Brominated and Chlorinated Norbornene Flame Retardants in Tributary Sediments of the Laurentian Great Lakes

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Introduction

Dechlorane 602 (Dec 602, $C_{14}H_4Cl_{12}O$), Dechlorane 603 (Dec 603, $C_{17}H_8Cl_{12}$), Dechlorane 604 (Dec 604, $C_{13}H_4Br_4Cl_6$), and Dechlorane Plus (DP, $C_{18}H_{12}Cl_{12}$) are flame retardant substitutes of mirex, which have fire retardant properties similar to mirex (http://www.inchem.org/documents/ehc/ ehc44.htm). These dechlorane compounds are either chlorinated or brominated/chlorinated norbornene derivatives containing a basic bicyclo [2,2,1]-heptene structure. DP is categorized by the United States EPA as a high production chemical (http:// www.epa.gov/ hpvis/index.html). Dec 602 and 604 are on the Non-domestic Substances List published by Environment Canada (http://www.ec.gc.ca/ CEPARegistry/subs_list/NonDomestic.cfm), which means that Dec 602 and 604 are likely in commercial use today.

Manufacture of DP began before 1970, and was first detected in air, sediment, and fish samples from the Laurentian Great Lakes in 2006 after being produced for four decades (Hoh et al. 2006). Similar to DP, Hooker Chemicals and Plastics Corp also patented Dec 602, 603, and 604 to improve the fire retardant properties of polymers in the late 1960s and 1970s (*e.g.* United States Patent 3392136, 3687983 and 3891599). These three dechloranes were recently found in sediment and fish in the Great Lakes with widespread occurrence, and Dec 602 is more bioavailable and/or bioaccumulated by fish than DP (Shen et al. 2010). Hexachloro-cyclopentadienyl-dibromo-cyclooctane (HCDBCO), another brominated/chlorinated norbornene flame retardant used in the past, was also recently detected in residential indoor air and dust (Zhu et al. 2008).

Levels of Dec 602, 603, 604, and DP in sediment of the Great Lakes reported in the literature are mainly focused on open water areas of the Great Lakes, and the Niagara River is suggested to discharge Dec 602, 604, and DP to Lake Ontario (Hoh et al. 2006, Qiu et al. 2007, Sverko et al. 2008, Shen et al. 2010). Currently, very few data are available that report dechlorane flame retardants in tributary sediments across the Great Lakes, which can directly indicate influence of urban/industrial land use activities on water quality of the lakes. In this study, we report concentrations and spatial trends of Dec 602, 603, 604, and DP in tributary sediments across the Great Lakes to assess sediment quality in each tributary prior to discharge to the Great Lakes and identify possible sources of contaminants from the watersheds. Temporal trends of Dec 602, 603, and 604 are also examined through archived Niagara River suspended sediments (1980 to 2006). The results presented combine the sediment survey of Canadian tributaries and the Niagara River upstream/downstream program conducted by Environment Canada (EC), and the Niagara River water quality monitoring and assessment program by the Ontario Ministry of the Environment (OMOE).

Materials and Methods

Chemicals. Dec 602 (95%, CAS# 31107-44-5), Dec 603 (98%, CAS# 13560-92-4), and Dec 604 (98%, CAS# 34571-16-9) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). DP (CAS# 13560-89-9) was purchased as *syn*-DP and *anti*-DP standards from Wellington Laboratories Inc. (Guelph, ON, Canada).

Sampling. Surficial sediments (top 3 cm) of tributaries were collected from more than 80 sites throughout the Great Lakes basins (Figure 1). Most of tributary sediments were sampled at the mouths of Canadian tributaries using a stainless steel spoon or a Wildco Petite Ponar sampler and placed in amber glass jars. All surficial sediments collected were immediately refrigerated for transport to the laboratory. Niagara River suspended sediments were collected in spring at the mouth of the Niagara River in Lake Ontario (Niagara-on-the-Lake station) by centrifuging large volumes of Niagara River water.

