

Historic Trends of Dechloranes 602, 603, 604, Dechlorane Plus and Other Norbornene Derivatives and Their Bioaccumulation Potential in Lake Ontario

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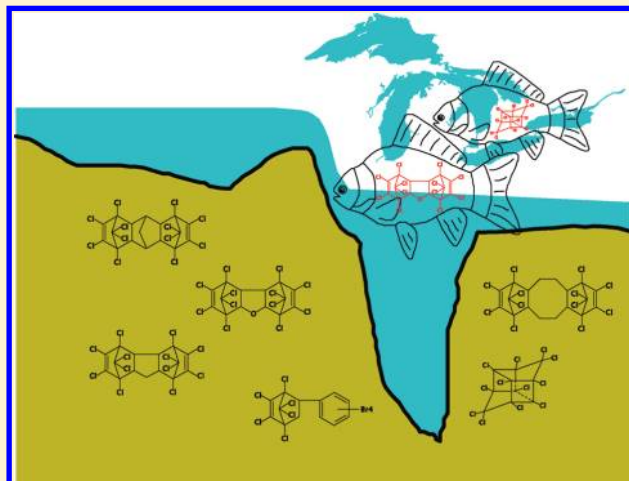
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S Supporting Information

ABSTRACT: Temporal trends and seasonal variation of Dechloranes (Dec) 602, 603, 604, and Chlordene Plus (CP) in Niagara River suspended sediment, a Lake Ontario sediment core, and Lake Ontario lake trout were investigated, with Mirex and Dechlorane Plus (DP) included for comparison. Temporal concentration trends were generally consistent in each of the media for all compounds with the lowest concentrations observed in or after the late 1990s. In Niagara River suspended sediments, all compounds showed seasonal variation over a year with distinct profiles observed. The relative concentration patterns observed were total DP > Mirex > Dec 602 and Dec 604 > Dec 603 > CP in suspended sediments and sediment cores, whereas Mirex was highest in lake trout, followed by Dec 602 and DP. Dec 602 concentrations were 50 to 380 times greater than those of DP in lake trout, indicating Dec 602 has a greater bioaccumulation potential. The estimated biota-sediment accumulation factor (BSAF) for Dec 602 was much greater than for DP in Lake Ontario, and was greater than those calculated for PBDEs, indicating that assessment of some dechlorane compounds is merited if use is ongoing or planned.



INTRODUCTION

Several highly chlorinated norbornene derivatives were patented and manufactured by Hooker Chemicals and Plastics Corp. (Hooker; currently OxyChem, Niagara Falls, New York) in the Niagara River area upstream of Lake Ontario. Mirex, a legacy organochlorine chemical, was manufactured and processed by Hooker from 1957 to 1976. About one-quarter of Mirex production was used as a pesticide and the rest was used as a fire retardant additive under the trade name Dechlorane.¹ Mirex was banned in the United States in the late 1970s because of its toxicity. Nonagricultural Mirex was replaced partially by other highly chlorinated compounds such as Dechlorane (Dec) 602, Dec 603, Dec 604, and Dechlorane Plus (DP), which reportedly had similar flame retardant properties to Mirex.² Dec 602, 603, 604, and DP are halogenated norbornene derivatives containing a basic bicyclo [2,2,1]-heptene structure.

DP, an in-use, high production volume (HPV) chemical,³ contains two isomers, *syn*- and *anti*-DP. Both isomers were first detected in air, sediment, and fish samples from the Laurentian Great Lakes in 2006 after four decades of production.⁴ Dec 602, 603, and 604 were also patented by Hooker in the 1960s and 1970s to improve the fire retardant properties of polymers (e.g., U.S. Patents 3392136, 3687983, and 3891599). Dec 602 and 604 are listed on Canada's Nondomestic Substances List⁵ and the European Chemical Substances Information System,⁶ indicating they are likely in commercial use today. Little information is available on production and usage of Dec 602, 603, and 604.

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However, they were recently reported in open lake sediments, tributary sediments, and fish of the Laurentian Great Lakes.^{7,8} CP (referred to as Chlordene Plus), another chlorinated norbornene derivative also patented by Hooker as a flame retardant, was also recently identified in Great Lakes tributary sediments.⁸

Dec 602, 604, and DP concentrations in sediments and fish collected from Lake Ontario were greater than those of other lakes^{4,7-9} and, together with their spatial trends in Great Lakes tributary sediments, indicated that the Niagara River area has been an important source of these compounds. The Niagara River area has a long history of industrial activity and related discharges and chemical waste disposal sites, which have resulted in contamination along the river and in Lake Ontario.

