TEMPORAL TRENDS OF DECHLORANE 602, 603 AND 604 IN NIAGARA RIVER SUSPENDED SEDIMENT AND LAKE ONTARIO LAKE TROUT

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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, $C_{18}H_{12}Cl_{12}$) (Figure 1) 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[1]. Similar to DP, Hooker Chemicals and Plastics Corp also patented Dec 602, Dec 603, and Dec 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[2]. Hexachlorocyclopenta-dienyldibromo-cyclooctane (HCDBCO), another brominated/chlorinated norbornene flame retardant used in the past, was also recently detected in residential indoor air and dust[3].

Levels of Dec 602, Dec 603, Dec 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, Dec 604, and DP to Lake Ontario[1,2,4,5]. DP in Niagara River suspended sediments and lake trout of Lake Ontario were reported by Sverko et al.[4] and Ismail et al.[6] In this study, we focus on concentrations and temporal trends of Dec 602, 603, and 604 in archived Niagara River suspended sediments collected between 1980 and 2006, as well as in archived lake trout samples collected from Lake Ontario between 1979 and 2004. For comparison, DP in the suspended sediment and lake trout samples are also determined.

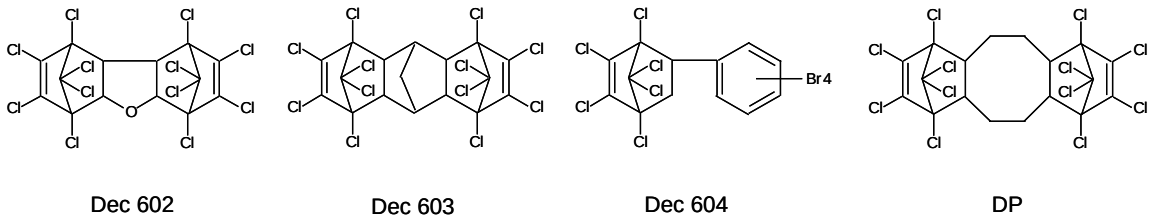

Figure 1. Structures of Dechlorane 602, Dechlorane 603, Dechlorane 604 and Dechlorane Plus.

Materials and Methods

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).

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. Lake trout were collected from Lake Ontario every four to six years (1979, 1983, 1988, 1993, 1998, and 2004) with five individuals (four in1979) per sampling time point.

Determination of Dec 602, Dec 603, Dec 604, and DP in suspended sediment and fish samples were performed on extracts previously prepared for determination of mono-ortho dioxin-like polychlorinated biphenyls (DLPCBs). The extraction and cleanup procedure for sediment and fish samples are described elsewhere[7]. 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 the extracts 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. 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, 102 ± 4% for *syn*-DP, and 82 ± 5% for *anti*-DP; and ten spiked standards in clean fish tissue 81 ± 5% for Dec 602, 68 ± 9% for Dec 603, 118 ± 7% for Dec 604, 96 ± 7% for *syn*-DP, and 84 ± 8% for *anti*-DP.

Results and Discussion

Temporal trends of Dec 602, Dec 603, Dec 604 and DP in Niagara River suspended sediments. Dec 602, Dec 603, Dec 604, and DP were consistently detected in suspended sediments over the period of 1980-2006 and ranged from 45 to 1400 pg/g dry weight (wt) for Dec 602, 15 to 280 pg/g dry wt for Dec 603, 30 to 1300 pg/g dry wt for Dec 604, and 5100 to 32000 pg/g dry wt for total DP.

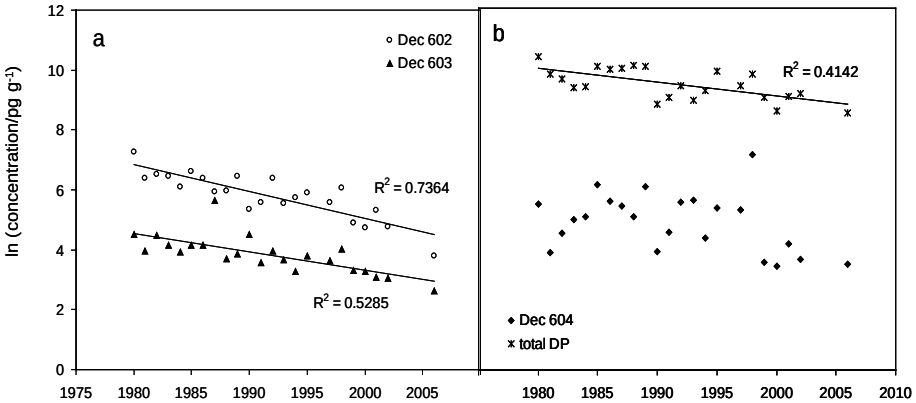

Figure 2. Concentrations of Dec 602, Dec 603, Dec 604 and total DP in Niagara River suspended sediments between 1980 and 2006.

Dec 602 and Dec 603 (Figure 2a) show a trend toward decreasing in concentrations ($p < 0.05$) over the study period; while Dec 604 does not show a significant decline over the same period of time (Figure 2b). The half-lives are approximately 8 years for Dec 602 and 11 years for Dec 603. Similar to Dec 602 and Dec 603, the concentration of total DP (Figure 2b) also shows a decline with a half-life of 15 years, which is slightly longer than those of Dec 602 and Dec 603. The *syn*-DP fraction (f_{syn}) is calculated as the concentration of *syn*-DP divided by the concentration of total DP. The f_{syn} of the technical DP were previously reported in the range of 0.20 to 0.36. The f_{syn} of suspended sediment samples were varied from 0.09 to 0.35; and no trend was observed over the period of 1980-2006. The temporal trend of DP in Niagara River suspended sediments (1980-2002) was reported by Sverko et al.[4] and a slight decline in total DP was also observed with a half-life of ~ 17 years. 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[4]. Unfortunately, information on production and actual use of Dec 602, 603 and 604 in polymers is very limited.

