CHAPTER 1

INTRODUCTION

This chapter is based on a review paper published recently in the journal Environmental Science and Technology, of which I was primary author along with Gregg T. Tomy, Eric J. Reiner, Yi-Fan Li, Jon Arnot, Robin Law, Brian E. McCarry and Ronald Hites. It depicts an overview of the rapid succession of publications to date stemming from the first report on DP's occurrence in the environment in 2006. My three publications (2008, 2008 and 2010) were not included in the Introduction.

Hoh et al. were the first to report on the environmental occurrence of Dechlorane Plus (DP) within the North American Great Lakes Basin. DP, chlorinated flame retardant chemical, has been manufactured by OxyChem in Niagara Falls, New York, for at least 40 years.[1] DP is produced by the Diels-Alder condensation of hexachlorocyclopentadiene with 1,5-cyclooctadiene at a 2:1 mole ratio; the resulting material consists of a mixture of the *syn* and *anti* isomers (Figure 1).

These two isomers are present in the technical product in a ratio between 1:2 and 1:3; that is, the *anti* isomer is about 65 – 75 % of the total. DP is used as a flame retardant in electrical hard plastic connectors in televisions and computer monitors, wire coatings and furniture.[2] DP is currently classified by the U.S. EPA as a high production volume (HPV) chemical, meaning that DP is produced or imported into the U.S. in quantities of at least 450,000 kg per year. This designation invoked the EPA's HPV challenge requiring the manufacturer to conduct a prescribed set of physico-chemical and

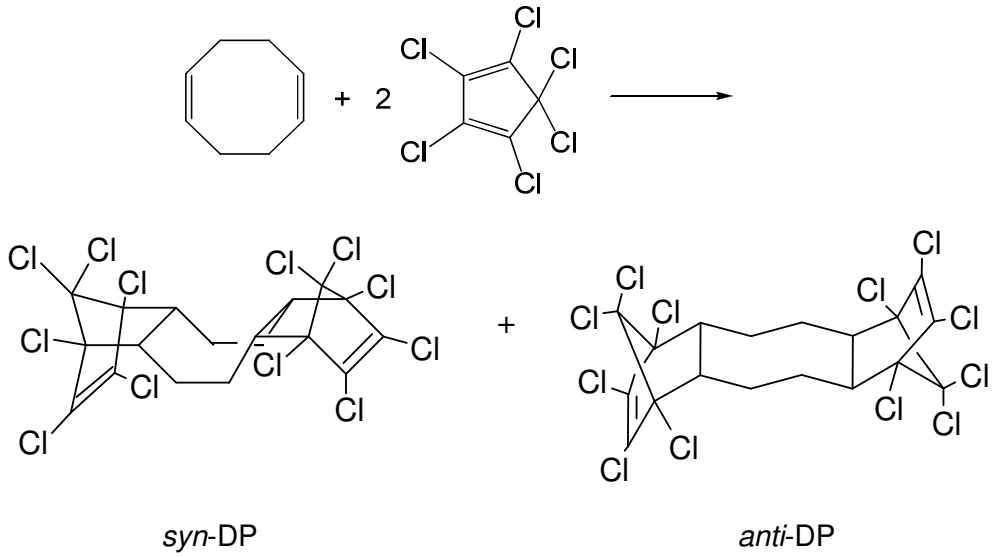

Figure 1: The reaction of 1,5-cycloctadiene to 2 moles of hexachlorocyclopentadiene creating *syn* and *anti* Dechlorane Plus.

toxicological studies. Carried out in 1979 and based on dated experimental methodologies, OxyChem reported on DP's highly lipophilic nature and therefore likely to sorb to sediment potentially adversely affecting benthic organisms. Further toxicological tests by OxyChem, including LC_{50} and LD_{50} tests, resulted in negligible effects. While the acute effects for the fish species targeted in these experiments were relatively insignificant, contemporary toxicity studies (e.g., involving P_{450} systems) have yet to be investigated. Furthermore, effects, acute or subtle, of human exposures to this widely produced flame retardant have not been studied.

Following the 2006 Hoh et al. paper,[1] other researchers measured DP in house dust.[3,4] The levels were at near or below concentrations of other HPV flame retardant formulations which were identified as toxic to humans and environmental organisms,

known as polybrominated diphenyl ethers (PBDE). This brominated flame retardant, was manufactured and sold as three commercial mixtures, pentabromo diphenyl ether (penta-BDE), octabromo diphenyl ether (octa-BDE) and decabromo diphenyl ether (deca-BDE), each possessing unique flame retardant properties for specific applications; the latter of which was similar to that of DP's. Both penta-BDE and octa-BDE have been restricted for use due to their toxic effects as identified by the Stockholm Convention.

While deca-BDE has been reported to be successful as a flame retardant, others reported on its susceptibility to dehalogenate to more toxic moieties thus leading the Stockholm Convention to restrict its use as well. Notably, DP was identified by the European Commission as a potential replacement candidate for the deca-BDE formulation.[5] It is therefore, important to measure current levels of DP in the environment and to determine what effects an increase in production and/or use would have on environmental and human health.

Evidence suggesting that DP may be a worldwide contaminant was first noted in 2008 by Qiu and Hites who detected the flame retardant in samples of tree bark from Spain, Korea and China.[6] More strikingly, Möller et al. recently detected DP in air sampled along an oceanic transect from Greenland to Antarctica; these data indicate that DP is a global pollutant, susceptible to long-range atmospheric transport.[7] This satisfies one of the three tenets which the Stockholm Convention requires a chemical to possess (persistence, bioaccumulation and toxic – PB&T) to include in its list of globally restricted chemicals.

Additionally, Wang et al. identified another DP production facility in China.[8]

More recently, "DP-like" substances (Dechlorane-602, Dechlorane-603, and Dechlorane-604) have also been detected in the Great Lakes.[9] Unlike DP, information on the production volumes and applications of these compounds is not available.

ENVIRONMENTAL LEVELS AND MEASUREMENTS OF DECHLORANE PLUS

Atmospheric Concentrations

There are a considerable number of measurements of DP in the atmosphere around the North American Great Lakes. Venier and Hites[10] and Hites et al.[11] have presented these atmospheric concentrations, which were measured as part of the Integrated Atmospheric Deposition Network (IADN) and which cover sampling sites near the shores of the Great Lakes. Their data were obtained from 2005 to 2008, inclusive. Air samples were taken for 24 hours at a frequency of once every 12 days over this 3-year period. The sampling site locations and the geometric averages of the total vapor and particle phase atmospheric DP concentrations are presented in Figure 1. The DP concentrations tend to be highest at the urban sites of Cleveland and Sturgeon Point (near Buffalo, NY, about 2 - 4 pg m^{-3}); the concentrations were much higher in the particle phase than in the vapor phase. Concentrations at remote sites in the IADN study are about 10 times lower (0.2 - 0.5 pg m^{-3}) than in the urban sites. All of these concentrations showed significant relationships to local population densities and to the distance from DP's manufacturing site in Niagara Falls. This is clearly an indication that

DP has sources associated with both its manufacturing plant in Niagara Falls and with human population density. The latter source may be due to the use of DP in electrical gear, the abundance of which is proportional to population.

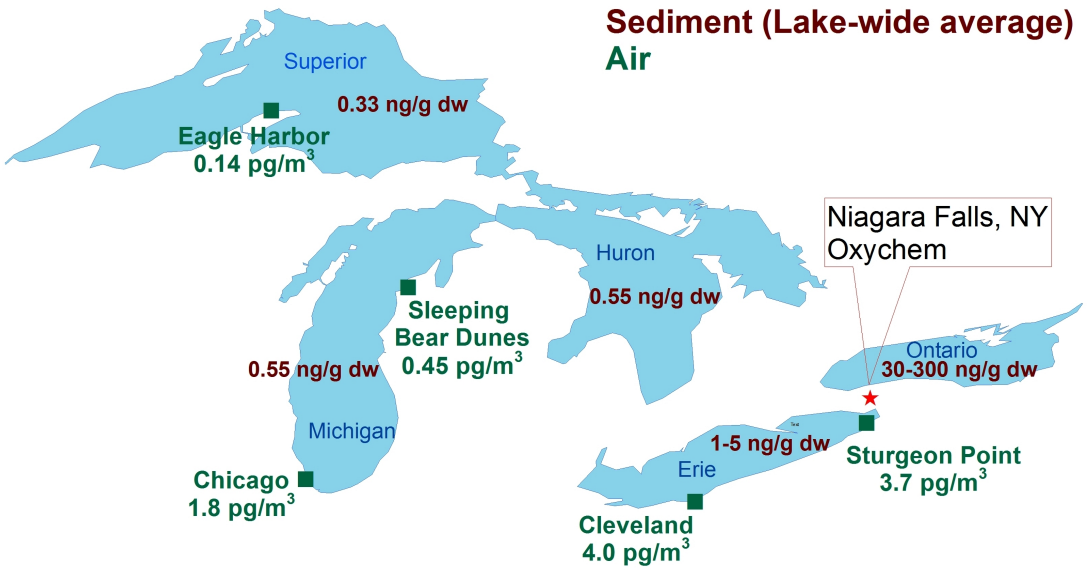

Figure 2: Map of the Great Lakes showing five current United States air sampling sites. The DP manufacturing plant is in the city of Niagara Falls, New York, which is on the Niagara River, a tributary connecting Lakes Erie and Ontario. The geometric means of DP's atmospheric concentrations (summed vapor plus particle phases) are given at each site (in pg m^{-3}). The lake-wide average sediment DP concentration is also given for each lake (in ng g^{-1} dw).

The Jiangsu Anpon Electrochemical Co. (Anpon) is a DP production facility located in the city of Huai'an, northwest of Shanghai.[8] Atmospheric concentrations The fraction of the *syn* isomer (ratio of the *syn*-DP concentration to the total DP concentration, or f_{syn}) in the particle phase samples from the Great Lakes region shows a significant relationship to distance from the manufacturing site in Niagara Falls (r^2 = 0.772, $p < 0.05$). The intercept of this regression line was close to the fraction of the *syn* isomer in the commercial product (0.35) but, 1000 km away from this presumed source, this fraction has decreased significantly to < 0.5.

This study applied the same active, discrete sampling technique as used by the researchers sampling near the North American OxyChem manufacturer. Atmospheric concentrations near the point source in China were 10^3-10^4 times higher than the atmospheric concentrations near the point source in North America, but this is likely not a fair comparison because the samples from China were collected much closer to the production facility than were the samples from North America. It is an open question if the Anpon facility in China has a higher or lower DP emission rate than the OxyChem facility in the United States.

