

PERSISTENT ORGANIC POLLUTANTS ASSOCIATED WITH SUSPENDED SEDIMENTS IN THE WESTERN LAKE ERIE – DETROIT RIVER CORRIDOR

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Introduction

The Detroit River lies in the heart of the Great Lakes basin and provides the link between western Lake Erie and Lake St. Clair. The binational watershed includes the metropolitan areas of Detroit, Michigan and Windsor, Ontario, with an associated population of approximately three and a half million people. The environmental health of the river has been identified as being impaired, in part due to the impacts of persistent organic pollutants (POPs).

Environment Canada is currently monitoring suspended sediment quality in the Detroit River corridor to assess the occurrence and spatial distribution of POPs in order to better understand the role anthropogenic activities play in discharging these compounds, and provide information to devise effective strategies to mitigate deleterious impacts. In this paper, we present the spatial distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs), non-ortho substituted and coplanar polychlorinated biphenyls (Co-PCBs), and polychlorinated naphthalenes (PCNs) in Detroit River suspended sediments.

Methods and Materials

*Analysis of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans and Polychlorinated Biphenyls*

Air-dried samples were spiked with ¹³C-labelled 2,3,7,8-substituted isomers and Soxhlet extracted in toluene for 16 hrs followed by an open column cleanup. The first column contained 1.5 g 10% silver nitrate; 1.0 g activated silica; 2.0 g 33% sodium hydroxide/silica; 1.0 g activated silica; 4.0 g sulphuric acid/silica; 2.0 g activated silica, and; 2.0 g anhydrous sodium sulphate. The column was eluted with hexane and transferred to a column containing 5.0 g of activated alumina and 2.0 g of 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-PCBs and remaining mono-ortho PCBs were eluted with 10% methanol/dichloromethane (v/v) (Fraction B). Fraction B was loaded onto a column containing 0.35 g 5% Amoco PX21-activated silica (w/w), eluted with 40 mL 25% dichloromethane/hexane and added to Fraction A. The column was inverted and eluted with 160 mL of toluene to isolate a PCDD/PCDF/Co-PCB fraction. Analyses were performed on a VG Autospec GC-HRMS with an HP6890 gas chromatograph with a 60m DB-5 0.25mm i.d 0.25µm film thickness (J&W Scientific). The GC-HRMS system was tuned to 10,000+ RP (10% valley definition).

Co-PCBs (BZ# - 77, 81, 126, 169) and PCDDs/PCDFs were analyzed in a 6-function MS experiment. Mono-ortho PCBs were analyzed as a separate fraction in a 4 function MS experiment. Samples were analysed in splitless mode with He carrier gas at a flow rate of 1.5 cm/s; injector temperature and transfer line temperature were maintained at 280°C and 300°C, respectively. Temp. program for Fraction A: 150°C for 1 min; 150°C to 200°C at 5°C/min; 200°C to 235°C at 3°C/min; 235°C for 10 min; 235°C to 300°C at 12°C/min; 300°C for 1 min. Temp. program for Fraction B: 100°C for 1 min; 100°C to 200°C at 30°C/min; 200°C to 235°C at 3°C/min; 235°C for 10 min; 235°C to 300°C at 6°C/min; 300°C for 12 min.

Analysis of Polychlorinated Naphthalenes

Dry samples were extracted in dichloromethane at 100°C and 2,000 psi using an Accelerated Solvent Extractor (ASE, Dionex Inc.). Extracts were subjected to an open-column deactivated Florosil [2g] cleanup; elution with 10 mL 50% pentane in dichloromethane [Fraction A] followed by 10 mL dichloromethane [Fraction B] afforded two fractions. Surrogate standards applied to sediment prior to extraction included PCB #30 and PCB #204. Fraction B was analyzed in SIM mode on a MicroMass Autospec-Ultima operated at 10,000 (10% valley) resolution with a Hewlett-Packard 6890 GC using splitless injection and a 60-metre fused silica 0.25 mm i.d. DB-5 column with a 0.30 µm stationary phase. Carrier gas was helium at 1.5 cm/s and the injector temperature and transfer line temperatures were 280°C and 260°C, respectively. The following temperature program was used: 110°C for 1.5 min; 110°C to 180°C at 15°C/min; 180°C to 280°C at 2°C/min; 280°C for 5 min. Method blanks and standard reference materials (SRMs) were processed with each set of 10 field samples. Quantitation was based on an external standard method using 2 ions per congener. A 25-congener mixed standard was prepared from individual standards from Wellington Laboratories and Promochem.

Results and Discussion

Trends in the spatial distribution of all three classes of contaminants were similar. Figure 1 shows the spatial distribution of the combined PCDD/PCDF and Co-PCB TEQs in suspended sediments in the Detroit River corridor. The TEQs for PCDDs/PCDFs and Co-PCBs were calculated according to WHO TEFs¹. TEQs for Co-PCBs were based on analysis of 12 congeners (BZ# 81, 77, 123, 118, 114, 105, 126, 167, 156, 157, 169 and 189). At all eight stations, PCB# 126 was responsible for greater than 50% of TEQs calculated for Co-PCBs; the mean percent TEQs attributable to this congener was 73%. Kannan et al.² also observed PCB# 126 contributed greater than 50% of PCB-related TEQs in fish from Michigan waters, including the Detroit River.

