of 1 sec for each window, and equal dwell times for each ion monitored.

Analysis of Dioxin-like PCBs and Polychlorinated Naphthalenes. Methods for the analysis of dioxin-like compounds and PCNs have been described in detail previously^{2,3}. Samples were spiked with ¹³C-labelled surrogate PCDD/PCDF and DLPCB standards and extracted in toluene. Extracts were subjected to a sequential cleanup using a modified silica column, alumina column, and an Amoco PX21 – activated silica column. The first column contained 10% silver nitrate;

activated silica; 33% sodium hydroxide/silica; activated silica; sulphuric acid/silica; activated silica, and; anhydrous sodium sulphate. The column was eluted with hexane and transferred to a column containing activated alumina and anhydrous sodium sulphate. The column was eluted with hexane followed by 10% carbon tetrachloride/hexane (v/v) to collect most mono-ortho PCBs (Fraction A). The PCDDs/PCDFs, co-planar (Co-PCBs), PCNs and remaining mono-ortho PCBs were eluted with 10% methanol/dichloromethane (v/v) (Fraction B). Fraction B was loaded onto a column containing 5% Amoco PX21-activated silica (w/w), eluted with 25% dichloromethane/hexane and added to Fraction A. The column was inverted and eluted with toluene to isolate a PCDD/PCDF/Co-PCB/PCN fraction. The HRMS system was tuned to ~10,000 RP. Co-PCBs (BZ# - 77, 81, 126, 169) and PCDDs/PCDFs (fraction B), mono-ortho PCBs (fraction A), and PCNs (fraction B) were analyzed in separate GC-HRMS runs. Analyses for PCDDs/PCDFs and DLPCBs were performed on a Micromass Autospec HRMS with a Hewlett-Packard HP6890 gas chromatograph using a 60m DB-5 column (0.25 mm i.d, 0.25 µm film thickness), while PCNs were analyzed using a Micromass Ultima-NT HRMS with a Hewlett-Packard HP6890 gas chromatograph with a 40m RTX-5 column (0.20mm i.d, 0.18 µm film thickness). Samples were analysed in splitless mode with He at 1.5 cm/s; injector temperature and transfer line temperature were maintained at 280°C and 300°C, respectively. All PCDD/PCDF and DLPCB data was corrected for surrogate recoveries. Quantitation of PCN homologs was based on relative response factors relative to ¹³C-labelled 2,3,7,8-tetraCDD. Instrument calibration for PCNs was performed using a 25-congener PCN mixture prepared from standards from Wellington Laboratories and Promochem.

Analysis of Hexabromocyclododecane. Extracts for HBCDD were prepared according to extraction/cleanup procedure for PCAs described above. The F2 fractions were reduced in volume and subsequently exchanged into 80% acetonitrile/water. Analyses were conducted on a MicroMass Quattro Ultima triple quadrupole MS equipped with a Waters 2695 LC and operated in atmospheric pressure chemical ionization (APCI) negative ion mode. Cone gas flow was 120 L/hr and the desolvation gas flow was 250 L/hr. The source temperature was 110°C and probe temperature was 500°C. Corona discharge amperage was 1 µa and cone voltage was 10 V. The mobile phase was 80% acetonitrile/water; the separation was performed isocratically on a 25 cm X 4.6 mm i.d. Vydac 218MS reversed-phase analytical HPLC column. The mass spectrometer was operated in SIR mode while monitoring the m/z 640.6 and m/z 642.6 ions. Quantitation was by external calibration using individual HBCDD isomer standards from CIL. A detailed description of some of our LC-MS methodology can be found elsewhere in these proceedings.