Temporal studies are important indicators of production, emission, and exposure history in aquatic systems. Although temporal variations of DP have been reported in Niagara River suspended sediments, sediment cores and Lake Ontario lake trout,^{7,9-11} information on Dec 602, 603, 604, and CP is not available. In this study, historical concentration trends of Dec 602, 603, 604, and CP were examined and compared to Mirex and DP in archived Niagara River suspended sediments (1980–2006), Lake Ontario lake trout (1979–2004), and a sediment core collected from the Niagara basin in western Lake Ontario. Because Dec 602 was previously reported to have higher concentrations than DP in fish,⁷ biota-sediment accumulation factors (BSAFs) of the dechlorane compounds were calculated. These and their modeled octanol–water partition coefficients (K_{OW}) were compared as a means to assess their relative bioaccumulation potential in Lake Ontario lake trout.

EXPERIMENTAL SECTION

Chemicals. Dec 602 (95%), 603 (98%), and 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). CP, *syn*-DP, and *anti*-DP standards were from Wellington Laboratories Inc. (Guelph, ON, Canada), and Mirex from Cambridge Isotope Laboratories Inc. (Andover, MA, USA).

Sample Collection. Niagara River suspended sediments were collected near the river mouth at Niagara-on-the-Lake, Ontario (Figure SI-1 in the Supporting Information) using a large-volume 24 h time-integrated dissolved/particulate phase sampling protocol detailed elsewhere.¹² Pumped water was passed through a Westphalia centrifuge assembly to collect suspended sediment followed by a Goulden extractor for dissolved analytes. Weekly/biweekly suspended sediment samples were freeze-dried and archived, and the temporal study was conducted on spring composites of these prepared from April and/or May samples from 1980 to 2002. Samples collected over the period April 2006 to March 2007 were combined into monthly composites to examine seasonal variation.

Lake trout were sampled from Lake Ontario north of Main Duck Island as part of long-term monitoring by the Great Lakes Laboratory for Fisheries and Aquatic Sciences (GLLFAS, now part of Environment Canada). Fish were collected every four to six years (1979, 1983, 1988, 1993, 1998, and 2004), with four or five individuals per time point. Individual whole fish were homogenized then stored frozen in glass jars at -80°C in the Great Lakes Specimen Bank until analysis.

The sediment core was collected from Lake Ontario (LO4; Figure SI-1 in the Supporting Information) using a mini-box core sampler from aboard the Canadian Coast Guard Ship (C.C.G.S.) *Limnos*, followed by subsampling using push cores and extrusion

and sectioning on board into 1 cm (for first 15 cm) and 2 cm intervals. A replicate core from the same box was dated by determining the ^{210}Pb activity as a function of the chronological age of the sediments.¹³ Data were calculated using both the Constant Initial Concentration (CIC) model (assumes a constant sedimentation rate) and the Constant Rate of Supply (CRS) model (assumes a variable sedimentation rate). Porosity and density analyses indicated changes in sediment composition that could indicate a variable accumulation rate, thus the CRS chronology was considered most accurate.

Sample Preparation. This study utilized sample extracts previously prepared for determination of mono-ortho dioxin-like polychlorinated biphenyls (DLPCBs) according to previously described extraction and cleanup procedures for sediment and fish.^{14,15} Briefly, frozen homogenized fish tissue samples were thawed, and sediment samples were air-dried, ground, and homogenized. Fish samples (~ 5 g, wet weight (wt)) were digested with hydrochloric acid and extracted with hexane. Sediment samples (5–10 g, dry wt) were Soxhlet-extracted with toluene. Sample extracts were processed using a 2 stage column procedure (multilayer silica and Amoco PX21 carbon/silica) for fish and 3 stages for sediment (multilayer silica, alumina, and Amoco PX21 carbon/silica), resulting in 2 fractions in nonane. Fraction A from each of these methods (the mono-ortho PCB fraction) contained the target norbornenes.

Chemical Analysis. Determination of Mirex, Dec 602, 603, 604, CP, and DP were performed on a Waters Autospec high-resolution mass spectrometer (HRMS; Milford, MA, USA) equipped with a Agilent 6890 gas chromatograph (GC; Wilmington, DE, USA) using a 15 m DB-5HT column (0.25 mm i.d., 0.10 μm film thickness, J&W Scientific, USA) using previously reported GC oven and HRMS parameters.^{7,8} Selected ion monitoring (SIM) utilized the two most abundant ions of the fragment cluster, which were m/z 271.8102/273.8072 for Mirex, Dec 602, CP, *syn*- and *anti*-DP, m/z 262.8570/264.8540 for Dec 603, and m/z 417.7026/419.7006 for Dec 604.

