

ENVIRONMENTAL LEVELS AND TRENDS

SPATIAL AND TEMPORAL TRENDS IN PERSISTENT ORGANIC POLLUTANTS IN LAKE ONTARIO SEDIMENTS

Chris Marvin¹, Gary Stern², Eric Reiner³, Karen MacPherson³, Terry Kolic³, Eric Braekvelt² and Scott Painter¹

¹Environment Canada, 867 Lakeshore Road, PO Box 5050, Burlington, ON, Canada L7R 4A6

²Freshwater Institute, Department of Fisheries and Oceans, 501 University Crescent, Winnipeg, MB, Canada R3T 2N6

³Ontario Ministry of the Environment, 125 Resources Road, Toronto, ON, Canada M9P 3V6

Introduction

A sediment survey was conducted to assess spatial and temporal trends in sediment contamination in Lake Ontario. The survey was also designed to assess changes in environmental quality since the advent of measures to reduce pollutant discharges, and to assist in the tracing of potential sources and vectors of contaminants. The suite of POPs analyses included polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs), dioxin-like PCBs (DLPCBs), toxaphene and polychloro-*n*-alkanes (PCAs).

Methods and Materials

Sediment samples were collected in Lake Ontario in 1998 using a mini box core sampling procedure. Samples consisted of fine-grained sediments classified as glacio-lacustrine clay, sand, silt or mud. The top 3 cm of the sediment was sub-sampled for analyses of POPs. At an index station in the central basin, a mini box core was collected to obtain both surficial and depth-integrated sediment samples; the core was sub-sampled in 1 cm increments from the surface to 16 cm, and every two cm thereafter to the bottom of the core.

Methods for the analysis and quantitation of toxaphene and PCAs are described in detail elsewhere^{1,2}. Dry sediment samples were extracted in dichloromethane; extracts were treated with mercury to remove sulphur and separated into three fractions on deactivated Florisil (1.2 % v/w water). Analyses were carried out using splitless injection with helium as a carrier gas on a Hewlett-Packard 5890 Series II gas chromatograph fitted with a 30m- or 60m X 0.25 mm i.d. (0.25 mm stationary phase) DB-5 column. Extracts were analysed for both PCAs and toxaphene congeners in separate analytical runs using high resolution gas chromatography/electron capture negative ionization - high resolution mass spectrometry (HRGC/ECNI-HRMS) carried out in selected ion mode (SIM) on a Kratos Concept (EBE geometry) at a resolving power of ~12,000. For toxaphene analysis, the moderating gas was argon; methane was used for analysis of PCAs

Analyses of sediments for PCDDs/PCDFs and DLPCBs were carried out using Ontario Ministry of the Environment (OME) standard methods (OME 2000). Dry samples were spiked with ¹³C-labelled surrogate 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. Analysis by HRGC/HRMS was carried out in SIM using a VG Ultima or Autospec HRMS equipped with a Hewlett-Packard 5890 gas chromatograph with a 0.25 mm i.d. 60 m DB-5 column (0.25 µm stationary phase).

ENVIRONMENTAL LEVELS AND TRENDS

Results and Discussion

Polychlorinated dibenzo-p-dioxins and dibenzofurans: The lake-wide average sediment concentration of PCDDs/PCDFs was 91 pg/g TEQs (2.81 ng/g); highest contamination was observed in depositional areas of the major lake basins (Figure 1). Four sites exhibited concentrations in excess of 200 pg/g TEQs. Based on analysis of a core sample from the central basin, accumulation of PCDDs/PCDFs increased during the 1930s and 1940s; the greatest contamination occurred in the early 1950s to the late 1960s (Figure 2). 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 contamination in Lake Ontario.

Toxaphene: The spatial distribution of toxaphene was similar to PCDDs/PCDFs (Figure 3). Sediment concentrations ranged from 0.09 ng/g to 7.7 ng/g with a lake-wide average of 2.6 ng/g. The two-most prevalent individual toxaphene congeners were B6-923 (Hx-Sed, 0.6 pg/g to 160 pg/g) and B7-1001 (Hp-Sed, 1.2 pg/g to 260 pg/g). Other prevalent congeners included B7-1450 and B7-1474+B7-1440. Average relative contributions of hexa, hepta, octa and nona homologs were 14 %, 54 %, 30 % and 3 %, respectively. Ratios of individual congeners were also investigated; Muir et al.⁴ reported that a ratio of B6-923 to B8-1413+B9-1679 <2 to be characteristic of atmospheric inputs. In general, samples within the deepest areas of the depositional basins exhibited the highest toxaphene concentrations and B6-923 to B8-1413+B9-1679 ratios >2, while other sites exhibited lower toxaphene levels and ratios <2. These data suggest that different processes including atmospheric deposition influenced toxaphene distributions in offshore depositional vs inshore sediments of Lake Ontario.