Some data are emerging on DP levels in air from Europe. Levels in Spain have recently been reported by de la Torre et al.[12] These samples were obtained using PUF disk passive sampling, and the concentrations were about 0.8 pg m^{-3} in rural areas and about 11 pg m^{-3} in the city of Madrid. These levels are somewhat higher than in the Great Lakes region but lower than in China.

Global background levels have recently been reported over the Atlantic Ocean by

Möller et al.[7] In air over the East Greenland Sea and over the northern and southern Atlantic Ocean, DP concentrations ranged from 0.05 - 4 pg m^{-3}, clearly indicating that DP is subject to long-range atmospheric transport. In air from the northern Atlantic, the highest concentrations were observed near the English Channel, indicating Western Europe as a source region to the marine environment. The f_{syn} values for the samples from the East Greenland Sea ranged from 0.05 - 0.7, and the values for samples from the southern Atlantic Ocean were all about 0.35. All of these latter values are significantly lower than that of the commercial product. Like the data for the Great Lakes, this result may indicate the selective atmospheric depletion of the *anti* isomer. It is interesting to note that the high end of these concentrations (approximately 4 pg m^{-3}) is about the same as the concentrations observed in air sampled near the eastern Great Lakes.

Sediment Concentrations

DP concentrations have been measured in many surficial sediment samples from the Great Lakes. These dry-weight (dw) averages are: Lake Superior, 0.33 ng g^{-1}; Lake Michigan, 0.55 ng g^{-1}; Lake Huron, 0.87 ng g^{-1}; Lake Erie 1.2 ng g^{-1}; and Lake Ontario 26 ng g^{-1}.[9] Lake Ontario is downstream of DP's manufacturing plant in Niagara Falls, and the sediment concentrations there are greater than in the other lakes. Both of these observations are clear indications of the impact of this source on the environment. DP concentrations in surficial sediments from various locations in China have also been measured. It is interesting to note that even the highest of these concentrations is lower than DP levels measured in Lake Ontario.

While surficial sediment samples are useful for understanding the spatial variations of DP concentrations as a function of geography, sediment cores are necessary for understanding the temporal variations; in other words, sediment cores help us determine how much of this material has entered the environment as a function of time. Such data are available only for the North American Great Lakes.[1,13] In general, concentrations maximized in about 1980 - 1990 and have tended to decrease in the recent past, perhaps reflecting reductions in either DP's production at the Niagara Falls facility or its release into the environment. As with the surficial sediments, the concentrations in the cores are much higher in Lake Ontario (particularly its western-most basin) compared to the four up-stream lakes, clearly indicating the effect of the manufacturing plant in Niagara Falls. A regression analysis of all of the f_{syn} values found in each section of these sediment cores as a function of year of deposition shows a weak, but significant correlation ($r^2 = 0.0942$, $p < 0.01$) with the fraction of the *syn* isomer increasing with depth (time) in the core, perhaps indicating preferential degradation of this isomer. However, this assumption does not consider the possibility that f_{syn} values in the technical mixture may have changed over time due to modifications in DP's production chemistry.

Soil Concentrations

DP concentrations have only been measured in soil samples from China. Typical DP levels at rural locations in China are 0.1 to 1 ng g^{-1} dw,[14] while typical urban concentrations are about 5 ng g^{-1} dw.[14,15] There was one atypically high DP level at 3300 ng g^{-1} dw in soil sampled near an e-waste recycling workshop in Qingyuan, China.[14]

Wang et al.[8] also found relatively high levels of DP in soil samples from the city of Huai'an, which turned out to be the home of the Chinese manufacturer of DP. At this location, concentrations were typically 10 ng g^{-1} dw except very near the manufacturing site itself; Figure 3 shows a maxima of 13,000 ng g^{-1} dw. In all of these Chinese soil samples, the f_{syn} is about 0.30. Given that the Chinese product has an f_{syn} value of 0.40, these somewhat lower f_{syn} soil values may indicate the preferential environmental enhancement of the *anti* isomer.

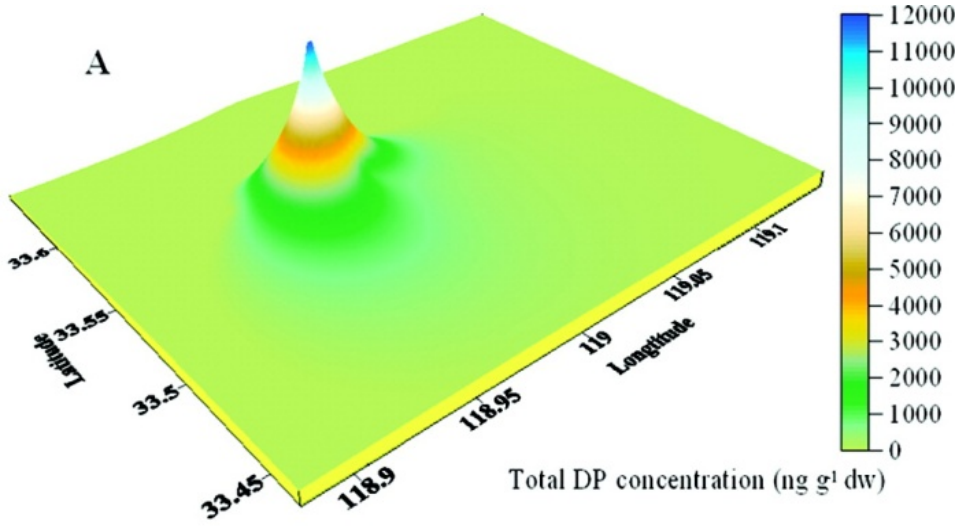

Figure 3: Concentrations of DP in soil samples in the vicinity at a Chinese manufacturing site plotted as a function of latitude and longitude. The Chinese manufacturing source is in the city of Huai'an at 33.5783 °N, 118.9882 °E.

Water and Wastewater Concentrations

DP concentrations in water are available only for a few rivers in China and for the Atlantic Ocean. In China, the rivers that have been studied are in the relatively large cities of Dalian and Harbin, where the DP levels are on the order of 0.2 - 2 ng $L^{21-23,16}$ In water from the Atlantic Ocean, the levels are much lower, ranging from below the detection limit to 0.0013 ng L^{-1} in the East Greenland Sea.[7] DP was also measured in a waste water treatment plant in China; the concentrations were 2.7, 2.8, and 0.2 ng L^{-1} for the influent, primary effluent, and secondary effluent, respectively.[17] In this case, the treatment system appeared effective. DP was also present in biosolids from sewage treatment plants in Spain and North Carolina at levels of about 33 and 45 ng/g dw, respectively.[18,19]

Biota Concentrations

In the North American Great Lakes, the concentrations of DP in fishes do not vary much between the five lakes. For lake trout collected from Lake Ontario, the DP level is about 4 ng g^{-1} lipid and is decreasing with a half-life of about 14 years.[20,21] In another study of lake trout from Lake Ontario, Shen et al. found that the DP concentrations were lower at about 1 ng g^{-1} lipid and that the levels in trout collected in 1975 - 1995 were five times greater than post-1995 levels. For lake trout from Lake Erie, the DP concentrations were 0.1 - 1.0 ng g^{-1} lipid, similar to the concentrations in Lake Ontario.[1] Another study showed that DP levels in lake trout and whitefish collected from four of the Great Lakes were all about 0.2 ng g^{-1} lipid, except for whitefish from Lake Ontario, where it was about 1.3 ng g^{-1} lipid.[9] The concentrations of DP in the Lake Ontario whitefish (but not

in the lake trout) were significantly higher than in all of the other samples (ANOVA, $p < 0.005$). The difference between the whitefish and lake trout levels may be due to dietary differences.

DP concentrations in aquatic invertebrates (zooplankton, mussels) and vertebrates (various fishes) from Lake Winnipeg range from about 0.04 to 0.82 ng g^{-1} lipid. In higher trophic level (TL) organisms from Lake Winnipeg, concentrations of *anti*-DP were greater than those of *syn*-DP. For example, in walleye and goldeye, *anti*-DP concentrations accounted for greater than 90 % of the total body burden of DP. Conversely, in lower TL organisms like zooplankton and mussels, the *syn*-isomer accounted for 100 % of the total DP body burden.

DP levels in aquatic organisms collected from Asia are much higher than in fishes from the Great Lakes. For example, concentrations of 250 ± 50 ng g^{-1} lipid were measured in oysters from Dalian, and the median DP concentration in several species of fish from Korea was 11 ng g^{-1} lipid (with a range of 0.6 - 130 ng g^{-1} lipid).[22] Levels in biota collected near e-waste recycling sites in China were even higher at 20 - 2000 ng g^{-1} lipid.[16,23] These authors also demonstrated a strong positive relationship between the f_{syn} values and TL suggesting that there is either a preferential depletion of the *anti*-isomer relative to the *syn*-isomer with increasing TL and/or that the *syn*-isomer is less bioaccumulative.[16,23]

Bird eggs represent a convenient way to sample the terrestrial food web. For example, herring gull eggs from the Great Lakes and from other parts of Canada have been studied for years. DP levels have been reported to be 1.5 - 15 ng g^{-1} wet weight

(ww) by Gauthier et al.[3,24] and 0.2 - 3 ng g^{-1} ww by Letcher et al.[25] with gull eggs from the Great Lakes at the high end of these ranges. Eggs collected nearest to Niagara Falls are particularly high, presumably because of proximity to the source. Conversely, eggs from Spanish storks showed concentrations much lower than those from the Great Lakes: 0.08 ng g^{-1} ww in a park and 0.31 ng g^{-1} ww in Madrid.[26] Falcon eggs from Spain and Canada have also been studied.[27] DP levels in these eggs from Spain were 0.8 - 2.5 ng g^{-1} lipid (note the different units than used above), which was about the same as gull eggs from outside the Great Lakes region. Levels in falcon eggs from Canada were 38 - 65 ng g^{-1} lipid, which was higher than those found in herring gulls, when the units are adjusted. DP has also been detected in serum (not eggs) taken from young bald eagles nesting in the Great Lakes region at concentrations of 0.2 ± 0.1 ng g^{-1} ww,[28] indicating that DP is accumulating in these high trophic level animals.