QA/QC. The criteria for quantification of target compounds included the following: (1) approximate Gaussian-shaped sample peaks; (2) GC retention times within ± 0.1 min of standard compounds; (3) signal-to-noise ratios of $>5:1$; (4) isotope ratios within 15% of theoretical values; and (5) that amounts in samples must be five times blank values, if detected in blanks. The method detection limits (MDL) in sediments were 0.5–1 pg/g dry wt and 5–15 pg/g lipid for fish. Only low levels of Mirex, Dec 602, *syn*- and *anti*-DP were detected in procedural blanks. Mass-labeled surrogates, available for Mirex and DP, were not added as the limited archived samples were originally analyzed for DLPCBs and PCDD/Fs prior to study conception. Spike tests ($n = 6$) using clean Ottawa Sand were performed to evaluate if Dec 602, 603, 604, CP, and DP were extracted, cleaned, and fractionated quantitatively in a similar manner to DLPCBs in sediments. Recoveries were $82 \pm 3\%$ (mean \pm one standard deviation) for Mirex, $85 \pm 4\%$ for Dec 602, $80 \pm 8\%$ for Dec 603, $71 \pm 10\%$ for Dec 604, $85 \pm 5\%$ for CP, $102 \pm 4\%$ for *syn*-DP, and $82 \pm 5\%$ for *anti*-DP. Similarly, recoveries of nine spiked standards in clean fish tissue were $34 \pm 4\%$ for Mirex, $81 \pm 5\%$ for Dec 602, $68 \pm 9\%$ for Dec 603, $118 \pm 7\%$ for Dec 604, $83 \pm 5\%$ for CP, $96 \pm 7\%$ for *syn*-DP, and $84 \pm 8\%$ for *anti*-DP. Reported concentrations were not corrected for recoveries. Reported Mirex concentrations in fish may be biased low based on the spike recovery test due to the reduction of extract volume to dryness and reconstitution, although interpretations of Mirex temporal trends,

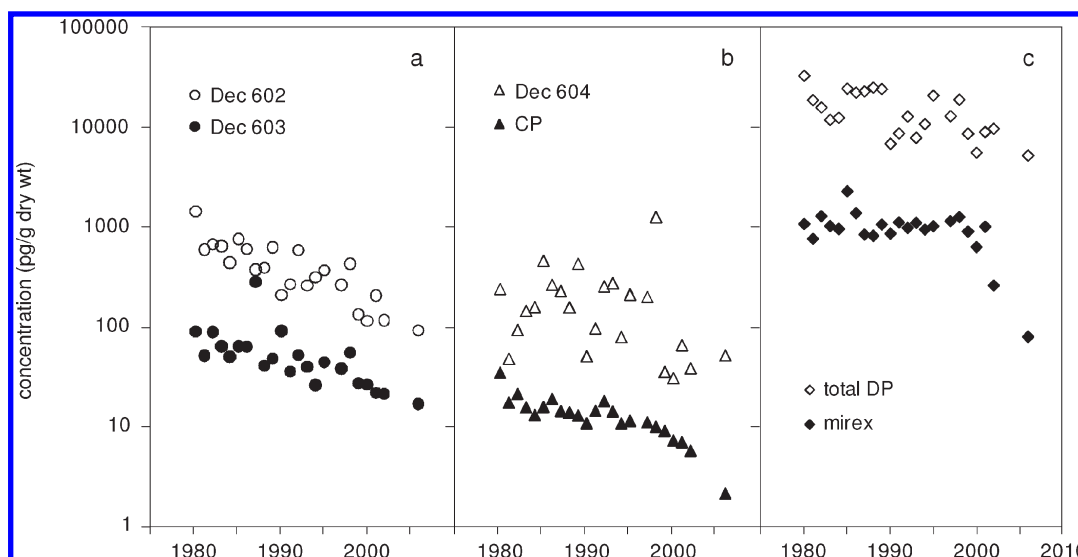


Figure 1. Temporal trends of Mirex, Dec 602, 603, 604, CP, and DP in Niagara River suspended sediments over the period of 1980 – 2006 (Note: The dechlorane concentrations for 2006 are the averages of the April and May 2006 samples).

relative concentration patterns, and relative bioaccumulation potentials are not affected.

RESULTS AND DISCUSSION

Concentrations of Dechloranes in Sediments and Fish. Mirex, Dec 602, 603, 604, CP, and DP were detected in all Niagara River suspended sediment samples and in the top 10 cm of the sediment core from LO4 (concentrations listed in Tables SI-1 to SI-3 of the Supporting Information). In general, the relative concentration pattern of these dechloranes in suspended sediments and sediments cores was total DP > Mirex > Dec 602 and 604 > Dec 603 > CP. DP, an in-use HPV chemical, had much higher concentrations compared to other dechloranes. Total DP concentrations (5.4–9.5 ng/g dry wt) were similar to those of BDE 209 (9.5–14 ng/g dry wt) in suspended sediments collected since 2000.¹² The average DP concentration (110 ng/g dry wt) in the top 3 cm of sediments of the Lake Ontario sediment core was greater than that of BDE 209 (3–29 ng/g dry wt),^{10,16} and the average Dec 602 concentration (12 ng/g dry wt) was also similar to BDE 209.

