Chemosphere 123 (2015) 71–78

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Niagara River suspended sediments

D.A. Burniston *, P. Klawunn, B. Hill, C.H. Marvin

Water Science and Technology Directorate, Environment Canada, 867 Lakeshore Road, Burlington, ON L7R 4A6, Canada

HIGHLIGHTS

- Archived Niagara River suspended sediment was analyzed for dioxins and furans.
- Results indicate episodic discharges of dioxins and furans from identified hazardous waste sites.
- Congener profiles in Lake Ontario implicate the Niagara River as a source of dioxins.
- The temporal trend indicates little change since 1990.

ARTICLE INFO

Article history:
Received 21 May 2014
Received in revised form 29 September 2014
Accepted 27 October 2014
Available online 27 December 2014

Handling Editor: H. Fiedler

Keywords:
Polychlorinated dibenzo-*p*-dioxins
Niagara River
Suspended sediments
Great Lakes
POPs

ABSTRACT

Niagara River archived suspended sediments were analyzed for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) to investigate temporal trends and to assess congener profiles as source indicators. In general, concentrations ranged from 6 to 35 pg g^{-1} toxic equivalents (TEQs) and 1000–6000 pg g^{-1} total PCDDs/Fs and reflected a slight decline in the 1980s, but with little apparent change since that time. This temporal trend was consistent with those observed in Lake Ontario environmental compartments. The observed levels generally reflected ambient background levels in the Niagara River; however, three samples were substantially above ambient levels and a fourth sample, while not elevated, had a profile that was distinctly different from those typically observed at Niagara-on-the-Lake at the mouth of the Niagara River. Event-based concentrations ranged from approximately 160–620 pg g^{-1} TEQs; congener profiles for these samples were consistent with known source areas in the Niagara River watershed, including Pettit Flume and Bloody Run Creek. These qualitative and quantitative results indicated loadings of dioxins and furans from hazardous waste sites in the Niagara River are occurring episodically, and can be measured in suspended sediments downstream at the river mouth at Niagara-on-the-Lake.

1. Introduction

The Niagara River is the principal connecting channel between Lakes Erie and Ontario and has a drainage basin of almost 700 000 square kilometers with a long-term average flow of 6000 cubic meters per second. This flow accounts for 83% of the tributary flow and 50% of all fine grained sediment entering Lake Ontario. The two sides of the river are markedly different in their degrees of industrialization/urbanization. The New York watershed is highly urbanized and heavily industrialized between Buffalo and Niagara Falls, while on the Ontario side land use is primarily agriculture, parks, urbanized (23%) and forested.

During the early part of the 20th century Niagara Falls become home to an extensive array of chemical manufacturing due to the abundance of hydroelectric power and process water. During most of the century, and especially during the Second World War, plastic and chemical production along the River increased with the manufacturing of chemicals that included halogenated benzenes, toluenes, phenols and aliphatics. The manufacture of these chemicals produced massive amounts of waste by-products. There are 24 hazardous chemical waste dumps located along the Niagara River in New York believed to represent non-point source loadings of toxics as late as 1996. (Holland, 1996)

The Hyde Park Landfill is a 15 acre site located less than ½ mile from the Niagara River in northwestern Niagara Falls (Fig. 1). The drainage from the landfill formerly flowed through Bloody Run Creek (BRC), located 2000 feet northwest of the site and discharges into the Niagara River gorge. The landfill is owned by Occidental

* Corresponding author. Tel.: +1 905 336 4703.
E-mail addresses: debbie.burniston@ec.gc.ca (D.A. Burniston), paul.klawunn@ec.gc.ca (P. Klawunn), chris.marvin@ec.gc.ca (C.H. Marvin).

http://dx.doi.org/10.1016/j.chemosphere.2014.10.086
0045-6535/

Chemical Corporation, formerly Hooker Chemical and plastics. Approximately 80 000 tons of hazardous materials were dumped at the site from 1953 to 1974 (Koszalka et al., 1985). Chemical waste from 2,4,5-trichlorophenoxyacetic acid manufacture, used as a defoliant, was a significant source of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). An estimated 0.7–1.5 ton of 2,3,7,8-TCDD, the most toxic PCDD/F congener, may still reside in this landfill (National Research Council, 1987). These contaminants, along with other chlorinated organic chemicals, required installation of a clay cap and shallow leachate collection system around the landfill area in 1979 (USEPA, 2000). Since that time, additional work has been completed including a deeper leachate collection system around the existing landfill. Monitoring data showed that surface water and groundwater along BRC had been contaminated by wastes leaching from this landfill (USEPA, 2000).

Pettit Flume (PF) is a mile-long concrete box culvert installed along the bed of Pettit Creek (Fig. 1). It is a municipal storm sewer that drains the Occidental Durez plant, owned by Occidental Chemical (formerly owned by Hooker Chemical), and surrounding hazardous waste sites, as well as receiving urban runoff from North Tonawanda. PF discharges into the Inlet Cove, a ¾ acre lowland embayment area located at the outfall of PF. The plant, located in the city of North Tonawanda, has been in operation since 1926 producing various plastic formulations and disposing of its wastes on site; these chemical wastes include chlorinated benzenes, phenol, chlorinated phenols, chlorotoluenes and other organic compounds. Contaminants from the site migrated via the storm sewer system and contaminated the sediment at the PF outfall area. Remediation included containment of the plant site, cleaning of storm sewers and contaminated sediment excavation from the storm sewer outfall area (USEPA and NYSDEC, 1993; USEPA, 2000).