There have also been a few studies of DP concentrations in people from China. One such study for people living near an e-waste recycling facility showed median levels of about 43 ng g^{-1} lipid in their blood.[29] This was higher than levels in people from southern China, who served as control samples, who had a median of about 14 ng g^{-1} lipid. In some cases, a mono-dechlorination DP analogue was detected in the samples from the e-waste population. In all of these samples, f_{syn} was generally about 0.4, indicating little differential metabolism of the two isomers in people. In a more recent study, DP and its mono-dechlorination product have been found in hair from workers at an e-waste recycling plant in southern China at levels significantly exceeding those in control populations.[30]

As a method of determining the spatial distribution of DP in the atmosphere, Qiu and Hites measured the two DP isomers in tree bark collected from white pines throughout the northeastern United States.[6] The levels decreased in proportion to the square of the distance from Niagara Falls. Generally, f_{syn} did not change with distance and was 0.25. These authors also analyzed DP in a few samples from Europe (which showed levels about 10 times lower than the United States) and from Asia (which showed levels about the same as the United States). More recent work has demonstrated a significant correlation between DP concentrations in tree bark and those in the surrounding air.[31]

Bioaccumulation Parameters

Biomagnification factors (BMFs) > 1 indicate chemical biomagnification (increased lipid normalized concentrations with increasing trophic position), and BMFs < 1 indicate no biomagnification (decreased lipid normalized chemical with increasing trophic position). Trophic level adjusted biomagnification factors (BMF_{TL}) ranged from < 0.1 to 0.6 (*syn*-DP) and from 0.8 to 11 (*anti*-DP) for predator-prey relationships in Lake Winnipeg and from 0.1 to 12 (*syn*-DP) and from 0.1 to 11 (*anti*-DP) for predator-prey relationships in Lake Ontario. Trophic magnification factors (TMFs) reflect the "average" degree of biomagnification (increasing lipid normalized concentrations with increasing trophic position) or bio-dilution (decreasing lipid normalized concentrations with increasing trophic position) for all species sampled in the food web. Lake Winnipeg aquatic food web TMFs for *syn*-DP and *anti*-DP were 0.45 and 2.5, respectively. Lake

Ontario aquatic food web TMFs for *syn*-DP and *anti*-DP were 0.44 and 0.34, respectively. These data suggest that food web biomagnification may be occurring in some cases for DP; however, there is substantial variability between the BMF and TMF data which may be a result of species-specific differences in biotransformation, limited sample size, or a violation of the steady-state assumption required for calculating BMFs and TMFs, i.e., the chemical concentrations in the food web are not approximating steady-state conditions.

Dietary bioaccumulation testing of DP in lake trout has been conducted. These laboratory data can be examined to determine possible sources of uncertainty and variability in the field-derived bioaccumulation parameters. Fish were dosed with *anti*- and *syn*-DP in food in two separate exposures for 49 days followed by 112 days of depuration (uncontaminated diet). Neither isomer reached steady-state in the fish after 49 days of exposure; however, kinetic bioaccumulation parameters were calculated from the data. The kinetic laboratory based BMFs were 5.2 and 1.9 for the *syn*- and *anti*-DP isomers, respectively. The laboratory BMF data suggest that both isomers biomagnify in lake trout, i.e., high bioaccumulation potential. The measured first-order depuration data were used to calculate whole body (minus liver) biological half-lives of 53 days and 30 days for the *syn*- and *anti*-DP isomers, respectively.

RELATED COMPOUNDS

A number of DP-related compounds have recently been detected in a variety of environmental matrices. These compounds include other DP isomers, impurities formed

through side reactions in the synthesis of DP, dechlorination products of DP, or DP analogues formed by using an alternate dieneophile as a starting material.

Sediment and Soil Concentrations

When DP cannot be applied in selected materials because such flame retardant formulations do not meet specific voltage leakage and thermal standards, alternatives such as, Dec602 and Dec604 are suggested as alternatives. In these cases, a mixture of Dec602 and Dec604 (see structures below) at loading amounts between 2 % to 30 % by weight have been used to meet these standards.[32] Dec602 is also used in Fiberglass-Reinforced Nylon-6 at 18 % by weight,[33] and Dec604 is used in Molykote® AS-810 Silicone Grease made by Dow Corning (10 – 30 % by weight) for lubrication of metal-to-metal and metal-to-plastic substrates in electro-mechanical applications.[34]

Shen et al. found Dec602, Dec603, and Dec604 in 24 surficial sediment samples from all of the Great Lakes.[9] The concentrations of Dec602, Dec603, and Dec604 ranged from 0.001-11, 0.001-0.6, and 0.001-8 ng g^{-1} dw, respectively; see Figure 5. Dec602 and Dec603 were detected in all of the lakes, but Dec604 was detected primarily in Lakes Erie and Ontario.

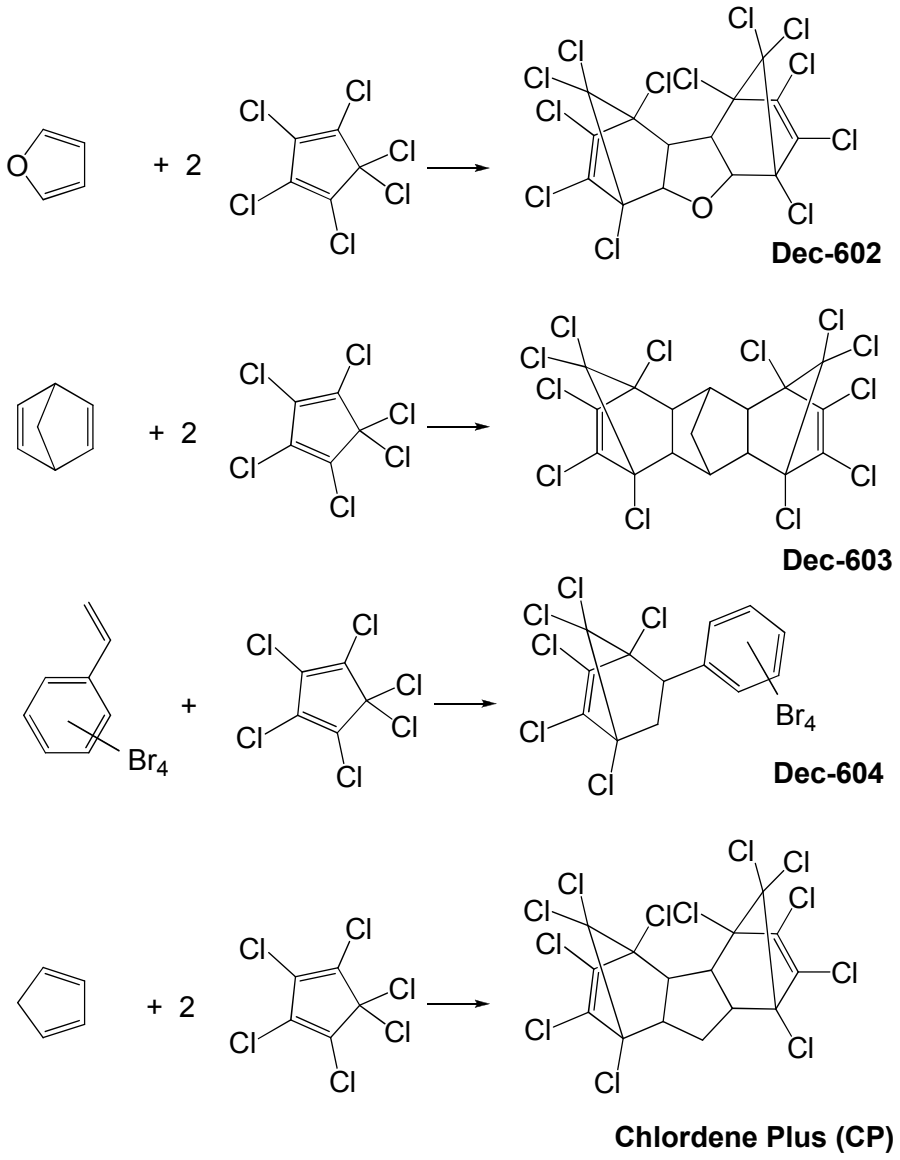

Figure 4: Synthesis reactions creating Dechloranes-602, -603, -604 and Chlordene Plus

Temporal trend measurements using sediment cores show that levels of these DP analogues increased until the mid-1980's; that these levels remained relatively steady until about 2000; and that these levels are increasing again.

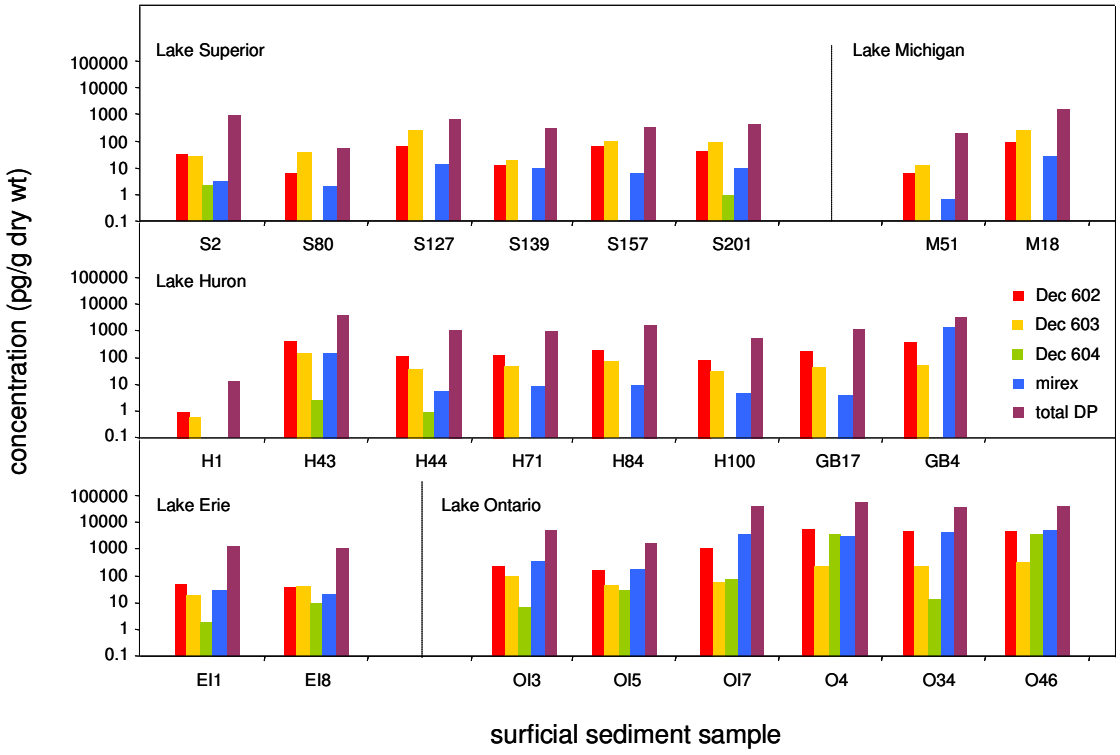

Figure 5: Concentrations of Dechloranes 602, 603, and 604, mirex and Dechlorane Plus in surficial sediment from the Great Lakes. S = Lake Superior, M = Lake Michigan, H = Lake Huron, GB = Green Bay, E = Lake Erie, and O = Lake Ontario.