After Mirex, Dec 602 and 604 were the next most abundant dechloranes found in sediment samples. Production and use information for Dec 602 and 604 is limited, but Dec 602 has been used in Fiberglass-reinforced Nylon-6 at 18%¹⁷ and is listed as having been a commercially used flame retardant.¹⁸ Dec 604 is listed as an ingredient in Molykote AS-810 Silicone Grease (10–30%) produced by Dow Corning Corp.¹⁹ Dec 602 and Dec 604 may be used together in wire insulation (U.S. Patent 3900533). Dec 603 and CP had much lower concentrations in suspended sediments and sediment cores. Although Dec 603 and CP appeared in U.S. patents of flame retardant polymer compositions, there is no information available on their actual use. Dec 603 is reported to be an impurity in technical Aldrin and Dieldrin products and CP in technical Chlordene and Chlordane, and their environmental occurrence is consistent with historical pesticide usage.⁸

Mirex, Dec 602, 603, and *syn*- and *anti*-DP isomers were detected in all lake trout between 1979 and 2004. CP was not

detected in half of the fish samples due to matrix effects, and Dec 604 was not found in any fish samples in this study (Table SI-4 of the Supporting Information). As expected, Mirex, listed for elimination on the United Nations Environment Program Stockholm Convention on Persistent Organic Pollutants, had elevated concentrations (83–4300 ng/g lipid) compared to other dechloranes because of its ability to bioaccumulate.^{1,2} In contrast to DP in sediments, DP concentrations in fish (180–1900 pg/g lipid) were much lower than those of Dec 602 (8000–180 000 pg/g lipid), indicating Dec 602 may be more bioavailable and/or more likely to bioaccumulate in fish compared to DP.

Temporal Trends of Dechloranes in Niagara River Suspended Sediments. Concentration trends of dechloranes in suspended sediments collected between 1980 and 2006 are shown in Figure 1. Both Dec 602 and 603 declined significantly over the study period (Pearson correlation, $R = -0.86$, $p < 0.01$ for Dec 602 and $R = -0.72$, $p < 0.01$ for Dec 603) (part a of Figure 1). The trend for CP ($R = -0.86$, $p < 0.01$) was similar to Dec 602 and 603, whereas Dec 604 concentrations fluctuated since 1980 ($R = 0.31$, $p > 0.05$) (part b of Figure 1). Mirex does not show any decline until the late 1990s (part c of Figure 1), which indicates that Mirex continued to leach from chemical production facility properties and/or waste storage sites along the Niagara River long after use of Mirex was prohibited in 1978. The declines since the late 1990s might reflect remediation efforts at several sites in the region through the 1990s.²⁰ A declining concentration trend for DP was reported previously⁹ for Niagara River suspended sediments and confirmed in this study ($R = -0.60$, $p < 0.01$), with results consistent with declines observed in a sediment core collected near the river mouth on the Niagara River bar.²¹ It is not clear if the decline in DP represent changes in production volumes at the manufacturing site or whether it reflects emission controls adopted over the past 20+ years at the site. The suspended sediment trends were also reflected in open lake sediment core trends, which generally decline since 1980 in the Niagara basin (this study, discussed below) and in the Mississauga basin.⁷

DP, Dec 602, and Dec 604 were found to be higher in tributary sediments from the Niagara River area and Lake Ontario than