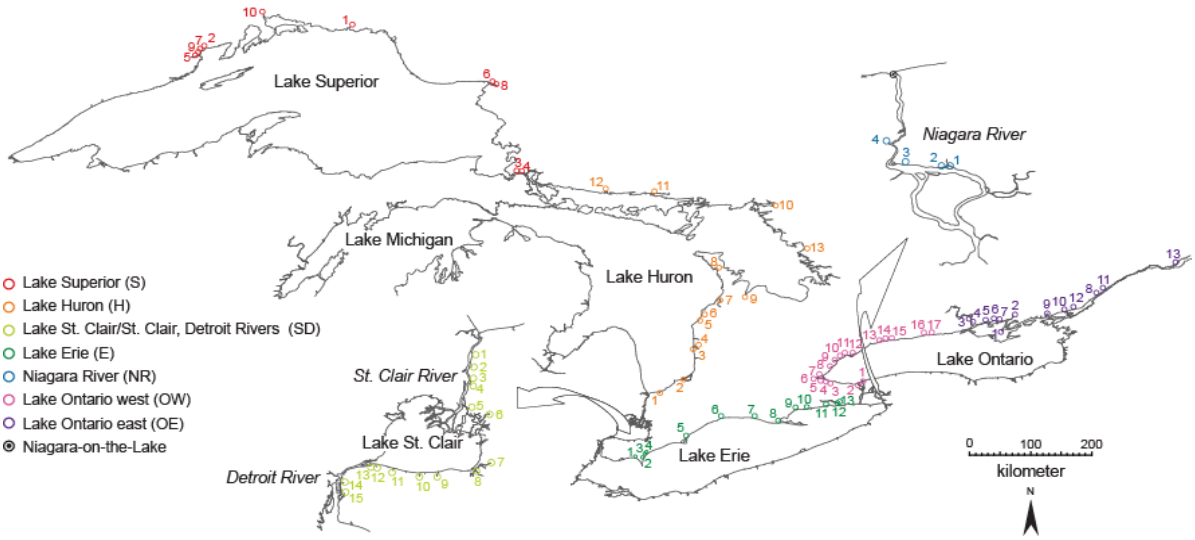

Figure 1. Map showing sampling sites for surficial sediment and suspended sediment

Sample preparation and chemical analysis. Determination of Dec 602, Dec 603, and Dec 604 in sediment were performed on extracts previously prepared for determination of mono-ortho dioxin-like polychlorinated biphenyls (DLPCBs). The extraction and cleanup procedure for sediment samples are described elsewhere (Shen et al. 2010). The sample extracts were analyzed on a Micromass Autospec high resolution mass spectrometer (HRMS) equipped with a Hewlett-Packard HP 6890 gas chromatograph (GC) using a 15 m DB-5HT column (0.25 mm i.d, 0.10 µm film thickness, J&W Scientific, USA). The HRMS system was operated in EI positive mode with electron energy of 40 eV and was tuned up to 10,000 resolving power (RP) according to 10% valley definition. Concentrations of Dec 602, Dec 603, Dec 604, and DP in sediment samples were determined by monitoring the two most abundant ions of the fragment cluster at *m/z* 271.8102/273.8072 for Dec 602 and DP, 262.8570/264.8540 for Dec 603, and 417.7026/419.7006 for Dec 604. The method detection limits (MDL) of the target compounds were 0.5 - 1 pg/g dry weight. Low levels of Dec 602 and DP were detected in the procedural blanks, and neither Dec 603 nor Dec 604 was detected in any procedural blanks. A spike test was performed to evaluate if Dec 602, 603, and 604 can be extracted quantitatively

in the similar manner to DLPCBs in sediments. Recoveries of six spiked standards in clean Ottawa Sand were 85 ± 4% (mean ± one standard deviation) for Dec 602, 80 ± 8% for Dec 603, 71 ± 10% for Dec 604, and 102 ± 4% for DP.

Results and Discussion

Spatial trends of Dec 602, 603, 604 and DP in tributary surfacial sediments. Dec 602 and 603 were detected in all tributary sediments except from S1 and SD13 for Dec 602 and S1, H6, and H12 for Dec 603. Dec 604 were detected in all samples from the Niagara River and Lake Ontario, and 50% of samples from Lake Superior. However, it was only found in 1 (H13) of 13 tributary sediments from Lake Huron and 4 (SD5, 11, 13 and 14) of 15 from the areas of the St. Clair River, Lake St. Clair, and the Detroit River and was not detected in any surficial sediments from Lake Erie. DP was detected in surficial sediments of all tributaries in this study. Concentrations of Dec 602, 603, 604 and total DP in tributary sediments are varied across the Great Lakes basin (Figure 2). The highest concentrations of Dec 602, 604, and total DP were found in Niagara surficial sediments at 12 ng/g dry weight, 4.8 ng/g dry weight, 310 ng/g dry weight, respectively. Dec 602 and DP had similar spatial trends in tributary sediments across the Great Lakes basin. The levels and spatial trends of Dec 602, 604, and DP in tributary sediments support the findings previously reported that manufacturing plants along the Niagara River are or were important sources of Dec 602, 604 and DP to Lake Ontario. The *syn*-DP fractions (f_{syn}), calculated as the concentration of *syn*-DP divided by the concentration of total DP, were in the range of 0.20 to 0.36 for the technical DP. In this study, the f_{syn} of surficial sediments vary from 0.03 to 0.43. The f_{syn} of the Niagara River sediments are 0.03 (NR1), 0.14 (NR2), 0.09 (NR3), and 0.11 (NR4), which are lower than those of the technical DP reported in the literature. More research is needed to investigate the fate of *syn*- and *anti*- DP after they are released to the environment.