In a second study, Shen et al. reported an extensive survey of Dec602, Dec603, Dec604 and Chlordene Plus (CP) in sediment from North American Great Lakes tributaries.[35] Dec602 was reported in tributaries from all lakes at levels ranging from not detected (ND) to 13 ng g^{-1} dw with the highest concentrations found in the Niagara River suspended sediment. Dec603 was detected in most samples with concentrations ranging

from ND to 1.1 ng g^{-1} dw. The highest relative concentrations of Dec603 were detected in Lake Erie. Dec604 was detected in all Niagara River/Lake Ontario samples, 60 % of the Lake Superior samples, one of the Lake Huron samples, and not detected in the Lake Erie samples. The concentrations of Dec604 in these samples ranged from ND to 4.8 ng g^{-1} dw. CP had the lowest overall concentrations, but it was detected in most samples at levels ranging from ND to 0.27 ng g^{-1} dw. The CP pattern of detection was different than the other three DP analogues.

Shen et al. also analyzed a number of hexachlorocyclopentadiene-derived pesticides for the presence of Dec602, Dec603, Dec604, CP, and DP.[35] Dec602, Dec604, and DP were not detected in any of the pesticides; Dec603 was detected in aldrin and dieldrin; and CP was detected in chlordene and chlordane. The distribution of Dec602 and Dec604 in the environment appears to be related to the use of consumer products, while the distribution of Dec603 and CP appear to be related to the use of these now banned organochlorine pesticides. The concentrations of DP and DP analogues were greater than those of BDE-209 in the Niagara River, similar to BDE-209 in Lakes Erie and Ontario, and less than BDE-209 in Lakes Superior and Huron.[35]

In still another study, Shen et al. reported annual trends for these compounds in Niagara River suspended sediment. Samples were taken yearly in March from 1980 to 2007. Levels ranged from 0.45 - 1.3, 0.15 - 0.28, and 0.3 - 1.3 ng g^{-1} dw for Dec602, Dec603, and Dec604 respectively. Dec602 and Dec603 showed decreasing trends over that time period with half-lives of 8 and 11 years, respectively. A definitive trend for Dec604 could not be determined. Shen at al.[36] also analyzed Niagara River suspended

sediments collected monthly from April 2006 to March 2007. The relative concentrations were DP > Dec602 > Dec604 > Dec603 > CP. Seasonal concentrations were reflective of the total organic carbon content.

There has been significant research on the environmental levels of DP analogues in China, which is currently a significant producer of DP and a leading electronics manufacturer and recycler. Wang et al. measured Dec602 concentrations of ~2 ng g^{-1} dw in sediment from a canal near the Anpon DP manufacturing plant in Huai'an, China.[8] This value is similar to the 6 ng g^{-1} dw in Lake Ontario surface sediment as reported by Shen et al.[9] Concentrations of Dec602 in soil samples from around the plant ranged from 0.1 to 53 ng g^{-1} dw with a mean of 7 ng g^{-1} dw. Values decreased by a factor of 10 within 7.5 km of the plant. Jia et al. detected Dec602 at 0.11 ng g^{-1} dw and Dec603 at 0.028 ng g^{-1} dw in seashore sediments from Bolai and Huanghai in Northern China. Dec604 was not detected. These levels are similar to those in Lakes Erie, Huron, and Superior, but significantly lower than in Lake Ontario.

Atmospheric Concentrations

There are currently no reports of DP analogues in North American air samples. Wang et al. reported about 0.1 pg m^{-3} in the vapor phase and 4.5 ng g^{-1} in the particulate phase for Dec602 in air samples taken 380 m from the Anpon manufacturing plant in China.[8] Recently, de la Torre et al. reported results from several air samples (8 urban, 11 rural) in Spain for Dec602, Dec603, and CP.[12] Dec604 and 1,5-DPMA were not detected. CP and Dec603 were only detected at three sites for each compound. The

average values for Dec602 were 0.27 and 0.28 pg m^{-3} for rural and urban sites, respectively. These levels are four times less than rural DP levels and 20 times less than urban DP levels.

Wastewater and biosolids

Qi et al. detected Dec602 in the primary effluent of a waste water plant at 0.020 ng L^{-1}, but this compound was not detected in the influent or secondary effluent.[17] Dec602 was detected at 0.002 ng g^{-1} dw in the primary and secondary sludge; this concentrations was just above the detection limit of 0.001 ng g^{-1} dw. Dec603 and Dec604 were not detected in any of the samples, whereas DP was detected in all of the samples. De la Torre et al. detected Dec602, Dec603, and CP in biosolids from 31 Spanish waste water treatment plants.[37] Dec604 and 1,5-DPMA were not detected in any of the samples. Levels of Dec602, Dec603, and CP ranged between ND and 0.02 ng g^{-1} dw for all samples, except two samples for Dec603, which were above 0.02 ng g^{-1} dw. CP was detected in only five samples.

Biota concentrations and bioaccumulation parameters

Shen et al. detected Dec602, Dec603, and Dec604 in Great Lakes fish at levels ranging from 0.47 - 34, 0.014 - 0.50, and 0.063 - 1.3 ng g^{-1} lipid, respectively.[9] The concentrations of Dec602 were higher than DP in all fish samples, indicating that Dec602 may be more bioavailable or bioaccumulative than DP. Shen et al. also determined temporal trends for these compounds in Lake Ontario lake trout samples collected

between 1979 and 2004. Dec602 and Dec603 were both detected at concentrations ranging from 8 to 180 and 0.03 to 0.4 ng g^{-1} lipid, respectively, and with a generally decreasing trend over that time period. Dec604 was not detected in any of the samples. Shen et al. determined biota-sediment accumulation factors for the DP analogues as well as for mirex using Lake Ontario lake trout samples.[36] Mirex had the highest accumulation factor (7400) followed by Dec602 (270) and CP (91), which were all greater than those calculated for the major PBDEs, the two DP isomers, and the other DP analogues.

Zitko conducted uptake and elimination experiments in fish for mirex, DP, and DP-like chemicals.[38] Atlantic salmon were exposed to these chemicals in water for 4 days (static conditions), and in a separate tank, they were exposed to these chemicals in their diet for 42 days. Dec602 was the only DP analogue (including Dec603, Dec604, and DP) other than mirex to be detected in the fish tissue after 4 days of aqueous exposure. There are several potential sources of error when interpreting aqueous based exposure information following the methods applied in the Zitko study, particularly for very hydrophobic chemicals;[39] therefore, the aqueous exposure data are of limited utility for determining the bioaccumulation characteristics of these chemicals. From the dietary exposure test data, the whole body biological half-lives were 58, 76, 63 and 68 days for DP, Dec602, Dec603, and Dec604, respectively. The half-life for total DP in salmon is similar to the half-life reported for the *syn*-DP isomer reported in rainbow trout.

Guerra et al. compared the levels of DP analogues in peregrine falcon eggs from Canada and Spain with aquatic and terrestrial diets (comprising primarily water-birds and

terrestrial birds).[27] Concentrations (ng g^{-1} lipid) showed the following relative pattern: 1,5-DPMA ≈ Dec602 > Dec603 ≈ DP > Dec604 > Cl_{11}DP ≈ Cl_{12}DP. Eggs from falcons with aquatic diets generally had higher concentrations of DP analogues than those with a terrestrial diet, and Canadian falcon eggs had higher concentrations than Spanish falcon eggs.

Munoz-Arnanz et al. analyzed white stork eggs from Spain.[26] The mono dechlorination product of DP was detected in about 10 % of the samples. Neither the di-dechlorination product nor 1,5-DPMA were detected in any of the samples. Jia et al. analyzed 45 oysters corresponding to seashore sediments from Bolai and Huanghai in Northern China. Dec602 was detected in 28 samples at an average concentration of 9.1 ng g^{-1} lipid, and Dec603 was detected in 10 samples at an average of 11 ng g^{-1} lipid. Dec602 levels were similar to those reported by Shen et al. for Great Lakes fish, while Dec603 levels were higher.

PHYSICAL-CHEMICAL PROPERTIES AND MODELS RELATING TO FATE AND BIOACCUMULATION

Solubility and partitioning

There is a lack of measured physical-chemical property data for DP and its analogues. Thus, quantitative structure-activity relationship (QSAR) models were used to estimate water solubilities (S_W), vapor pressures (P_S), octanol-water partition

coefficients (K_{OW}), air-water partition coefficients (K_{AW}), and octanol-air partition coefficients (K_{OA}) (see the Supporting Information). The models indicate that all of these chemicals are super-hydrophobic (S_W < 10 ng L^{-1}; log K_{OW} > 7) with very low vapor pressures (P_S < 10^{-6} Pa), and as a result, there are technical challenges in obtaining reliable measurements of these physical-chemical properties.

Environmental half-lives, persistence, and long-range transport potential

Available screening-level models indicate that these chemicals are not readily biodegradable and that the half-lives in water, soil, and sediment are greater than screening criteria used in the Stockholm Convention.[40] The modeled half-lives in air for some of these chemicals are less than the Stockholm Convention screening criteria (i.e., < 2 d); however, these half-lives are predicted for the gas phase only and use default OH radical concentrations.[41] Due to the low vapor pressures of these chemicals, DP and its analogues will be associated with particles in the atmosphere (i.e., > 99 % particle bound), and this is supported by the monitoring data. Therefore, the actual half-lives in air may be greater, allowing for the long-range transport of these chemicals on particles. Other chemicals with similar properties (i.e., low vapor pressures), such as decabromodiphenyl ether, are also known to have a significant long-range transport potential.[42]

The OECD Tool[43] was used to calculate the characteristic travel distance and overall persistence of DP and DP analogues and to compare these estimates with benchmark chemicals. The results of the OECD Tool are uncertain because the

environmental half-lives for air, water, and soil required as input for the OECD Tool calculations are largely from QSAR estimates; however, in general, the OECD Tool results suggest that DP and its analogues have comparable transport and persistence properties as many listed Stockholm Convention pollutants. The screening-level model results also support available monitoring data indicating the long-range transport potential of these chemicals.

Biotransformation half-lives and bioaccumulation

Biotransformation half-lives in fish were estimated from an *in vivo* depuration test for DP[44] and from a screening-level QSAR model.[45] These biotransformation half-lives are slow and comparable to biotransformation half-lives associated with chemicals that are known to biomagnify and bioaccumulate in aquatic food webs.[45] Bioaccumulation factors (BAFs; L-water/kg-wet weight) calculated by a screening-level QSAR model show that steady-state BAFs in fish are > 5000 (L-water/kg-wet weight) for DP and its analogues.