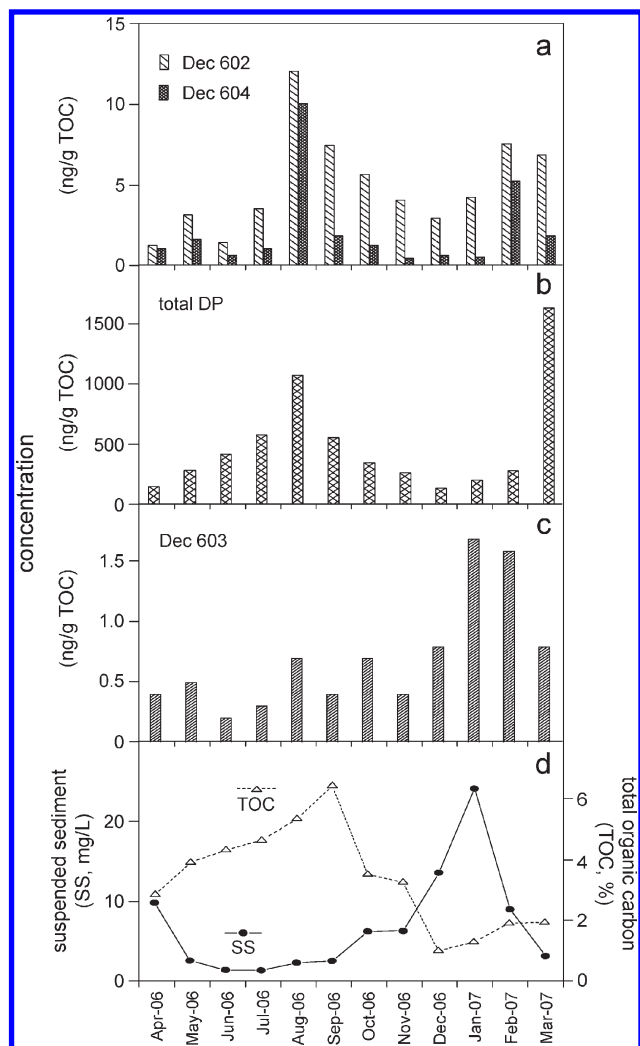


Figure 2. Seasonal variation of total organic carbon (TOC)-adjusted concentrations of Dec 602, 603, 604, and DP in Niagara River suspended sediment over the period of April 2006–March 2007.

Lake Erie tributaries,⁸ and higher in lake sediments and fish from Lake Ontario than Lake Erie,⁷ suggesting similar sources for these compounds. Concentration ratios of these compounds in suspended sediments with year were compared to further assess relative contributions to the Niagara River and Lake Ontario (Figure SI-2 of the Supporting Information). The ratio of DP/Dec 602 shows a considerable increase to present ($R = 0.66$, $p < 0.01$), indicating that Dec 602 concentrations are declining more rapidly than for DP (part a of Figure SI-2 of the Supporting Information). This is consistent with continued manufacture, emissions, and/or use of DP and possibly reduced or ceased production of Dec 602 in the area. The ratio of Dec 602/Dec 604 was more variable ($R = -0.41$, $p > 0.05$), and there was no trend in the DP/Dec 604 ratio ($R = -0.06$, $p > 0.05$) (part b of Figure SI-2 of the Supporting Information). It is difficult to interpret these results in terms of source contributions without more knowledge of production history and use. The periodic manufacture in the area of Dec 602 and/or Dec 604 at different times could account for the more variable results, or the relative influence of uses and sources (i.e., ongoing use and emissions in certain applications compared to manufacture and emissions

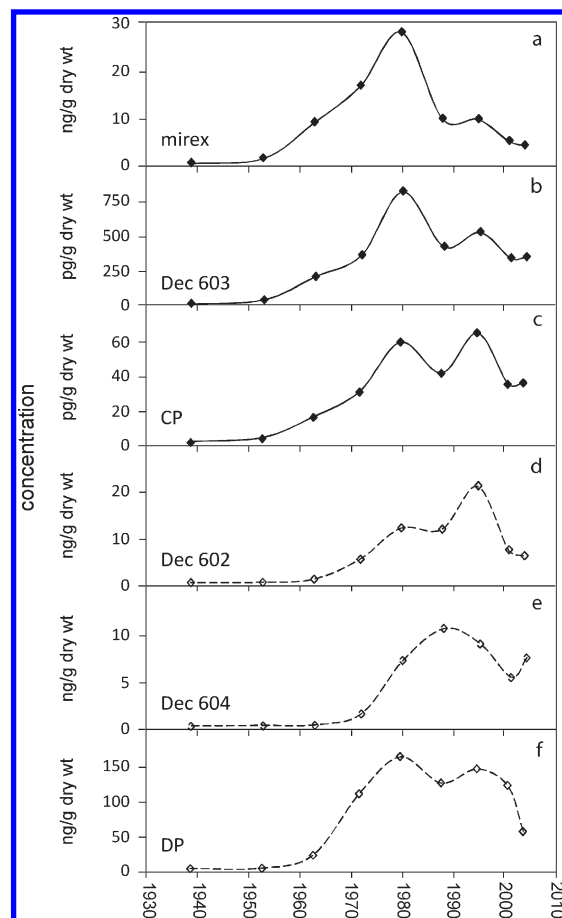


Figure 3. Temporal trends of Mirex, Dec 602, 603, 604, CP, and DP in Lake Ontario sediment core.

in the region), could influence concentrations and occurrence patterns. The use of Dec 604 individually compared to the use of Dec 602 and Dec 604 together (noted above) could account for the greater variability in the Dec 602/Dec 604 ratios (part b of Figure SI-2 of the Supporting Information) and in the concentration trend for Dec 604 (part b of Figure 1).