Temporal trends of Dec 602, Dec 603 and DP in Lake trout. Dec 602, Dec 603, and DP were detected in all lake trout collected from Lake Ontario between 1979 and 2004 and ranged from 8 to 180 ng/g lipid for Dec 602, 30 to 400 pg/g lipid for Dec 603, and 180 to 1900 pg/g lipid for total DP. Dec 604 was not found in any fish samples in this study.

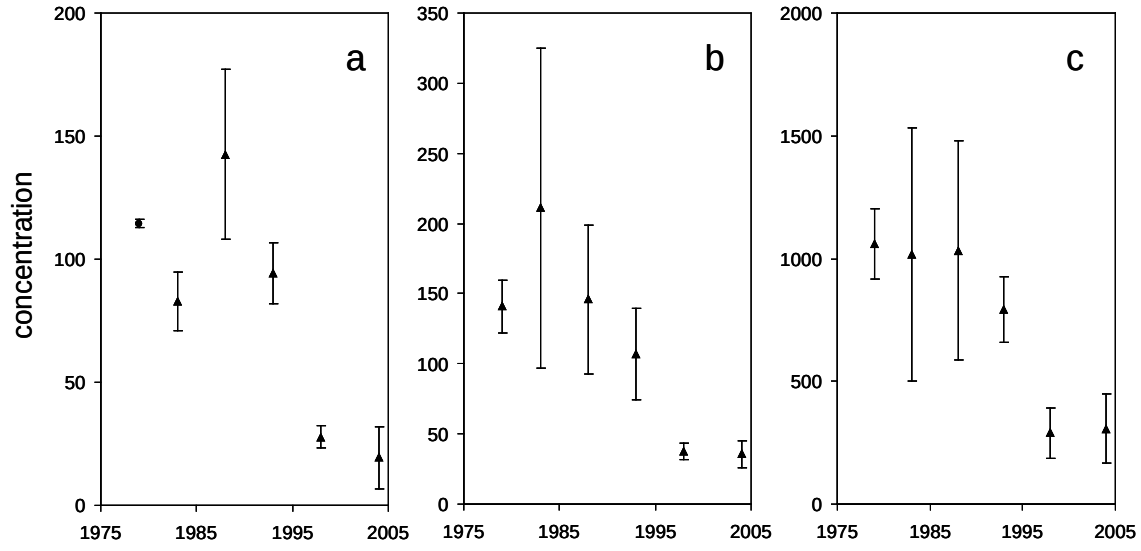

Figure 3. Concentrations of Dec 602 (ng/g lipid, 3a), Dec 603 (pg/g lipid, 3b), and total DP (pg/g lipid, 3c) in Lake Ontario lake trout between 1979 and 2004.

The temporal trends of Dec 602, Dec 603, and DP in lake trout are presented in Figure 3. For Dec 602 and Dec 603, the highest average concentrations of individuals per time point were found in 1988 and in 1983, respectively. The average concentrations of total DP during 1979-1988 were very similar. Generally, the levels of Dec 602, Dec 603, and DP decrease dramatically beginning from the late 1980s. *syn*-DP is considered more bioavailable and/or bioaccumulated than *anti*-DP in fish[1,2]. The f_{syn} of lake trout samples are all above the highest f_{syn} of technical DP products (0.36) in this study, ranging from 0.42 to 0.56, which is consistent

with previous observations. It is important to note that Dec 602 might be much more bioavailable and/or bioaccumulated compared to DP in fish. In suspended sediments of the Niagara River, the pattern of relative concentrations of dechlorane compound is DP > Dec 602 > Dec 604 > Dec 603; and the DP concentrations were 20 to 120 times greater than those of Dec 602. In lake trout of Lake Ontario, the pattern of relative concentrations is Dec 602 > DP > Dec 603; and the Dec 602 concentrations were 50 to 380 times greater than those of DP.

Acknowledgement

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References

1. Hoh E., Zhu L., Hites R. *Environ. Sci. Technol.* 2006; 40:1184
2. Shen L, Reiner E, Macpherson KA, Kolic TM, Sverko E, Helm PA, Bhavsar SP, Brindle ID, Marvin CH. *Environ. Sci. Technol.* 2010; 44:760
3. Zhu J., Hou Y., Feng Y., Shoeib M., Harner T. *Environ. Sci. Technol.* 2008; 42:386
4. Sverko E., Tomy G.T., Marvin C.H., Zaruk D., Reiner E., Helm P.A., Hill B., McCarry B.E. *Environ. Sci. Technol.* 2008; 42:361
5. Qiu X, Marvin CH, Hites RA. *Environ. Sci. Technol.* 2007; 41:6014
6. Ismail N, Gewurtz SB, Pleskach K, Whittle DM, Helm PA, Marvin CH. Tomy GT. *Environ. Toxical. Chem.* 2009; 28:910
7. Ontario Ministry of the Environment. *Laboratory Services Branch Method DFPCB-E3418.* 2008