For screening-level purposes, the biotransformation half-lives and high BAFs predicted by the models are in general agreement with the measured half-life, BMF, and TMF data, and they all indicate a high bioaccumulation potential. Collectively, these data suggest that DP and DP-like chemicals discussed in the present review have the potential to bioaccumulate in aquatic food webs. The predicted BAF values exceed bioaccumulation hazard criteria outlined in the Stockholm Convention (i.e., > 5000).[40] BAFs for these chemicals are difficult to measure because water concentrations in the

environment are usually near or below detection limits, and the dissolved (bioavailable) fraction of the chemical in the water will also be low. For example, the bioavailable fraction (i.e. concentration dissolved/total concentration measured) for DP (log K_{OW} ~9) is estimated to be about 0.005 based on typical environmental concentrations of dissolved and particulate organic carbon.[1]

Air-surface exchange

Wang and co-workers measured both air and soil samples collected concurrently near a DP manufacturing facility.[8] DP concentrations in both the gas and particle phases for three air samples were measured for three consecutive days in October, 2009. It is interesting to note that, while the levels of particle-bound DP in air during the three sampling days varied widely (7330 - 26,300 pg m^{-3}) due to local wind direction and speed, the levels of gas-phase DP were quite stable (390 - 430 pg m^{-3}). Furthermore, the values of f_{syn} for gas-phase DP was 0.26 ± 0.04, close to that in soil (0.22 ± 0.11), but higher than those for particle phase DP (0.36 ± 0.01), which is close to that of DP produced by the Chinese manufacturer. This may indicate different sources of DP in the two phases; therefore, we suggest that the particle-phase DP, in air measured near this DP manufacturer, originated from the DP production facility, while the gas-phase DP originated from soil volatilization.

In order to explore this further, the ratio of C_A/C_S was calculated. If we use DP's log K_{OA} value from Table SI-4, we get an equilibrium ratio of (see SI for details):

$$C_A / C_S \approx 3.2 \times 10^{-5}$$

where C_A is the DP concentration in air (in pg m^{-3}) and C_S is the DP concentration in soil (in pg g^{-1} dw). The concentration of DP in a soil sample collected nearest the air sampler was 13,400 ng g^{-1} dw. Using the above equation, air concentrations of DP in the gas-phase at equilibrium were calculated to be 430 pg m^{-3}, which is close to the measured value (390 - 430 pg m^{-3}).

Air-water exchange was also studied using the data measured by Moller et al. in the marine boundary layer air and in surface seawater from the East Greenland Sea and in the Northern and Southern Atlantic Oceans.[7] The mean gas-phase DP concentrations in air and in the dissolved-phase in the sea water were, respectively, 0.121 pg m^{-3} and 0.009 pg L^{-1} in the East Greenland Sea and 0.028 pg m^{-3} and 0.044 pg L^{-1}, respectively, along the Atlantic transect. These concentrations suggest that the fugacity fraction (*ff*) is 0.96 in the East Greenland Sea and 0.92 along the Atlantic transect. These values are near unity and indicate net gaseous deposition of DP to seawater and support the importance of long-range atmospheric transport as a major pathway for DP to reach the Arctic and Antarctica.

FOCUS OF RESEARCH AND OBJECTIVES

The analytical measurement of DP is not simple. *In situ* dechlorination occurs when GC injection liners becomes 'dirty'; discovered during the course of this research. One of our priorities has been to develop an analytically sound method to accurately measure DP concentrations and its isomers in various environmental matrices. After a publication by other researchers describing the occurrence of DP around the only known

manufacturing plant (OxyChem, Niagara Falls, NY) we set out to further investigate the fate of DP and its isomers in various environmental compartments located near the OxyChem plant. Furthermore, we wanted to look at whether DP was only a local phenomenon by analyzing air samples in the world utilizing the Global Atmospheric Passive Sampling (GAPS) study. If detected, this would suggest DP as a worldwide contaminant with sources stemming beyond that of the manufacturing plant.

This sandwich-based thesis is comprised of three published papers (Chapters 2,3 & 5) and two manuscripts currently submitted for review to the journal of Environmental Science and Technology (Chapters 4 & 6). Each chapter is preceded by a description of the co-authors' contribution to the paper as well as mine. This thesis describes the progression of my research including the discovery of several new compounds related to DP and their fate in the environment.

References

[1] Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40*, 1184-1189.

[2] Betts, K. S. A new flame retardant in the air. *Environ. Sci. Technol*. **2006**, 40, 1090-1091.

[3] Zhu, J.; Feng, Y. F.; Shoeib, M. Detection of Dechlorane Plus in residential indoor dust in the city of Ottawa, Canada. *Environ. Sci. Technol.* **2007**, *41*, 7694-7698.

[4] Ren, G. F.; Yu, Z. Q.; Ma, S. T.; Chen, L. G.; Luo, X. F.; Sheng, G. Y.; Fu, J. M. Dechlorane Plus in in-and outdoor air of an urban city in southern China. *Organohalogen Compd.* **2010**, *72*, 852-855.

[5] The European Commission report on potential alternatives to deca-BDE. http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE (accessed Jan 16, 2011).

[6] Qiu, X. H.; Hites, R. A. Dechlorane Plus and other flame retardants in tree bark from the northeastern United States. *Environ. Sci. Technol.* **2008**, *42*, 31-36.

[7] Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Large-scale distribution and transport of Dechlorane Plus in air and sea water of the Arctic to Antarctic. *Environ. Sci. Technol.* **2010**, *44*, 8977-8982.

[8] Wang, D. G; Yang, M.; Qi, H.; Sverko, E.; Ma, W. L; Li, Y. F; Alaee, M.; Reiner, E. J.; Shen, L. An Asia-specific source of Dechlorane Plus: Concentration, isomer profiles, and other related compounds. *Environ. Sci. Technol.* **2010**, *44*, 6608-6613.

[9] Shen, L.; Reiner, E. J.; MacPherson, K. A.; Kolic, T. M.; Sverko, E.; Helm, P. A.; Bhavsar, S. P.; Brindle, I. D.; Marvin, C. H. Identification and screening analysis of halogenated

norbornene flame retardants in the Laurentian Great Lakes: Dechloranes 602, 603, and 604. *Environ. Sci. Technol.* **2010**, *44*, 760-766.

[10] Venier, M.; Hites, R. A. Flame retardants in the atmosphere near the Great Lakes. *Environ. Sci. Technol.* **2008**, *42*, 4745-4751.

[11] Hites, R. A.; Salamova, A.; Venier, M. Dechlorane Plus in Great Lakes air. *Organohalogen Compd.* **2010**, *72*, 423-426

[12] de la Torre, A.; Pacepavicius, G.; Shen, L.; Reiner, E.; Jiménez, B.; Alaee, M.; Martinez, M. A. Dechlorane Plus and related compounds in Spanish air. *Organohalogen Compd.* **2010**, *72*, 929-932

[13] Qiu, X. H.; Marvin, C. H.; Hites, R. A. Dechlorane Plus and other flame retardants in a sediment core from Lake Ontario. *Environ. Sci. Technol.* **2007**, *41*, 6014-6019.

[14] Yu, Z.; Lu, S.; Gao, S.; Wang, J.; Li, H.; Zeng, X.; Sheng, G.; Fu, J. Levels and isomer profiles of Dechlorane Plus in the surface soils from e-waste recycling areas and industrial areas in south China. *Environ. Pollution* **2010**, *158*, 2920-2925.

[15] Wang, B.; Iino, F.; Huang, J.; Lu, Y.; Yu, G.; Morita, M. Dechlorane Plus pollution and inventory in soil of Huai'an City, China. *Chemosphere* **2010**, *80*, 1285-1290.

[16] Wu, J. P.; Zhang, Y.; Lou, X. J.; Wang, J.; Chen, S. J.; Guan, Y. T.; Mai, B. X. Isomer-specific bioaccumulation and trophic transfer of Dechlorane Plus in the freshwater food web from a highly contaminated site, South China. *Environ. Sci. Technol.* **2010**, *44*, 606-611

[17] Qi, H.; Liu, L. Y.; Ren, N. Q; Sverko, E.; Huang, J.; Shen, X. D.; Jia, H. L.; Reiner, E. J.; Shen, L.; Li, Y. F. Occurrence of Dechlorane in a wastewater treatment plant of northeast China. Presented at Dioxin, San Antonio, TX, Sept 12-17, 2010; #1484.

[18] Davis, E. F.; Klosterhaus, S. L.; Stapleton, H. M. Measurement of current use flame retardant chemical in biosolids. *Organohalogen Compd.* **2010**, *72*, 1121-1224

[19] de la Torre, A.; Sverko, E.; Alaee, M.; Angeles Martinez, M. Concentrations and sources of Dechlorane Plus in sewage sludge. *Chemosphere* **2010**, 82, 692-697.

[20] Ismail, N.; Pleskach, K.; Marvin, C.; Whittle, M.; Keir, M.; Helm, P.; Tomy, G. T. Temporal trends of flame retardants in Lake Ontario lake trout (1979-2004). *Organohalogen Compd.* **2006**, *68*, 1808-1811.

[21] Ismail, N.; Gewurtz, S. B.; Pleskach, K.; Whittle, D. M.; Helm, P. A.; Marvin, C. H.; Tomy, G. T. Brominated and chlorinated flame retardants in Lake Ontario, Canada, lake trout (*Salvelinus Namaycush*) between 1979 and 2004 and possible influences of food-web changes. *Environ. Toxicol. Chem.* **2009**, *28*, 910-920.

[22] Kang, J. H.; Kim, J. C.; Chang, Y. S. Dechlorane Plus in fish from urban-industrial rivers. *Organohalogen Compd.* **2009**, *71*, 1356-1359.

[23] Zhang, X. L.; Luo, X. J.; Liu, H. Y.; Yu, L. H.; Chen, S. J.; Mai, B. X. Bioaccumulation of several brominated flame retardants and Dechlorane Plus in water-birds from an e-waste recycling region in south China: Associated with trophic level and diet sources. *Environ. Sci. Technol.* **2011**, *45*, 400-405.

[24] Gauthier, L. T.; Letcher, R. J. Isomers of Dechlorane Plus flame retardant in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America: Temporal changes and spatial distribution. *Chemosphere* **2009**, *75*, 115-120.

[25] Letcher, R. J.; Burgess, N.; Champoux, L.; Elliott, J. E.; Hebert, C. E.; Martin, P. A.; Wayland; M.; Weseloh, D. V. C.; Wilson, L. Isomers of Dechlorane Plus in the eggs of

four species of gulls (*Larids*) from colonies across Canada and the influence of diet on spatial distribution. Presented at Dioxin, San Antonio, TX, Sept 12-17, 2010; #1523.