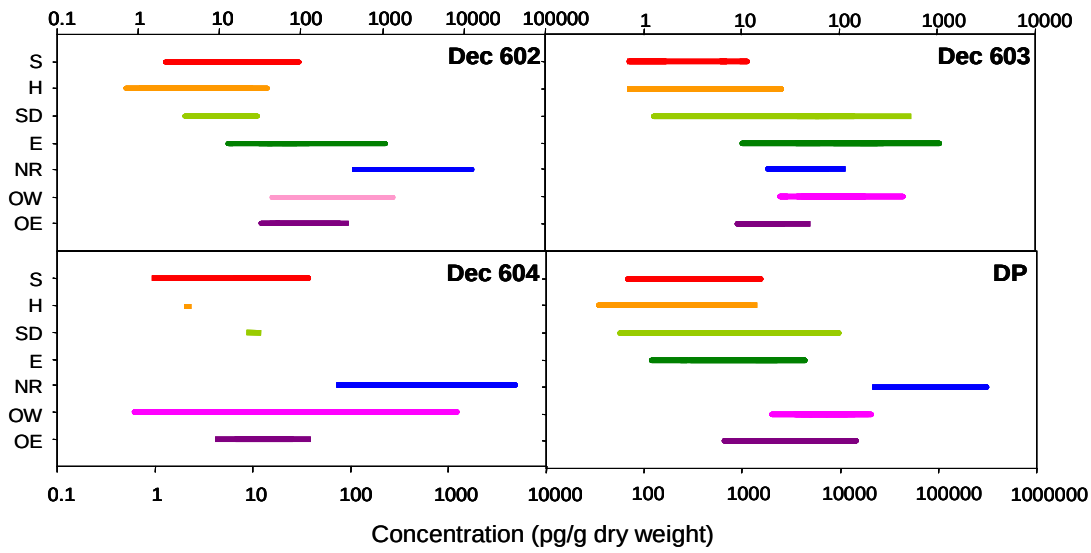

Figure 2. Concentration ranges of Dec 602, 603, 604, and DP in surficial sediments of the Great Lakes tributaries

The highest concentration of Dec 603 (1.1 ng/g dry weight) was detected at E2 of Lake Erie. As shown in Figure 2, the spatial trend of Dec 603 is different from those of Dec 602, 604, and DP. The source of

Dec 603 to the Great Lakes requires further investigation. The spatial trends of all dechlorane compounds in tributary sediments observed in this study are different from that of PBDEs across the Great Lakes (Gewurtz et al. 2009).

Temporal trends of Dec 602, 603 and 604 in Niagara River suspended sediments. The temporal trend of DP in Niagara River suspended sediments (1980-2002) was previously reported by Sverko et al (2008) and a slight decline in total DP was observed with a half-life of ~ 17 years. Similar to DP, Dec 602 and 603 show a trend toward decreasing in concentrations ($p < 0.05$) over the period 1980-2006 (Figure 3a); while Dec 604 does not show a significant decline over the same period of time (Figure 3b). The half-lives are approximately 8 years for Dec 602 and 11 years for 603, which are slightly shorter than that of DP. DP is still in use today, and the decline of DP might be due to decreasing usage/production of DP or that modern manufacturing processes release less DP into the environment (Sverko et al., 2008). Unfortunately, information on production and actual use of Dec 602, 603 and 604 in polymers is very limited.

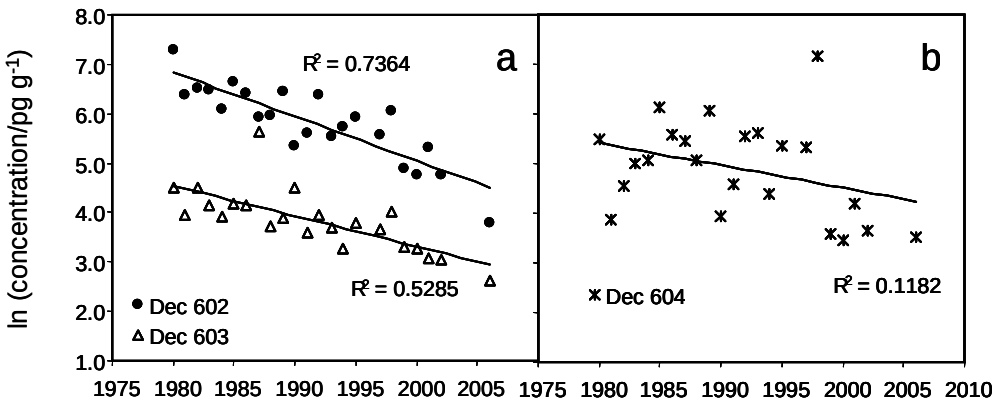

Figure 3. Concentrations of Dec 602, 603, and 604 in Niagara River suspended sediments over the period 1980-2006.

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