There was a gradient toward increasing concentrations of PCDD/PCDF and Co-PCB TEQs moving downstream through the Trenton Channel. Highest concentrations of all three compound classes were detected at a site in the upper Trenton Channel near Monguagon Creek (Station 1161), which discharges a highly industrialized watershed. Levels of contaminants at the two sites in the Trenton Channel were elevated, compared to a site on the eastern side of the river near Fighting Island (Stn 804). The Fighting Island site exhibited TEQ values similar to stations upstream in the upper reaches of the river (Stns 1162 and 803), and in southern Lake St. Clair (Stn 1160). The influence of the Trenton Channel was also evidenced by elevated contaminant levels at a site on the western side of the river at the outflow to Lake Erie (Stn 1157). Concentrations of TEQs at this site were roughly three-fold higher than a corresponding site on the Canadian side (Stn 1156).

AQUATIC ENVIRONMENT

Spatial trends in PCN contamination were similar to those of PCDDs/PCDFs and Co-PCBs. The highest concentrations of PCNs were detected at Station 1161 near Monguagon Creek in the Trenton Channel. Figure 2 shows levels of some predominant PCN congeners in relation to sample sites. Additional congeners present at levels greater than 1 ng/g at Station 1161 included PCNs 13, 36, 27 and 48. Levels of total PCNs, based on the sum of congeners meeting ion abundance ratios for confirmatory identification, ranged from 1.25 ng/g at Fighting Island (Stn 804) to 400 ng/g at Monguagon Creek (Stn 1161).

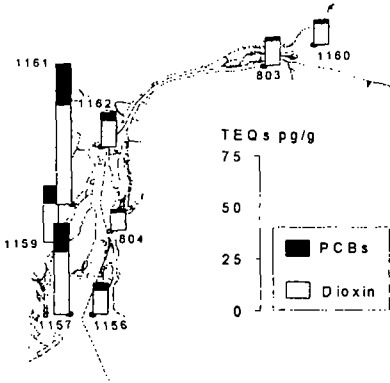


Figure 1. Spatial distribution of toxic equivalents of co-planar PCBs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans determined in suspended sediments from the Detroit River.

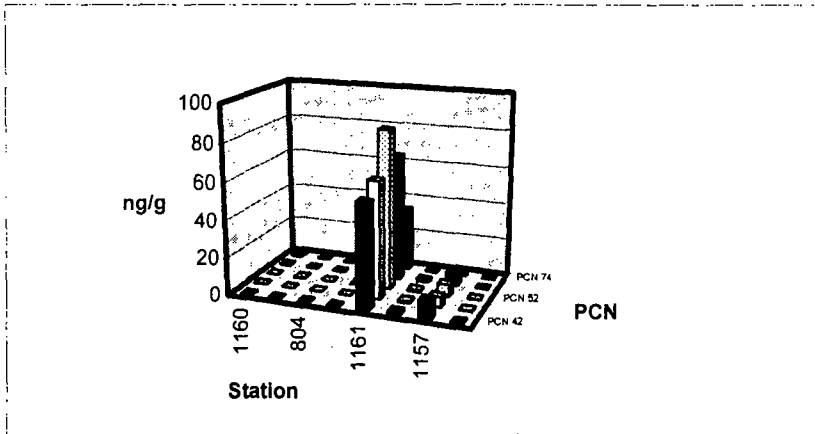


Figure 2. Spatial distribution of selected PCN congeners (ng/g dry wt.) in Detroit River suspended sediments.

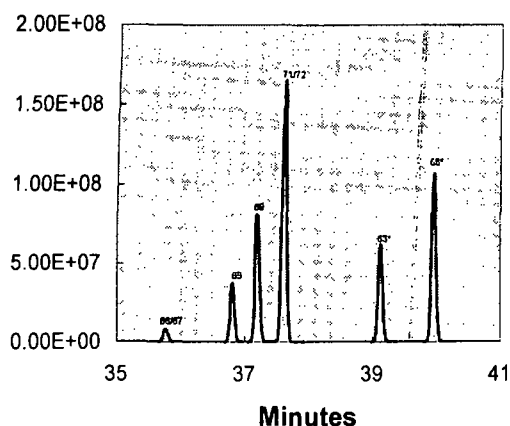


Figure 3. Ion chromatogram (sum of m/z 333.8288 and m/z 335.8210) showing tentatively identified hexa-substituted PCN congeners in suspended sediment from the Trenton Channel (Station 1161), Detroit River. *Denotes congener identifications assigned through retention time and mass spectral comparisons with congeners in Halowax 1014.

The PCN analyses also indicated the presence of other congeners, including congeners 66/67 and 69, which are reported to be the most biologically active³. The presence of interfering compounds resulted in some ion abundance ratios falling outside criteria, which precluded definitive quantitation of some congeners. Figure 3 shows the ion chromatogram for the hexa-substituted PCN congeners, tentatively identified by molecular mass and retention time. Kannan et al.² observed PCN profiles in fish from the Detroit River that were similar to that of Halowax 1014. Two congeners (PCN 63 and PCN 65) were tentatively identified based on a comparison with the hexa-substituted congener profile of Halowax 1014.

Acknowledgments

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