[26] Munoz-Arnanz, J.; Sáez, M.; Pacepavicius, G.; Alaee, M.; Jiménez, B. Dechlorane Plus and possible environmental metabolites in white stork eggs. *Organohalogen Compd.* **2010**, *72*, 933-936

[27] Guerra, P.; Fernie, K.; Jiménez, B.; Pacepavicius, G.; Shen, L.; Reiner, E. J.; Eljarrat, E.; Barceló, D.; Alaee, M; . Dechlorane Plus and related compounds in peregrine falcon (*Falco peregrines*) eggs from Canada and Spain. *Environ. Sci. Technol.* **2011**, *45*, 1284-1290.

[28] Venier, M.; Wierda, M.; Bowerman, W. W.; Hites, R. A. Flame retardants and organochlorine pollutants in bald eagle plasma from the Great Lakes region. *Chemosphere*, **2010**, *80*, 1234-1240.

[29] Ren, G.; Yu, Z.; Ma, S.; Li, H.; Peng, P.; Sheng, G.; Fu, J. Determination of Dechlorane Plus in serum from electronics dismantling workers in south China. *Environ. Sci. Technol.* **2009**, *43*, 9453-9457.

[30] Zheng, J.; Wang, J.; Luo, X. J.; Tian, M.; He, L. Y.; Yuan, J. G.; Mai, B. X.; Yang, Z. Y. Dechlorane Plus in human hair from an e-waste recycling area in south China: Comparison with dust, *Environ. Sci. Technol.* **2010**, *44*, 9298-9303.

[31] Salamova. A.; Hites, R. A. Evaluation of tree bark as a passive atmospheric sampler for flame retardants, PCBs, and organochlorine pesticides. *Environ. Sci. Technol.* **2010**, *44*, 6196-6201

[32] Krackeler, J. P.; Biddell, W. G. Insulated high voltage wire coated with a flame retardant composition, U.S. Patent #3,900,533, 1976.

[33] Chanda, M.; Roy, S. K. *Plastics Technology Handbook*, 4th, ed.; CRC Press: Florida, 2007.

[34] Material Safety Data Sheet: Molykote®AS-810, Dow Corning Corporation, Midland MI, 2009.

[35] Shen, L.; Reiner, E. J.; MacPherson, K. A.; Kolic, T.M.; Helm, P.A.; Richman L.A.; Marvin C. H.; Burniston D; Hill, B,; Brindle, I.D.; McCrindle, B.; Chittim B. G.; Dechloranes 602, 603, 604, Dechlorane Plus and Chlordene Plus, a newly detected analogue, in tributary sediments of the Laurentian Great Lakes. *Environ. Sci. Technol.* **2011***, 45,* 693-699.

[36] Shen, L.; Reiner, E. J.; Helm, P. A., Marvin, C. H.; Hill, B.; Zhang, X., MacPherson, K. A.; Kolic, T. M.; Tomy, G. G.; Brindle. I. D. Historic trends of Dechloranes 602, 603, 604, Dechlorane Plus and other norbornene derivatives and their bioaccumulation potential in Lake Ontario, *Environ. Sci. Technol.* **2011,** *45*, on-line .

[37] de la Torre, A.; Shen, L.; Reiner, E.; Alaee, M.: Martinez, M. A.; New halogenated norbornene flame retardants in sewage sludge. *Organohalogen Compd.* **2010**, *72*, 1060-1063

[38] Zitko, V. The uptake and excretion of mirex and dechloranes by juvenile Atlantic salmon. *Chemosphere* **1980**, *9*, 73-78.

[39] Arnot, J. A.; Gobas, F. A. P. C. A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in fish. *Environ. Rev.* **2006,** *14*, 257-297.

[40] UNEP, Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants. In United Nations Environment Program: Geneva, Switzerland, 2001; p 44.

[41] U.S. EPA *Exposure Assessment Tools and Models, Estimation Programs Interface (EPI) Suite, Ver. 4.0*; U. S. Environmental Protection Agency, Exposure Assessment Branch: Washington, D.C., 2009.

[42] Breivik, K.; Wania, F.; Muir, D. C. G.; Alaee, M.; Backus, S.; Pacepavicius, G. Empirical and modeling evidence of the long-range atmospheric transport of decabromodiphenyl ether. *Environ. Sci. Technol.* **2006,** *40*, 4612-4618.

[43] Wegmann, F.; Cavin, L.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. The OECD software tool for screening chemicals for persistence and long-range transport potential. *Environmental Modeling and Software* **2009,** *24*, 228-237.

[44] Arnot, J. A.; Mackay, D.; Bonnell, M. Estimating metabolic biotransformation rates in fish from laboratory data. *Environ. Toxicol. Chem.* **2008,** *27*, 341-351.

[45] Arnot, J. A.; Meylan, W.; Tunkel, J.; Howard, P. H.; Mackay, D.; Bonnell, M.; Boethling, R. S. A quantitative structure-activity relationship for predicting metabolic biotransformation rates for organic chemicals in fish. *Environ. Toxicol. Chem.* **2009,** *28*, 1168-1177.

CHAPTER 2

Dechlorane Plus Levels in Sediment of the Lower Great Lakes

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Extracts provided by Brad Hill, Chris Marvin and Paul Helm were analysed by Donna Zaruk on the GC/MS and confirmed by high resolution mass spectrometry in Eric Reiner's laboratory. Editorial contributions were made by Gregg Tomy. I conceived and developed this research writing 90 % of the paper while under the supervision of Brian McCarry. This paper was published in the journal of Environmental Science and Technology (2008) and hi-lited in the journal's cover story; currently cited 38 times.

ABSTRACT

A recently discovered chlorinated flame retardant, Dechlorane Plus (DP), was reported in air and a sediment core within the North American Great Lakes region. To further reveal the fate of DP in the Great Lakes, 40 surficial sediments from Lakes Erie and Ontario and two additional cores were analyzed using newly available analytical grade DP isomer solutions. The maximum total concentration in Lake Ontario was over 60-fold higher than Lake Erie, 586 ng g^{-1} and 8.6 ng g^{-1}, respectively. Additionally, analysis of archived suspended sediments collected from the Niagara River (1980 – 2002) showed a declining total DP concentration of 89 ng g^{-1} to 7.0 ng g^{-1}, suggesting a possible decrease in production or the reduction of free DP released into the environment during manufacturing. The average *syn*-DP fractional abundance (f_{syn}) in our study was less than the commercial DP composition indicating a stereo selective enrichment of *anti*-DP in the environment. Mean f_{syn} profiles were uniquely similar to both Lake Ontario and the Niagara River in comparison to Lake Erie. During the course of our analysis we noticed an increasing f_{syn} value in the calibration standard which became exacerbated as the liner got dirtier and suggested the prospect of DP degradation. Follow-up studies indicated these compounds were dechlorinated DP species produced on the injection liner. Using a clean injection liner these degradates were also detected in sediments from the Niagara River and Lake Ontario; tentatively identified as [-Cl+H] and [-2Cl+2H] by high resolution mass spectrometry. The observed similarity of f_{syn} profiles between Lake Ontario and Niagara River and the detection of the degradates only in their locations,

suggest to us that the river is a major source to Lake Ontario's DP burden. To our knowledge, this is the first report of DP degradates in the environment.

INTRODUCTION

Dechlorane Plus is an additive chlorinated flame retardant used primarily in wire cable coatings and plastic roofing material. The United States EPA has categorized this chemical as a High Production Volume Chemical (HPVC) with estimated production volumes at more than one million pounds annually.[1] In the last few years flame retardants have received considerable attention from environmental scientists, and more recently regulators as the physical-chemical properties that make compounds useful as flame retardants also give rise to environmental concern. Brominated flame retardants, especially the penta and octa diphenyl ether formulations, now face regulation worldwide. Although focus has been on the brominated flame retardant chemicals, the chlorinated flame retardant, Dechlorane Plus (DP, CAS #13560-89-9), was recently measured in air and sediment samples in the Great Lakes region where it has been produced for over 40 years.[2]

An earlier chlorinated flame retardant developed by Hooker Chemical (now OxyChem, Niagara Falls, NY, USA), called Dechlorane or Mirex ($C_{10}Cl_{12}$), was banned because of its toxicity to marine invertebrates. The DP ($C_{18}H_{12}Cl_{12}$) formulation replaced the banned flame retardant with subsequent production volumes estimated to be one million pounds annually and potentially as high as 10 million.[1,3] The flame retardant is sold worldwide, including Europe and the Far East. The technical DP formulation, containing 65 % (by weight) chlorine, is an additive flame retardant that is compatible with a range

of polymers primarily used in wire coatings and plastic roofing materials; other reported minor uses include automotive, textile and connectors in computer applications.[4,5] The percent composition of DP in commercial polymer products range from 10 – 35 %. While DP is on the Canadian Domestic Substances List it does not rank highly in terms of risk for bioaccumulation because of its high molecular weight and high log K_{OW}, 9.3. However other data suggest that these reported by Tomy et al. show bioaccumulation for certain organisms in food webs of Lakes Winnipeg and Ontario.[4,6] Additionally, OxyChem's submission to the voluntary EPA HPV Challenge Program indicates that DP has ecotoxicological effects in fish and may affect sediment bearing organisms due to its adsorptive properties.[4] Sediments in the Great Lakes are the main repository for hydrophobic and persistent organic pollutants such as polychlorinated biphenyls (PCBs) and decabromodiphenyl ethers (PBDEs).[7,8]

Although Hoh et al. reported DP levels in several environmental compartments, limited sediment spatial information was available for Lake Erie and no levels were reported in Lake Ontario, downstream of the manufacturing plant. In this paper we present DP levels in two Lake Erie cores, the spatial distribution in surficial sediments for Lakes Erie and Ontario, and the temporal trend of DP in Niagara River suspended sediment.

MATERIALS AND METHODS

Sample Collection

Surficial sediment samples for Lake Erie and Lake Ontario were collected in 1997/1998 and 1998, respectively, aboard the *CCGS Limnos* via the mini box coring technique as described previously.[9] Briefly, samples comprised of the top three centimeters of lake-bottom sediment were freeze dried, transferred to a Teflon-lined, capped glass jar and frozen (-20 ^{o}C) until analysis. Benthos gravity core samples were collected at Lake Erie's two index stations in 1997 according to Marvin et al. (2003). Core samples were treated similar to suspended sediment procedures. Niagara River suspended sediments were collected by centrifuging large volumes of Niagara River water at Environment Canada's Niagara-on-the-Lake monitoring station, near the mouth of the river.[10] Samples have been collected every two weeks since 1980, with a portion archived frozen. For this study, samples collected mid-March (1980 – 2002) were analyzed to capture spring runoff with higher particulate loads.