Dioxin-like polychlorinated biphenyls: The distribution of DLPCBs 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. These data are in contrast to those reported for fish; Lake Ontario TEQ ratios of DLPCBs to PCDDs/PCDFs are roughly 4 on average⁵, 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.

C₁₀-C₁₃ Polychloroalkanes: In contrast to the other compounds, PCAs exhibited a more consistent lake-wide distribution (Figure 4). The lake-wide average PCA sediment concentration was 36 ng/g, which was similar to the lake-wide average for SDDT (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. Relative average contributions of the formula groups to total PCAs were as follows: $\Sigma C_{10} = 24 \%$, $\Sigma C_{11} = 35 \%$, $\Sigma C_{12} = 34 \%$, $\Sigma C_{13} = 6.6 \%$. Core samples are currently being analyzed in order to assess the relative importance of atmospheric vs potential local sources.

References

1. Braekvelt, E., Tomy, G.T. and Stern, G.A. (2001) Environ Sci Technol. 35, 3513.
2. Tomy, G.T., Stern, G.A., Muir, D.C.G., Fisk, A.T., Cymbalisty, C.D. and Westmore, J.B. (1997) Anal Chem. 69, 2762.
3. Ontario Ministry of the Environment. (2000). The determination of polychlorinated dibenzo-p-dioxins, polychlorinated furans and dioxin-like PCBs in environmental matrices by GC-MS. Environment Ontario Laboratory Services Branch Method DFPCB-E3418. Toronto, ON, Canada.
4. Muir, D.C.G., Stern, G.A. and Karlsson, H. (1999) Organohalogen Compounds. 41, 565.
5. Kolic, T.M., MacPherson, K.A., Reiner, E.J., Gobran, T. and Hayton, A. (2000) Organohalogen Compounds. 46, 562.

ENVIRONMENTAL LEVELS AND TRENDS

Legend

- 0 - 10
- 10 - 20
- 20 - 100
- 100 - 200
- 200 +



Figure 1. Distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (pg/g TEQs) in Lake Ontario surficial sediments in 1998.

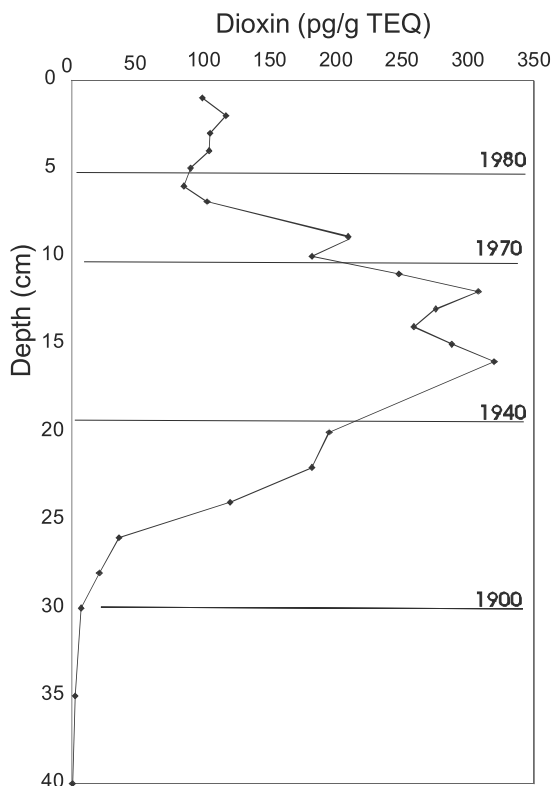


Figure 2. Profile of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (pg/g TEQs) in a Lake Ontario box core sampled from the Mississauga Basin.

ENVIRONMENTAL LEVELS AND TRENDS



Figure 3. Distribution of total toxaphene (ng/g) in Lake Ontario surficial sediments in 1998.



Figure 4. Distribution of C₁₀-C₁₃ polychloroalkanes (ng/g) in Lake Ontario surficial sediments in 1998.