Seasonal Variation of Dechloranes in Niagara River Suspended Sediments. The dechloranes varied seasonally over the period of April 2006 to March 2007 with some distinct patterns observed as illustrated by Dec 602, 603, 604, and DP (Figure 2). Total organic carbon (TOC)-normalized concentrations of Dec 602 and 604 were highest in late summer (August–September) and in late winter (February–March) (part a of Figure 2). Mirex exhibited a similar seasonal pattern to Dec 602 and 604. Relatively higher TOC-normalized concentrations of DP were observed in August–September, similar to Dec 602 and 604, but the March 2007 composite had the highest TOC-adjusted DP concentration (part b of Figure 2). The seasonal pattern of Dec 603 differed from those of Dec 602, 604, and DP, with the highest TOC-adjusted concentrations observed in January–February (part c of Figure 2). CP did not exhibit a clear pattern.

TOC concentrations were highest during late summer (part d of Figure 2) when Dec 602, 604, DP and Mirex concentrations also increased. However, normalization to TOC did not fully account for the observed trends (parts a and b of Figure 2), consistent with the influence of localized sources, and that these compounds are not strongly associated with sorption to algal

matter, which increases throughout summer in upstream Lake Erie (the main source of Niagara River water). Lake Erie is also stratified during this period resulting in relatively lower suspended sediment concentrations (part d of Figure 2). Possible explanations for the trends may include the mobilization of sediments/soils from the local Niagara region that may contain higher chemical concentrations during summer rain events, contributing to the sediment load of the river in addition to upstream lake sediments. Similarly, during late winter rain and melt events, sediment/soil particles with elevated concentrations may be washed into the river. DP may additionally have emissions occurring at different times of the year depending on when batches are manufactured. The Dec 603 trend showing higher winter concentrations is consistent with a greater proportion of suspended particles from Lake Erie during winter. The lake is no longer stratified in winter when storms and ice scour increases particle concentrations,²² and elevated Dec 603 concentrations were observed in Lake Erie tributary sediments relative to Lake Ontario and the Niagara area.⁸ There was no trend apparent in the f_{syn} of DP (fraction of *syn*-DP relative to the sum of *syn*-DP + *anti*-DP) to aid interpretation.

Temporal Trends of Dechloranes in Lake Ontario Sediment Cores. Figure 3 shows the concentration trends for Mirex, Dec 602, 603, 604, CP, and total DP in the sediment core from the Niagara basin of Lake Ontario. Downward concentration trends were observed in the upper slices since 1980 and were generally consistent with trends in Niagara River suspended sediments over the same period. However, core results were more variable and had lower resolution as each core slice integrates inputs over 5–7 years compared to annual values for the Niagara River suspended sediments. The Niagara basin is also influenced by other inputs (industrial, municipal, tributary, and atmospheric) to the western end of Lake Ontario. Smaller declines in the core for DP and Dec 604 compared to Dec 602 are consistent with observations in the suspended sediments. The lowest concentrations (post-1980) in both suspended sediments and the sediment core occurred since 2000. There was a more substantial decline in Mirex in the core that differed from the suspended sediment trends for reasons which are unclear.

Sediment cores provide an indication of input trends for the target compounds prior to the 1980s when detailed monitoring programs were established. For example, Mirex concentrations gradually increased from the early 1950s, peaked in the early 1980s, and declined considerably since then (part a of Figure 3). Dec 603 had a temporal trend similar to Mirex (part b of Figure 3) as Mirex, Aldrin, and Dieldrin were manufactured beginning in the late 1940s and/or early 1950s and their registered uses were limited by the mid-1970s in North America. Concentrations of CP also increased between the mid-1950s and early 1980s, but declined only since the mid-1990s (part c of Figure 3). Most uses of Chlordane were limited by the mid-1970s and the U.S. EPA banned all approved uses in 1988, but manufacture for export still continued until 1997. There are 23 Chlordane-contaminated hazardous waste sites located in the Great Lakes Basin, and the Niagara River area is on the list of Areas of Concern (AOC), with Chlordane listed as one of the pesticides which is a Chemical of Concern.²³

Dec 602, 604, and DP concentrations increased in sediments between the early and mid-1960s (parts d–f of Figure 3, respectively), approximately 10 years after Mirex. The maximum concentration of Dec 602 occurred in the mid-1990s followed by a subsequent decline. Dec 604 peaked around the late 1980s, but