Sample Extraction and Analysis

Bottom sediment samples were processed at Environment Canada's National Water Research Institute in Burlington, ON. After the addition of recovery surrogates (CB30 and CB204, Accustandard, New Haven, CT, USA), the samples (5 g) were extracted using pressurized fluid extraction (Dionex Corp., Mississauga, ON, Canada) with acetone:hexane, 1:1 (v/v). Extracts were purified with modified silica gel,

fractionated into A and B with hexane and DCM:hexane, 1:1 (v/v), respectively. Fraction-B, which contains the DP isomers, was injected onto an Agilent (Mississauga, ON, Canada) 5980 GC, fitted with a 30 m DB-5 capillary column (0.25 μm film thickness x 0.25 mm i.d.; J&W Scientific, Folsom, CA, USA), coupled to an Agilent 5973 mass selective detector in negative ion chemical ionization mode using methane as the reagent gas. Confirmation analyses were conducted using DB-35 with the same dimensions to the DB-5 column. Split/splitless injections of 1 μL were made onto an injector set isothermally at 265 ºC. The initial oven temperature was set at 80 ºC with a 2 min hold time, ramped at 10 ºC/min to 285 ºC, and held for 5 min. Source and quadrupole temperatures were set to 150 ºC and 106 ºC, respectively. The dominant peak in the molecular ion cluster of the *syn* and *anti* isomers (*m/z* 651.8; spectra were identical) was used for quantitation while the second most abundant peak (*m/z* 653.8) was used for confirmation. Measurements of the dechlorinated Cl_{11} and Cl_{10} moieties were conducted by monitoring *m/z* ions 617.7/619.7 and 583.8/585.8, respectively. An Agilent GC/ECD measured the chlorinated biphenyl surrogates for sample extraction efficiencies during organochlorine pesticide analysis. Niagara River suspended sediments were extracted and analyzed at the Ontario Ministry of Environment's Laboratory Services Branch. Samples were Soxhlet extracted for 18 h using toluene. The raw extracts were reduced in volume then cleaned by silica column chromatography eluted with 50:50 DCM:hexane. The DP stereoisomers were detected and quantified using the same procedures as described above. All concentrations are given on a dry weight of sediment basis.

UV Exposure Study

An analytical grade *syn*- and *anti*-DP isomer solution in high purity isooctane (> 98 %, Caledon Inc., Caledon, ON, Canada) at 100 ng mL^{-1} each was exposed for 24 h per day to UV-A, 365 nm, light at 30 W (Spectroline Inc, Westbury, NY, USA) at a distance of 20 cm for 31 days. The solution was placed in a borosilicate vessel sealed with a Teflon lined cap and intermittently subsampled during the exposure event.

Identification of Dechlorinated Moieties

Identified suspect peaks were analysed for exact mass using the Agilent 5890 GC coupled to a Micromass (Mississauga, ON, Canada) TOF-MS in both negative ion chemical ionization and electron ionization modes (resolving power @ 5000). Elemental compositions of the unknown compounds were determined within 3.7 ppm error.

Quality Assurance/Quality Control

All recoveries for CB30 and CB204 were 78 ± 12 % and 97 ± 14 %, respectively (±1 SD). Method detection limits (MDLs) were calculated by conducting a replicate spike study (n = 7), which included the addition of the DP isomers at 0.5 ng each into Ottawa sand (~5 g). Once the spikes had been extracted and analysed, the calculated standard deviation was applied to determine detection limits using a one-sided student's t-test @ 95 % confidence, which gave rise to MDLs of 30 pg g^{-1} and 25 pg g^{-1} for the *syn*-

and *anti*- isomers, respectively. The linear dynamic range of the instrument was 10 pg to 2500 pg on column ($r^2 > 0.995$) for both isomers. The ratio of the quantitation and confirmation ions in samples was within 15 % of measured standard values in all cases. Procedural blanks were added at a rate of one for every 12 samples – neither DP isomer nor their dechlorinated moieties were detected.

RESULTS AND DISCUSSION

Spatial and Temporal Levels of syn- and anti-DP

The total dry-weight DP concentration ranges (ng g^{-1}) for Lakes Erie and Ontario were 0.061 – 8.62 and 2.23 – 586, respectively (Figure 1). The lake-wide average in Lake Ontario was more than 50 times greater than Lake Erie. In comparison, Li et al. (2005) reported Lake Ontario surficial sediment total PBDE levels of only four fold over Lake Erie.[11] A previous study suggests that inter-lake differences based on dry weight surficial PBDE concentrations were minimized when data were normalized to total organic carbon.[8] When applying this normalization to the inter-lake DP concentration difference, the levels are still 10-fold higher in Lake Ontario. This strongly suggests that the Niagara River is a likely source, being an area in which DP is manufactured. The central basin in Lake Erie exhibited the highest concentrations throughout the lake, however these concentrations were approximately five times lower than for BDE209 surficial concentrations reported by Zhu and Hites (2005) and Song et al. (2005).[8, 12] Sediments are therefore more susceptible to redistribution due to influences from wind,

convective currents and, additionally, benthic organisms may become more active which can exacerbate the lake bottom disturbance.[8] Reported sediment down flux rates in Lake Erie's shallow western basin are much greater than in Lake Ontario due to substantial resuspension of bottom sediments.[13] Interestingly, the spatial PCB pattern measured from the same 1997/98 sampling event showed a distinctly western basin maximum resulting from discharges from the Detroit River and other local tributaries.[14] Although Hoh et al. (2006) suggested an eastern basin point source near the OxyChem plant, we did not measure a similar, expected eastern basin DP maximum in our surficial sediment study. This may be due to recent reduction in production volumes, or the plant's influence on Lake Erie sediment DP burden is not locally significant. Although current available literature suggests that DP's only manufacturing location is in Niagara Falls, New York, there appears to be a second historical DP manufacturing plant. According to a Final Plan of Remedial Action document prepared by the Delaware's state Department of Natural Resources and Environmental Control in 2005, DP was reportedly produced during BP Amoco's Polymer plant operation from 1961 to 1980 site in New Castle, Delaware.[15] This brings into question whether there may be other possible, current or historical, production plants which produced DP and may present the possibility of a non-single point source for air transport as another environmental compartment input.

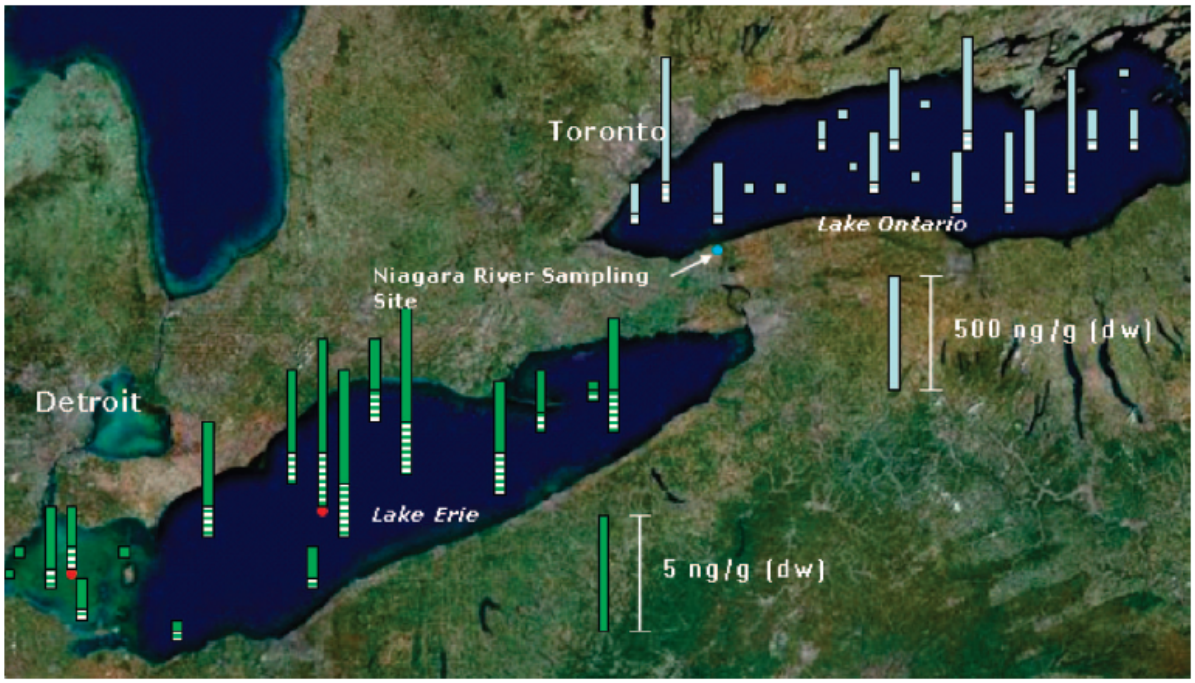

Figure 1. Total *syn*- and *anti*-DP levels in surficial sediment. Red dots represent core sample sites, lined and solid colors represent *syn*- and *anti*-DP, respectively.

The spatial distribution of DP in Lake Ontario was generally related to bathymetry, with the highest concentrations associated with fine grained sediments in the three major deep-water depositional basins (Figure 1). The non-depositional sill zones, including the Whitby-Olcott sill separating the Niagara and Mississauga basins, and the Scotch Bonnet sill separating the Mississauga and Rochester basins, exhibited the lowest levels. These sill zones are characterized by coarse sand that adsorb hydrophobic contaminants less effectively than fine silts and clays in depositional areas.[16] In contrast to the lower comparative Lake Erie DP levels to the BDE209 concentrations reported by

Song et al., Lake Ontario DP values were approximately twice the BDE209 concentrations.

The Niagara River has been identified as the source for several organic contaminants into the receiving waters of Lake Ontario, including polychlorinated dibenzo-*p*-dioxins/dibenzofurans, PCBs and mirex.[9, 17] The spatial distribution of DP observed in our study is similar to those of other contaminants, including PCBs. The highest concentration measured in Lake Ontario was near the city of Toronto. This is somewhat puzzling if one was to consider the Niagara River as the primary source in conjunction with the counter clock-wise gyre flow pattern of the lake.[18] A potential contribution to the lake's DP burden would be manufacturers who include DP in their product formulation resulting in secondary sources into the lake. However, these preliminary observations and the corresponding conclusions regarding potential sources remain speculative, and greater spatial resolution during follow-up sampling is required to further identify if industrial sources associated with urban centers are contributors to the DP burden in Lake Ontario. At present, the significant difference in DP concentrations between lakes, strongly points to the Niagara River as a main DP contributor to Lake Ontario.

