TEMPORAL TRENDS IN POLYCHLORINATED DIOXINS AND FURANS, DIOXIN-LIKE PCBS AND POLYBROMINATED DIPHENYL ETHERS IN NIAGARA RIVER SUSPENDED SEDIMENTS

Marvin Chris[1], Donald Williams[1], Ken Kuntz[1], Eric Reiner[2], Terry Kolic[2], Corina Lucaciu[2], Karen MacPherson[2]

[1]Environment Canada, Burlington
[2]Ontario Ministry of the Environment, Toronto

Introduction

Monitoring of surface water in the Niagara River has been conducted over the past 25 years to track changes/trends in concentrations/loads of toxic chemicals in response to implemented control measures. Concentrations of pollutants are measured in both dissolved and particulate phases from weekly water samples collected at the head of the river at Fort Erie, and the mouth at Niagara-on-the-Lake. Analyses have focused on a number of priority toxics including PCBs, PAHs, organochlorine pesticides, industrial by-products and metals. We have analyzed archived particulate samples from the period 1980 – 2002 at Niagara-on-the-Lake to assess trends in contaminants associated with historical industrial activities in the watershed (polychlorinated dibenzo-*p*-dioxins and dibenzofurans, dioxin-like PCBs), compared to more modern industrial chemicals (polybrominated diphenylethers).

Methods and Materials

Water at the mouth of the Niagara River was collected using a large-volume 24-hour time-integrated dissolved/particulate phase sampling protocol under the auspices of the Niagara River Upstream/Downstream Program[1]. Freeze-dried archived samples analyzed in this study represent April and/or May samples.

Methods for analysis of dioxin-like compounds and PBDEs are described in detail elsewhere[2]. For analysis of PCDDs/PCDFs and DLPCBs, samples were spiked with ^{13}C-labelled surrogate standards (Wellington Laboratories Inc.,Guelph, ON, Canada) 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, which 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), 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 fraction. The HRMS system was tuned to ~10,000 RP. Co-PCBs and PCDDs/PCDFs (fraction B) and mono-ortho PCBs (fraction A) were analyzed in separate runs. Analyses were performed on a Micromass Autospec with a Hewlett-Packard HP6890 gas chromatograph using a 60m DB-5 column (0.25 mm i.d, 0.25 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.

For analysis of PBDEs, samples were fortified with ^{13}C-labelled PBDE quantification standards with one congener for each homologue group. Fortified samples were Soxhlet extracted overnight in toluene for approximately 12-16 hours. Cleanup was performed using an acid/base/silver nitrate silica column. After initial elution with hexane, the PBDEs were eluted with hexane followed by hexane/DCM (50:50). Chromatographic separation for the tri-BDEs to deca-BDE was achieved on a DB-5HT 15m X 0.25mm X 0.10 μm (J&W Scientific, USA), and the GC-HRMS system was tuned to greater that 9000 RP. Total PBDEs represent the sum total of the following 16 congeners: BDE-17; BDE-28; BDE-47; BDE-49; BDE-66; BDE-71; BDE-77; BDE-85; BDE-99; BDE-100; BDE-119; BDE-126; BDE-138; BDE-153; and BDE-183.

Results and Discussion

Trends in PCDDs/PCDFs and DLPCBs: Assessment of homologue profiles and ongoing bottom sediment and biomonitoring have implicated non-point source discharges within the Niagara River as primary contributors to PCDD/PCDF and DLPCB contamination in Lake Ontario. The temporal trends in PCDDs/PCDFs and DLPCBs at the mouth of the Niagara River are shown in Figure 1. Data for 1980 have been omitted, as inclusion of these relatively high concentrations (43.6 pg/g TEQ for PCDDs/PCDFs and 39.5 ng/g for DLPCBs) made trend analysis more difficult. General profiles for both PCDDs/PCDDs and DLPCBs are similar, and show a general trend toward decreasing concentrations, which is presumably due to implementation of control measures in the watershed, including remediation of hazardous waste facilities. Based on a previous study of sediment contamination in Lake Ontario, maximum accumulation of PCDDs/PCDFs and DLPCBs occurred in the early 1950s to the late 1960s; levels subsequently declined from the late 1960s to the early 1980s, but further declines since the 1980s were not apparent[3]. The current data indicate that loadings of PCDDs/PCDFs and DLPCBs are decreasing, and that further reductions in contamination on a lake-wide basis are to be expected.

