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Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans associated with settling particles in Lake Ontario

Christopher H. Marvin [a,*], Deborah A. Burniston [a], Li Shen [b], Paul A. Helm [b], Eric J. Reiner [b]

[a] Water Science and Technology Directorate, Environment and Climate Change Canada, 867 Lakeshore Road, Burlington, Ontario, L7S 1A1, Canada
[b] Ontario Ministry of Environment and Climate Change, 125 Resources Road, Toronto, Ontario, M9P 3V6, Canada

HIGHLIGHTS

- Sediment traps in Lake Ontario were used for assessment of dioxins and furans from the Niagara River.
- Seasonal samples showed influences of water column characteristics on concentrations and fluxes.
- Sediments in Lake Ontario were more contaminated than particulate material from the Niagara River.
- Congener profiles indicated the Niagara River episodically contributed loadings to Lake Ontario.
- Dioxin and furan inputs originated from both atmospheric and non-atmospheric sources.

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ABSTRACT

Sediment traps were deployed at seven sites in the western and central basins of Lake Ontario for calculation of concentrations and down fluxes for polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) to assess ongoing loadings to Lake Ontario from the Niagara River watershed. Traps were deployed at multiple depths (beginning at 20 m) during two seasonal time periods at stations impacted by the outflow of the Niagara River, and stations reflecting deeper water offshore conditions. Settling particles were collected seasonally to assess the influence of physical characteristics of the water column, i.e., isothermal conditions vs. stratified conditions, on concentrations and fluxes of PCDD/Fs. At all stations and for all depth intervals, PCDD/F concentrations were higher in the winter sampling period (range of 3120–10,600 pg g^{-1}), compared to the spring – summer – fall time period (range of 320–6900 pg g^{-1}). These results indicated bottom sediments in central and western Lake Ontario were more highly-contaminated, compared to contemporary particulate material entering the lake via the Niagara River or resulting from shoreline erosion. However, assessment of PCDD/F congener profiles and ratios also indicated source areas within the Niagara River watershed continued to episodically contribute loadings to Lake Ontario. The results also indicated changes in discharges of PCDD/Fs from sources in the Niagara River result in changes in congener profiles in settling particles, which can be detected by continued monitoring.

1. Introduction

Settling particles are an important vector for contaminant transport through the water column in the Great Lakes. Contaminants originating from a variety of sources, including watershed-based activities and atmospheric deposition (wet, dry and indirect) (Cohen et al., 2002; Norstrom, 2005; Pearson et al., 1997, 1998), can enter the lakes thru sorption on particulate material, or can be partitioned onto settling particles from the dissolved phase. Settling particles are subject to prevailing lake circulation patterns before ultimately settling in depositional areas. Common methods for sampling of settling particles include centrifugation and sediment traps. Sediment traps offer the advantage of time-integrated sampling over a period of weeks or months, thereby enabling estimates of contaminant down fluxes useful in investigating pathways and assessing loading patterns and inventories. Sediment traps deployed in areas of relatively high sedimentation collect material reflecting current loadings that may not be manifest in

* Corresponding author
E-mail address: .chris.marvin@canada.ca (C.H. Marvin).

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bottom sediments until a substantially later point in time. Sediment traps have been used for studies of contaminants, nutrients, and sedimentation rates in the Great Lakes (Baker et al., 1991; Chambers and Eadie, 1981; Charlton, 1983; Eadie et al., 1984; Marvin et al., 2004; Oliver and Charlton, 1984; Oliver et al., 1989).

The impacts of the Niagara River on Lake Ontario from a chemical contamination perspective are well documented (Allan et al., 1983). The Niagara River contributes over 80% of tributary inflow (Eadie and Robertson, 1976), 85% of the total input water budget and approximately 50% of fine-grained sediments (Kemp and Harper, 1976). In the late 1960s, hazardous waste sites and chemical industry outfalls were implicated as primary sources of toxics, including PCBs, PCDD/Fs and organochlorines to the Niagara River (Oliver et al., 1989; Allan et al., 1983; Eadie and Robertson, 1976); perhaps the most notorious of these sites was Love Canal, which before remediation was one of the largest chemical dumps in the United States (International Joint Commission, 2002). In the early 1980s, a major study was conducted that determined environmental compartments in the river to be heavily contaminated with a range of persistent toxics including PCBs, PCDD/Fs and organochlorines (NRTC, 1984). As a result of these toxics issues, the Canadian and American state, provincial and federal environmental agencies implemented the Niagara River Toxics Management Plan in 1987 to cooperate in reducing loadings to the river from both point- and non-point sources. The focus on selected hazardous waste sites (26 sites) on the American side of the river judged at the time to have the greatest potential for loadings of toxics to the river, and subsequent remedial activities, resulted in demonstrable and significant reductions in contamination in the Niagara River (Williams et al., 2000; Niagara River Secretariat, 2007).