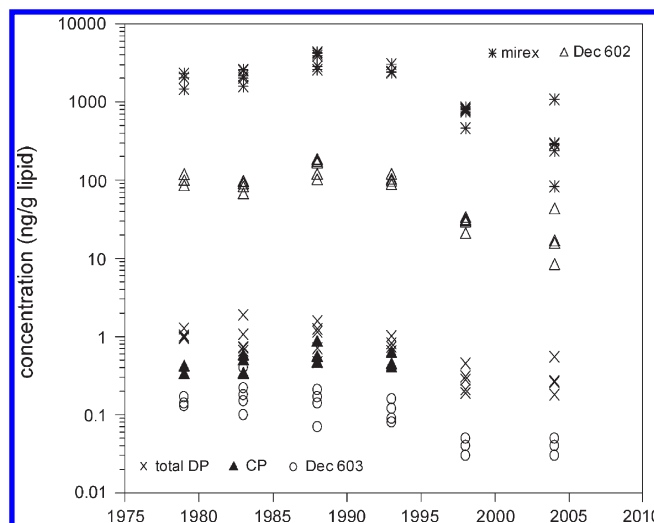


Figure 4. Temporal trends of Mirex, Dec 602, 603, CP, and DP in Lake Ontario lake trout.

concentrations have not dropped as rapidly as Dec 602, with 2/3 of the maximum concentration found in the top 1 cm. The maximum DP concentration was observed around 1980, but appreciable declines did not occur until recently. No trend was observed for the f_{syn} in sediment cores.

Sediment core profiles for the dechlorane compounds in the Niagara basin were similar to those observed in a core from the Mississauga basin,⁷ consistent with the broad influence of Niagara River inputs to Lake Ontario depositional basins. Both exhibited bimodal peaks for most analytes around 1980 and again in the mid-1990s. Without knowledge of the production history for these compounds, it is difficult to relate production and use to core observations. Observed trends in the Niagara basin core may be influenced by production changes, but also industrial emission abatement efforts and remedial actions at contaminated locations which have impacted other historical contaminant levels in the area.²⁰

Temporal Trends of Dechloranes in Lake Ontario Lake Trout. Mirex was found at the highest concentrations in the lake trout, followed by Dec 602 and DP, similar to results reported previously for a small number Lake Ontario lake trout.⁷ Peak concentrations for each compound studied occurred in the early or late 1980s with subsequent declines to 2004 (Figure 4). Mean concentrations declined 6-fold, 5-fold, and 4.5-fold from peak year to 2004 for Mirex, Dec 602, and Dec 603 respectively, but only 2.5-fold for total DP. Consistent with observations in the sediment core and suspended sediments, the lowest concentrations occurred in recent years (1998/2004).

syn-DP bioaccumulates to a greater extent or is more bioavailable than *anti*-DP in fish,^{4,7,24} but this may vary depending on the foodweb studied.^{25,26} In this study, the measured f_{syn} in lake trout (Table SI-4 of the Supporting Information) were all above the reported f_{syn} of technical DP products (0.2–0.36)^{4,7,27} ranging from 0.42 to 0.56, consistent with previous observations in fish,^{4,7,25} and were greater than sediment f_{syn} values. A decreasing trend in f_{syn} was found with time ($R = -0.81$, $p \ll 0.001$) with lower f_{syn} values in fish collected in 1998 and 2004 (Table SI-4 of the Supporting Information). This was in contrast to the sediment core and suspended sediments where no trends were noted. Modulations of f_{syn} by trophic interactions in the foodweb

Table 1. Estimates of Biota-Sediment Accumulation Factors (BSAF) and log K_{OW} for Mirex, Dec 602, Dec 603, Dec 604, CP, and DP

chemical	formula	MW	BSAF ^a	Estimated log K_{OW}		
				EPI Suite ^b	SPARC ^c	ABSOLV- ppLFER ^d
Mirex	C ₁₀ Cl ₁₂	545.54	7400	7.0 ^e	9.4 ^e	7.0 ^e
Dec 602	C ₁₄ H ₄ Cl ₁₂ O	613.62	270	8.1	9.4	7.9
CP	C ₁₅ H ₆ Cl ₁₂	611.64	91	9.8	9.9	9.1
Dec 603	C ₁₇ H ₈ Cl ₁₂	637.68	12	11.2	10.8	9.8
Dec 604	C ₁₃ H ₄ Br ₄ Cl ₆	692.50	4.5	10.6	8.7	9.9
<i>syn</i> -DP	C ₁₈ H ₁₂ Cl ₁₂	653.72	0.8	11.3 ^f	11.1 ^f	10.7 ^f
<i>anti</i> -DP	C ₁₈ H ₁₂ Cl ₁₂	653.72	0.3	11.3 ^f	11.1 ^f	10.7 ^f

^aBSAF = C_B/C_S ; C_B are average wet lake trout concentrations reported in this study (1998 and 2004) and/or previously,⁷ C_S are average dry weight concentrations in surface sediments (top 3 cm) from stations O4, O34, and O46 from Lake Ontario.⁷ ^bEstimated using KOWWIN v1.67 in EPI Suite 4.0 (<http://www.epa.gov/oppt/exposure/pubs/episuite.htm>, Accessed December 2009). ^cEstimated using SPARC Online Calculator v4.0 (<http://sparc.chem.uga.edu/sparc>, Accessed December 2009). ^dEstimated using poly parameter linear free energy relationships (ppLFER) with phase descriptors given by Goss³⁴ and solute descriptors predicted by ABSOLV Module of ACD/ADME Suite (<http://pharma-algorithms.com/index.html>, Accessed December 2009). ^eMeasured log K_{OW} of Mirex is 6.89.³⁵ ^fAll the three K_{OW} prediction tools are based on 2D chemical structures as input and cannot distinguish isomers.