Trends in PBDEs: Total PBDEs are expressed as the total of 18 congeners. The temporal trend in PBDEs (Figure 2) contrasted with those of PCDDs/PCDFs and DLPCBs. Prior to 1988, PBDEs were generally detected at low-ppb concentrations, but appear to show a trend toward increasing concentrations over the period 1981 – 1988. Prior to 1989, most of the PBDE burden was attributable to decaBDE (Figure 2); average contribution of decaBDE to total PBDEs over this period was 89%. After 1988, PBDE concentrations showed a more rapidly increasing trend to a maximum of approximately 35 ng/g in 1995. Despite the considerable inter-year variability in PBDE concentrations during the mid- to late-1990s, there is still a definitive trend toward increasing concentrations. An explanation for this variability is that spring samples are influenced

to varying extents by sediments originating upstream in Lake Erie; future work will focus on summer samples with greater contributions of particulate derived locally within the watershed, which may result in a more consistent temporal trend. An increase in PBDEs in the late-1980s and early 1990s was similarly observed by Luross et al.[4] in Lake Trout from the Great Lakes, which was attributed to increased PBDE usage as a result of the banning of polybrominated biphenyls and Mirex in the late-1970s.

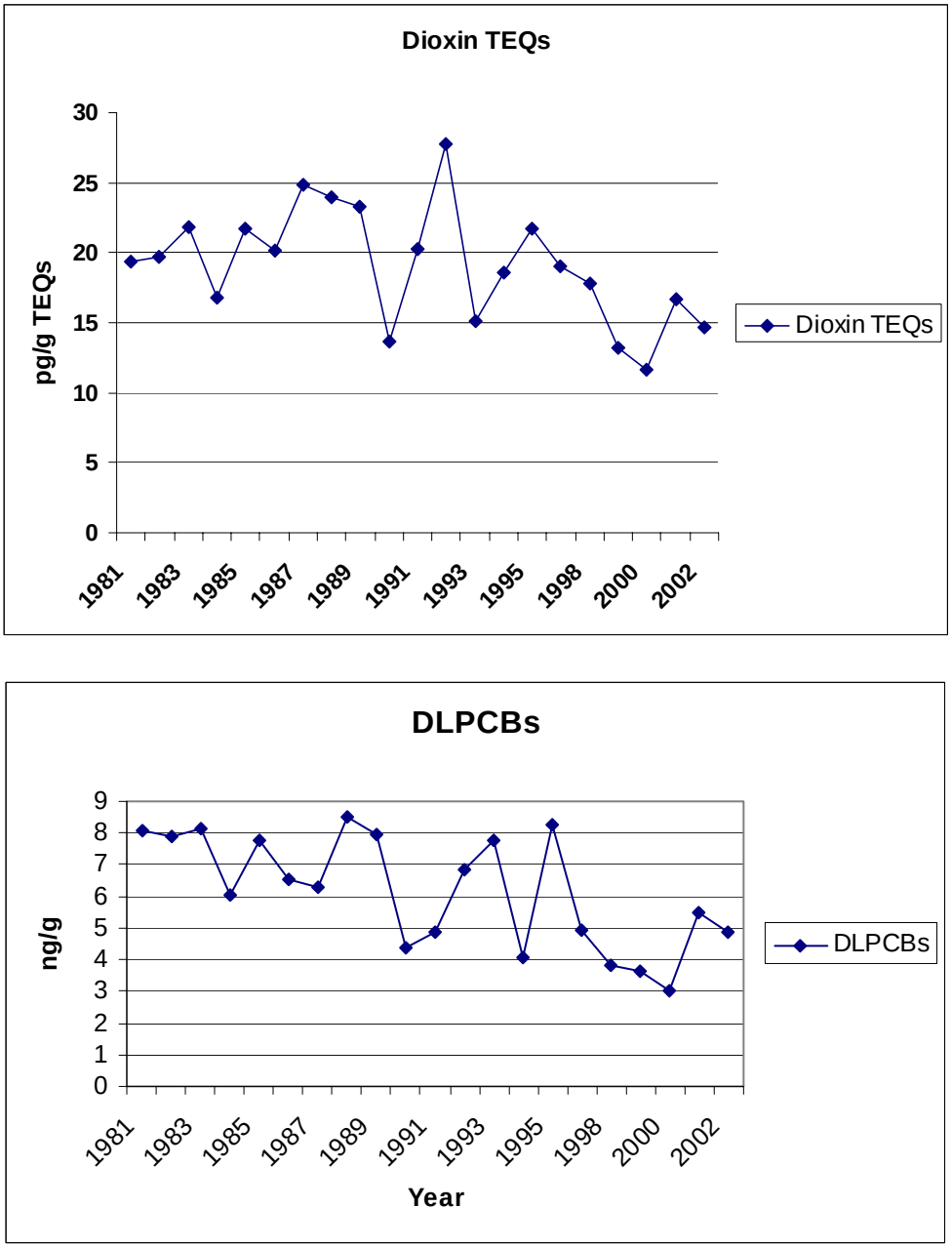
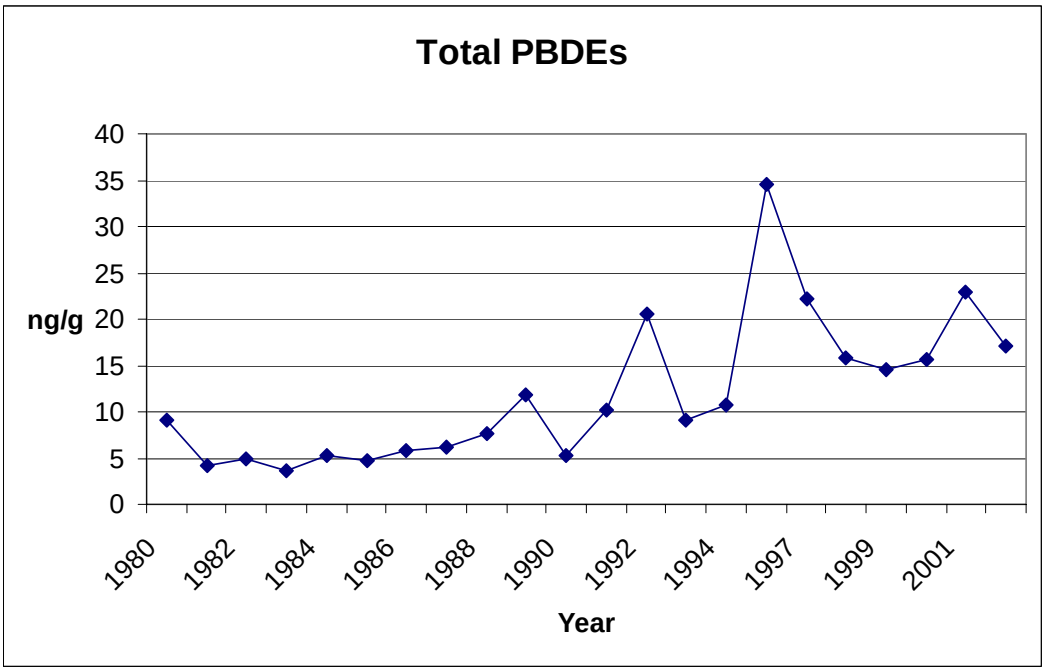
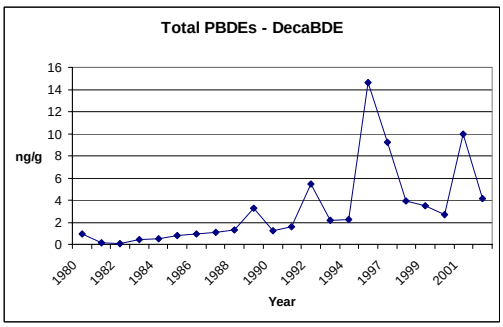


Figure 1: Concentrations of PCDDs/PCDFs (top) and DLPCBs (bottom) in Niagara River suspended sediments over the period 1981 – 2002.





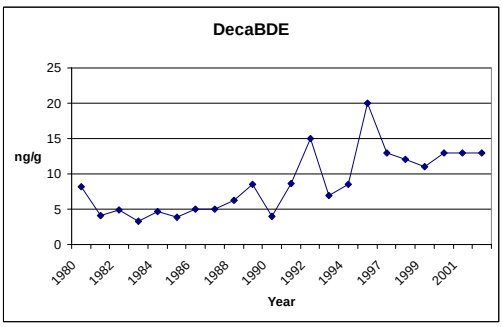


Figure 2: Concentrations of PBDEs in Niagara River suspended sediments over the period 1980 – 2002. Bottom panels also show trends for total PBDEs without decaBDE (left), and decaBDE exclusively (right).

References

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