Results and Discussion

Dioxin-like Polychlorinated Biphenyls: The distribution of DLPCBs in Lake Ontario sediments was similar to PCDDs/PCDFs. DLPCBs included 4 coplanar (BZ# 77, 81, 126, 169) and 8 mono-ortho substituted congeners (BZ# 105, 114, 118, 123, 156, 157, 167, 189). The lake-wide average DLPCB concentration (9.4 pg/g TEQs) was roughly 10-fold lower than PCDDs/PCDFs (110 pg/g TEQs). These data are in contrast to those reported for fish; Lake Ontario TEQ ratios of DLPCBs to PCDDs/PCDFs are roughly 4 on average, indicating that DLPCBs are bioaccumulated to a greater extent than PCDDs/PCDFs. Relative concentrations among coplanar congeners were 77>126>169, however, PCB 126 generally accounted for more than 75% of sediment TEQs. The lake-wide average sediment concentration of PCDDs/PCDFs was 110 pg/g TEQs (2.81 ng/g); highest contamination was observed in depositional areas of the major lake basins. Based on analysis of a core sample from the central basin of Lake Ontario, accumulation of PCDDs/PCDFs and DLPCBs increased during the 1930s and 1940s; the greatest contamination occurred in the early 1950s to the late 1960s. Levels declined from the late 1960s to the early 1980s; further declines since the 1980s are not apparent. Assessment of homolog profiles and ongoing bottom

sediment and biomonitoring have implicated point source discharges within the Niagara River as primary contributors to PCDD/PCDF and DLPCB contamination in Lake Ontario.

C₁₀-C₁₃ Short-Chain Chlorinated Paraffins: SCCPs are used primarily as extreme temperature additives in metal working fluids, and in a variety of other applications including drilling, machining, drawing and stamping. These compounds are also used as additives, flame-retardants and plasticizers. SCCPs were found to be widespread in Lake Ontario sediments. The Lake Ontario lake-wide average PCA sediment concentration was 49 ng/g, which was slightly higher than the lake-wide average for Σ DDT (32 ng/g). Two individual stations in the northern area of the central basin and the southern area of the eastern basin exhibited concentrations of 154 ng/g and 147 ng/g, respectively. Fluxes of SCCPs to Lake Ontario sediments, estimated using sediment cores, were much higher in the western basin (170 $\mu\text{g}/\text{m}^2/\text{yr}$), compared to the central area of the lake (8.0 $\mu\text{g}/\text{m}^2/\text{yr}$); the high flux associated with the western basin indicated the presence of significant local sources. Maximum accumulation of SCCPs occurred in the period of the late 1960s to the early 1970s, with subsequent decreases during the period 1970 – 1998 of roughly 50%. Relative average contributions of the carbon chain groups to total PCAs were as follows: $\Sigma\text{C}_{10} = 24\%$, $\Sigma\text{C}_{11} = 35\%$, $\Sigma\text{C}_{12} = 34\%$, $\Sigma\text{C}_{13} = 6.6\%$. Relative contribution of the C₁₃ carbon chain appeared to be related to source type; some samples exhibited relatively low C₁₃ contributions, and exhibited SCCP profiles typical of urban residential areas while other samples exhibited high C₁₃ contributions and corresponding profiles indicative of highly industrialized areas. Figure 1 shows the relative contributions of the carbon chains in samples corresponding to urban residential and industrial areas. The averaged Lake Ontario profile is indicative of general urban residential activity.

Hexabromocyclododecane: HBCDD is the most heavily produced of the aliphatic BFRs, and is the primary flame retardant used in polystyrene. The technical mixture contains three isomers, the most predominant of which is the gamma (~80-90%), while the alpha (~5-10%) and beta (~5-10%) are minor components. Due to the fact HBCDD is an additive flame retardant, leaching could be a primary vector for release into the environment. Little is known of the distribution and fate of HBCDD in the North American environment. The HBCDD isomers are thermally labile and partition poorly on GC columns; therefore, we based our method on negative APCI-LC-MS. A companion paper in these proceedings describes our work in the determination of TBBP-a, a reactive BFR used primarily in printed circuit boards. Some areas of the Detroit River are intensively urbanized and industrialized. The distribution of HBCDD in the Detroit River was similar to other POPs, including PCDDs/PCDFs, DLPCBs and PCNs³, and reflected land use patterns within the watershed. Interestingly, only the alpha and gamma isomers were routinely detected while the beta was not detected, or found only at trace levels (Figure 2). Concentrations of HBCDD in Detroit River suspended sediments ranged from non-detect to 15 ng/g (alpha), 2.1 ng/g (beta) and 86 ng/g (gamma). These results indicate transformation processes in the sediments resulting in conversion of the beta isomer to one or both of the alpha and gamma.