at different times would need to be considered to understand this trend. For example, a major perturbation of the Lake Ontario foodweb occurred in the mid-1990s with the dreissenid mussel invasion. Although remediation of contaminated sites along the Niagara River occurred in the late 1990s²⁰ that may have contributed to reduced concentrations, changing f_{syn} values resulting from such efforts were not noted in suspended sediments.

It is important to note that the relatively high concentrations of Dec 602 in fish compared to other dechloranes indicate that it is more amenable to bioaccumulation, similar to Mirex. For example, in suspended sediments of the Niagara River, the DP concentrations were 20 to 120 times greater than those of Dec 602; while the Dec 602 concentrations were 50 to 380 times greater than those of DP in Lake Ontario lake trout.

Bioaccumulation of Dechloranes. Bioaccumulation of chemicals in apex species such as lake trout is a key element in considering if chemicals are an environmental concern. The octanol–water partition coefficient (K_{OW}) is one indicator of bioaccumulation potential. K_{OW} values have been estimated for DP and have not been otherwise measured. Empirically derived indicators, such as the trophic magnification factor (TMF) and the predator–prey biomagnification factor (BMF) also provide indications of bioaccumulation potential in aquatic food webs.²⁸ *anti*-DP was found to biomagnify in a Lake Winnipeg, Canada foodweb (TMF = 2.5), but no significant biomagnification was found in the Lake Ontario foodweb.²⁵ In foodweb samples from a source-influenced reservoir in China, TMFs for both *syn*- and *anti*-DP (11.3 and 6.6, respectively) indicated biomagnification.²⁶ BMFs determined for some predator–prey relationships in Lake Ontario²⁵ and in exposure studies²⁴ also indicated bioaccumulation potential for DP. However, no foodweb

accumulation or BMF studies to date have included Dec 602, 603, 604 or CP.

The biota-sediment accumulation factor (BSAF) is a common empirical measure that also provides an indication of bioaccumulation in aquatic systems and a means of comparing accumulation potential between compounds in that system, especially in the absence of more direct information. The BSAF is calculated by:²⁹

$$BSAF = \frac{C_B}{C_S}$$

where C_B is the contaminant concentration in biota (wet weight) and C_S is the corresponding concentration in sediment (dry weight). Lipid- (C_{BL}) and organic carbon-normalized (C_{SOC}) BSAFs (BSAF') are also a common means of expressing BSAFs.²⁹ Using data from this and our previous study⁷ reported on a dry weight (sediment) and wet weight (biota) basis, BSAFs were estimated for Mirex, Dec 602, 603, 604, CP, *syn*- and *anti*-DP for lake trout relative to sediments from Lake Ontario (Table 1). Estimates of log K_{OW} are also listed for comparison as determined using EPI Suite, SPARC, and ABSOLV-ppLFER estimation programs. Mirex was found to have the highest BSAF (7400) followed by Dec 602 (270) and CP (91). The DP isomers had the lowest BSAFs. For comparison, the corresponding BSAF for total PCBs for Lake Ontario lake trout is 5,³⁰ and calculated BSAFs for BDE 47, 99, 153, 154, and 183 are 58, 20, 22, 35, and 0.3 respectively using average lake trout data (wet weight) from 2000³¹ and average surface sediment concentrations (dry weight).¹⁶ The results were consistent with log K_{OW} estimates, with the lowest K_{OW} values associated with the higher BSAFs. Very high log K_{OW} values (≥ 8) have been shown to have lower BMFs and assimilation efficiencies.³²

The BSAFs and log K_{OW} estimates suggest that Dec 602, Dec 603, and Dec 604 have a greater potential for bioaccumulation than DP in the environment. There is little information available regarding the production history and current use of these compounds globally. Sediment cores and environmental trends in Lake Ontario and the Niagara region indicate that there may not be current production of at least Dec 602 and Dec 603 in the region, but they have been widely detected in environmental samples in the Great Lakes region and in China.³³ The BSAF comparison indicates that regulatory assessment of some of these chemicals is merited if use is ongoing or planned.

■ ASSOCIATED CONTENT

S Supporting Information. Tables of dechlorane concentrations for all samples, and figures of sampling sites and concentration ratios of total DP/Dec 602, Dec 602/Dec 604, and DP/Dec 604 in Niagara River suspended sediment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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