The PCDD/F levels began to increase in Lake Ontario sediment around 1940, coinciding with the rapid growth of the organic chemical manufacture in response to the outbreak of World War II (Czuczwa and Hites, 1984). The disposal of PCDDs/Fs as a waste products of chemical production reached a maximum in the late 1960s (Pearson et al., 1998; Marvin et al., 2002), followed by a decline marked by the beginning of closures to some hazardous waste dumps, including Love Canal (1952) and the Occidental Chemical Corporation S-area site (1961) (USEPA and NYSDEC, 1993). However, declines in concentrations of PCDDs/Fs in Lake Ontario since the 1980s appear to have leveled off (Pearson et al., 1997; Marvin et al., 2007). The lack of declines since the 1980s is unexpected given the amount of remediation activity in the Niagara River watershed. Assessment of PCDD/F profiles in Lake Ontario sediment indicates that both historic and current elevated levels of contamination can be largely attributed to inputs from the Niagara River (Shen et al., 2008). Profile analysis of bottom sediment in the open waters of Lake Ontario has attributed the high proportion of 2,3,7,8-TCDD and higher molecular PCDFs to Niagara River sources (Shen et al., 2008).

The publication of numerous reports on the magnitude of the hazardous waste site problem on the American side of the river, including the Love Canal environmental disaster, was the impetus that led to the signing of the "Four Party" Niagara River Declaration of Intent (1987) and subsequently the Letter of Support (1996). Eighteen "priority toxics", including 2,3,7,8-TCDD, were specifically targeted for reduction because they were thought to have significant sources in the Niagara River watershed. The Niagara River Toxics Management Plan (NRTMP) is the program designed to achieve these reductions; Environment Canada's (EC's) Niagara River Upstream/Downstream (NR U/D) program is one component of a monitoring plan intended to measure concentrations of chemicals in the river in order to determine loads of contaminants and report on trends, specifically in relation to implemented control measures. Under the auspices of the NR U/D program, EC has been

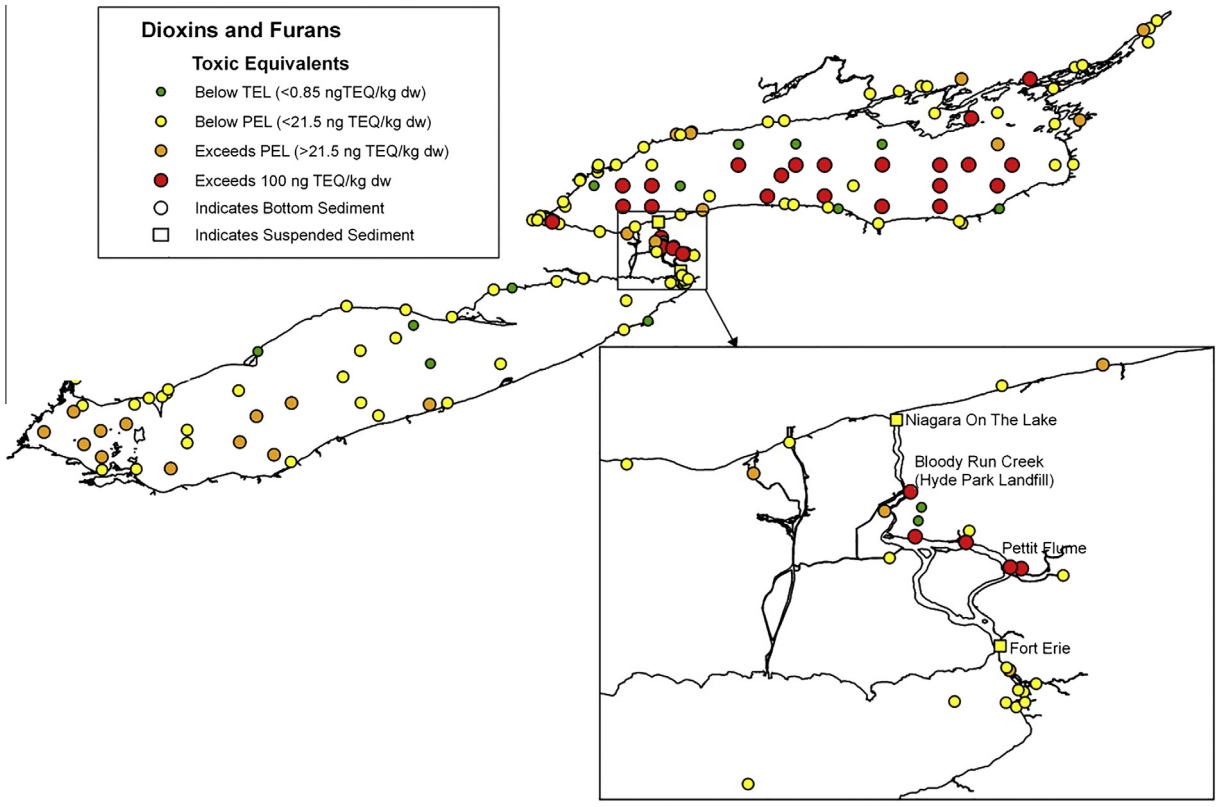

Fig. 1. Concentrations of dibenzo-*p*-dioxins and polychlorinated dibenzofurans in the lower Great Lakes and suspended sediment concentrations at Environment Canada's Niagara River Upstream/Downstream Program stations (Marvin et al., 2002; Richman and George, 2004; Richman et al., 2011; Richman, 2013).