References

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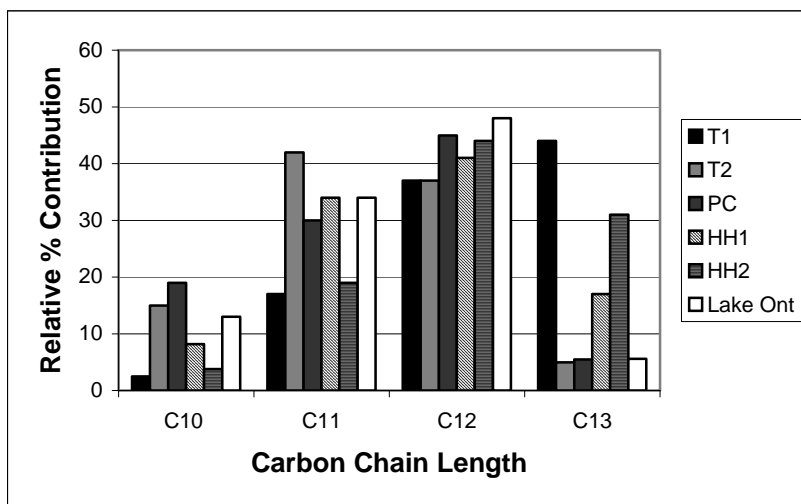


Figure 1: Relative contributions of SCCP carbon chain groups in sediments from Lake Ontario. T1 - Toronto industrial; T2 – Toronto residential; PC – Toronto residential; HH1 – Hamilton industrial; HH2 – Hamilton industrial, and; Lake Ont – lake-wide average for Lake Ontario.

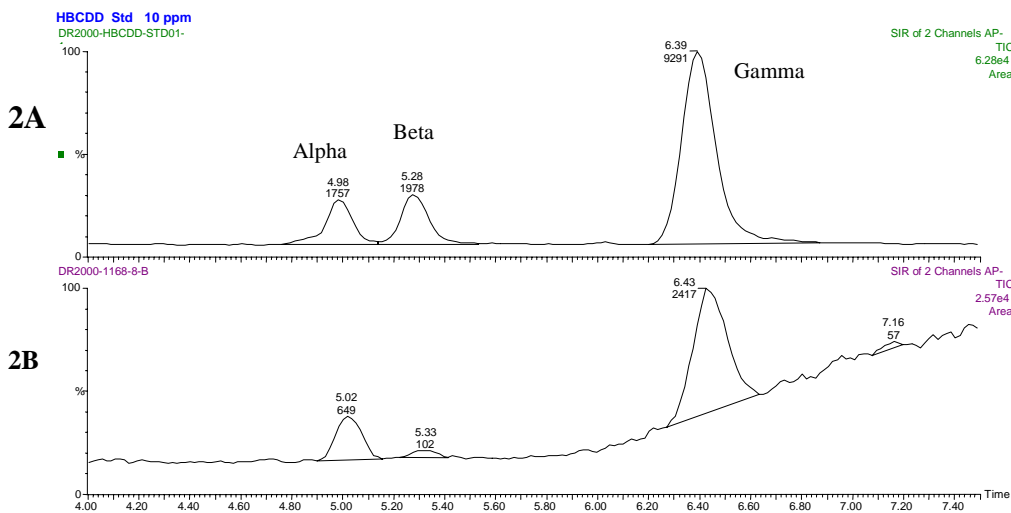


Figure 2: Negative APCI-LC-MS chromatograms showing a comparison of an HBCDD technical mixture (2A), and a suspended sediment sample from the Detroit River (2B).