Chlorinated dioxins and furans are chemical classes comprised of 75 polychlorinated dibenzo-*p*-dioxin (PCDD) congeners and 135 polychlorinated dibenzofuran (PCDF) congeners, of which 17 (7 PCDDs and 10 PCDFs) are substituted at the 2,3,7 and 8 positions resulting in physical/chemical properties conducive to increased bioaccumulation and toxicity (Reiner et al., 2006). The occurrence and distribution of PCDD/Fs in Lake Ontario have been previously reported (Marvin et al., 2003; Shen et al., 2008) and assessment of spatial distributions and statistical analyses of PCDD/F congener profiles have implicated the Niagara River watershed as a primary source of contamination. Atmospheric deposition (wet and dry) is the most predominant vector for PCDD/Fs entering the Great Lakes (Cohen et al., 2002; Norstrom, 2005) (80% of total loadings), of which 63% originates from outside of the Great Lakes basin (Cohen et al., 2002). Atmospheric deposition accounts for the majority of the PCDD/F inputs to Lake Erie (Norstrom, 2005; Czuczwa and Hites, 1986) and while the Niagara River transports 80% of tributary flow and 50% of fine-grained sediment to Lake Ontario, congener profiles in Lake Ontario sediment have indicated atmospheric deposition accounts for less than 10%–30% of PCDD/F inputs (Norstrom, 2005; Pearson et al., 1997). However, it should be considered these reports are based on data from samples collected in the mid-1990s.

The occurrence and distribution of PCDD/Fs have also been studied in the Niagara River itself. Marvin et al. (2007a) established a temporal trend toward decreasing concentrations of PCDD/Fs in suspended particles from the Niagara River Upstream – Downstream (U/D) Program sampled over the period 1980–2002; this decreasing trend was attributed to implementation of control measures in the Niagara River watershed. However, the limited data set ($N = 1$ annually) did not allow for a statistical analysis of the temporal trend, and the rate of decrease of PCDD/Fs was not as significant, compared to other industrial chemicals. More recently, Burniston et al. (2015) assessed bi-weekly samples from the Niagara RiverU/D Program and determined that loadings of PCDD/Fs from hazardous waste sites in the Niagara River watershed have occurred episodically; event-based concentrations were up to two orders magnitude greater than typical concentrations representative of baseline conditions (1000–6000 pg g^{-1}). The PCDD/F congener profiles of event-based samples were enriched in 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF) or 2,3,7,8-tetrachlorodibenzodioxin (TCDD), which provided further evidence of the influence of the Niagara River on contamination in open-water depositional areas of Lake Ontario (Burniston et al., 2015).

The Ontario Ministry of the Environment has conducted a long-term biomonitoring program in the river since 1983 using the freshwater mussel *Elliptio complanata* (Richman et al., 2011). The early stages of the program were focused on source identification, while in more recent studies the goal was to assess the efficacy of remedial actions at priority sites. The results from the biomonitoring program in terms of the success of remedial activities have been mixed; while some sites appear have been effectively remediated, others appear to continue to discharge PCDD/Fs to the river. Of particular note were indications of ongoing PCDD/F contamination in the lower reaches of Bloody Run Creek, which discharges the Hyde Park Dump (Howdeshell and Hites, 1996), and Pettit Flume Cove that has historically received discharges from chemical companies and hazardous waste sites (Richman et al., 2011). These two sites have distinct congener profiles which have been determined in previous studies to influence Niagara River suspended particles (Burniston et al., 2015; Richman et al., 2011).

Previous studies of contaminants associated with settling particles using sediment traps were conducted in the early 1980s to investigate the changes in loadings as a result of measures to reduce discharges from areas within the Niagara River area of western Lake Ontario during the 1960s and 1970s (Oliver and Charlton, 1984; Oliver et al., 1989). These studies provided information on contaminant transport that was used to assist in the interpretation of spatial trends in data from studies of contaminants in lake bottom sediments (Marvin et al., 2003; Shen et al., 2008). In this paper, we report the results of the analysis of settling particles collected at individual stations in the Niagara (western) and Mississauga (central) basins of Lake Ontario. An understanding of the behavior and pathways of settling particles in the water column is important for assessing the significance and extent that contaminated sediment acts as a source. Concentrations and down fluxes for PCDD/Fs were calculated. In addition, congener profiles and ratios were generated and compared with samples representing ambient background and source areas of the Niagara River in order to assess the ongoing loadings of PCDD/Fs to Lake Ontario.

2. Materials and methods

2.1. Sample collection

Settling particles were collected spatially over time at varying depth intervals (SI Tables S2 and SI Fig. S1) at individual stations in the western (Niagara) and central (Mississauga) basins of Lake Ontario. Stations were based on those studied previously by Oliver and Charlton (Chambers and Eadie, 1981) who positioned sediment traps to capture particulates originating from the Niagara River. Three of the stations (207, 208, 209) were arranged 8–10 km off the mouth of the Niagara River in a semi-circular pattern at the outer edge of the river plume; this plume was previously characterized by Charlton (1983); Charlton, 1983 based on transmission and temperature profiles. Water depths at these stations was approximately 70 m. Station 210 (70 m depth) was located roughly 14 km further east in an area influenced by the Niagara River as a result of the