As a means of elucidating temporal trends in DP accumulation in Lake Ontario sediments, archived samples from the Niagara River Upstream/Downstream program were analyzed. The maximum and minimum values for total DP values for archived Niagara River suspended sediments (1980 – 2002) ranged from 89 ng g^{-1} (1980) to 7 ng g^{-1} (1999). A slight but significant ($p < 0.05$) decline in total DP concentration with time

was observed with a half-life of approximately 17 years (Figure 2) corresponding to a 1 ng g^{-1} decline per year. This agrees well with the half-life of 16 years calculated for Lake Ontario trout during that same period.[19] Although the BDE209 levels in the Niagara River suspended sediments reported for the same sampling period showed an increasing trend, the maximum was less than that of total DP at approximately 21 ng g^{-1}.[20] Song et al. measured a doubling time for PBDEs of 5.3 years in Lake Erie attributable to increasing usage and manufacturing patterns. The DP half-life suggests that usage/production may be decreasing or that modern manufacturing processes release less free DP into the environment.

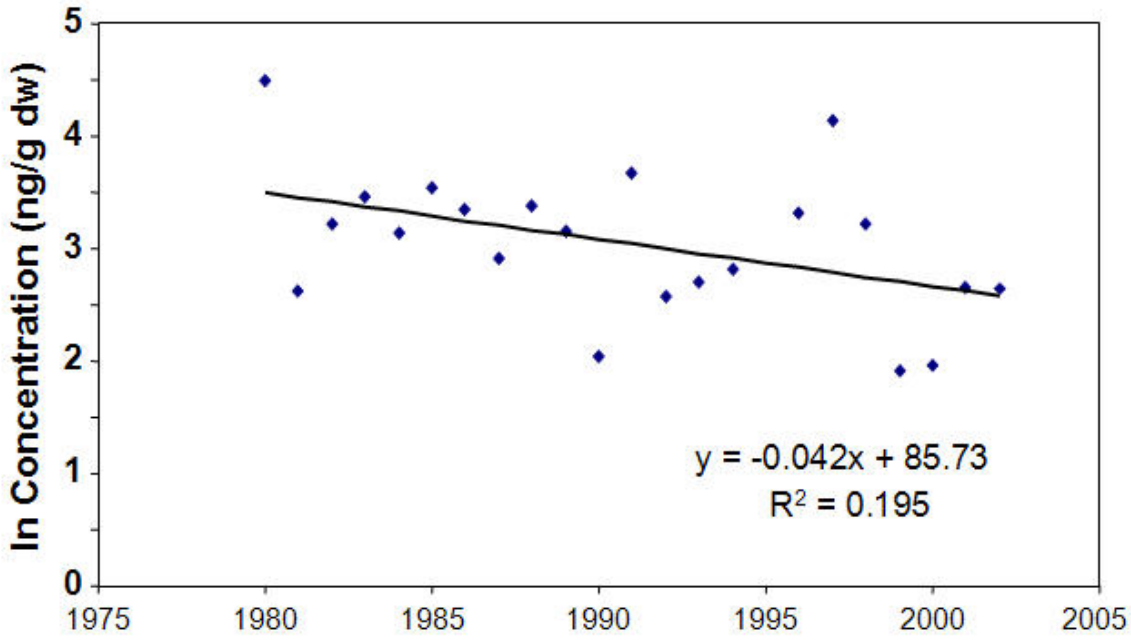

Figure 2: Decreasing trend for DP concentrations in Niagara River suspended sediments.

In sediment cores from Lake Erie, the total DP core maxima of the western and central basins were 4.43 ng g^{-1} and 38.2 ng g^{-1}, respectively. The western basin is relatively shallow, with an average depth of 10 – 15 m, allowing for severe mixing to occur and is evidenced by the comparatively uniform DP core depth profile (Figure 3).[13] The central basin is somewhat deeper at an average depth of 25 – 30 m, and some undisturbed stratification is evident (Figure 4). The core profile shows a bimodal pattern also observed for PCBs reported by Painter et al. A second, shallower maximum of 34.4 ng g^{-1} was also observed. Hoh et al. reported an eastern core maximum of 40.0 ng g^{-1} which suggests a west-to-east increase in DP concentration.

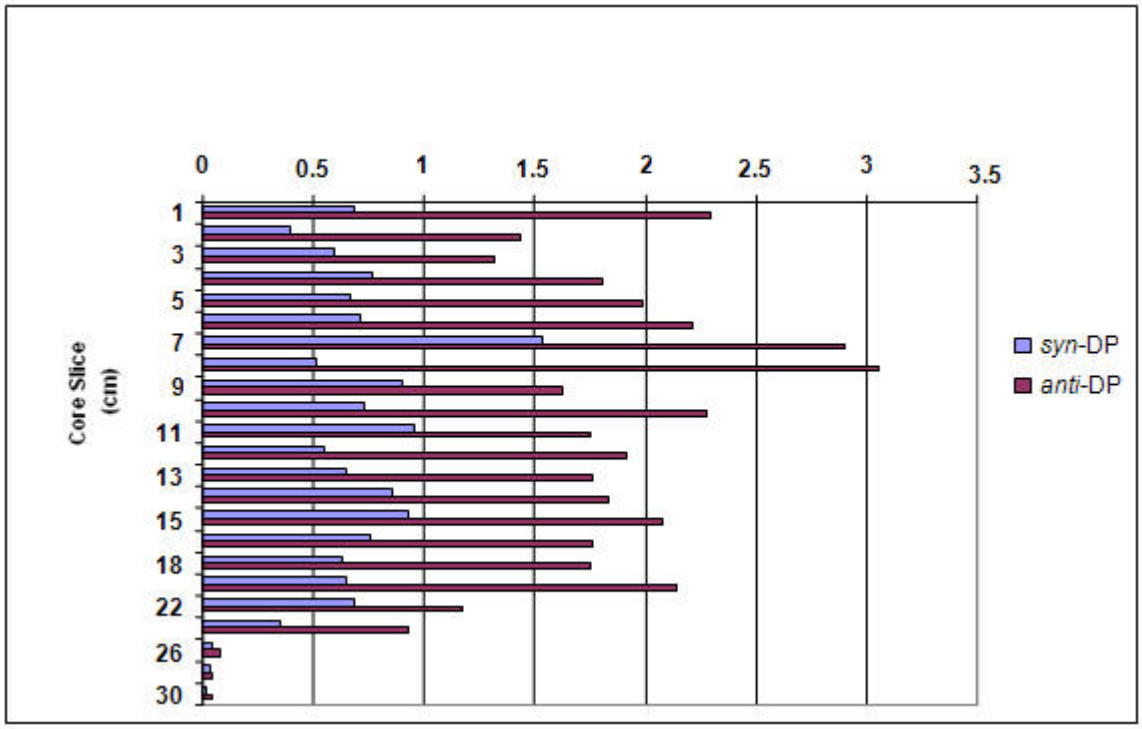

Figure 3. Lake Erie western basin core *syn*- and *anti*-DP profiles (ng g^{-1}).

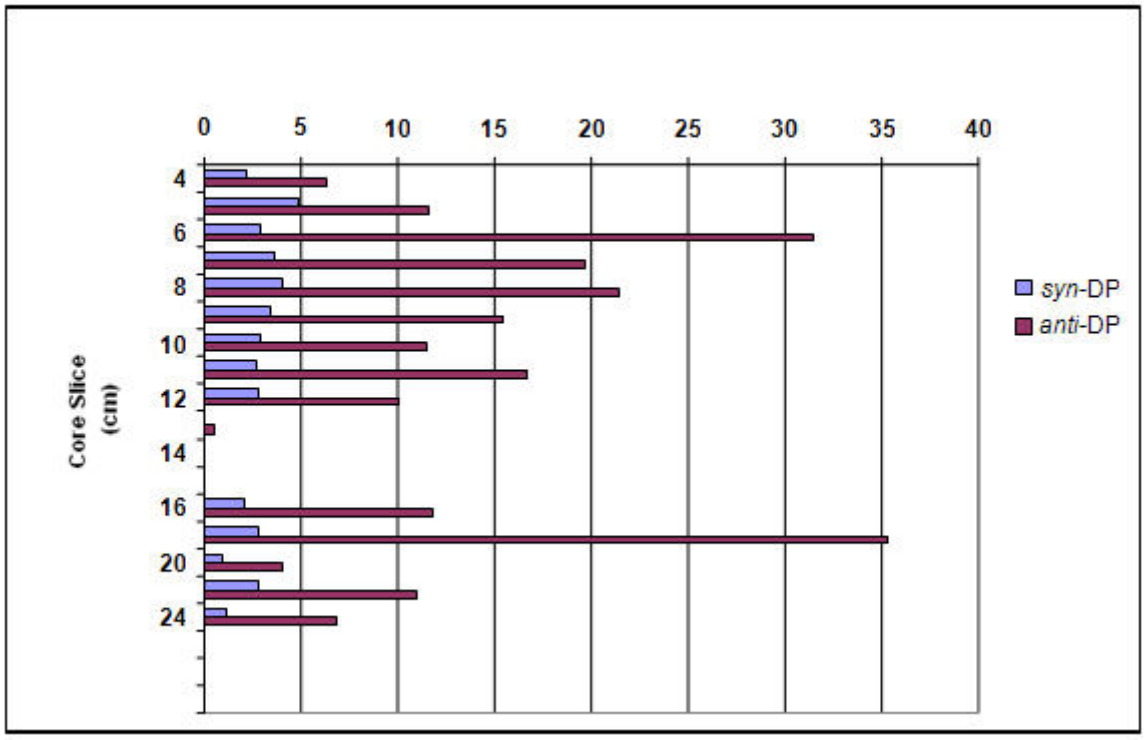

Figure 4. Lake Erie central basin core *syn*- and *anti*-DP profiles (ng g^{-1}).

Syn- and anti-DP Fractional Abundance

The main stereoisomer ratios in sediment as measured in the environment can be described as fractional abundance, given by:

$$f_{syn} = [syn\text{-DP}]/([syn\text{-DP}] + [anti\text{-DP}])$$

The fractional abundance of DP for Lakes Erie and Ontario, the Niagara River and commercial DP are shown in Table 1.

Table 1. Comparison of fractional abundances for *syn-/anti*-DP isomers between the technical mixture and lower Great Lakes sediment.

Location (Zone)	f_{syn}	+/- SD	*n*
Technical DP	**0.355**	**0.004**	**3**
Niagara River	**0.099**	**0.042**	**22**
Lake Ontario (depositional)	**0.167**	**0.061**	**14**
Lake Ontario (non-depositional)	**0.069**	**0.042**	**7**
Lake Erie (depositional)	**0.216**	**0.066**	**7**
Lake Erie (non-depositional)	**0.263**	**0.082**	**11**
Lake Erie Cores			
Central Basin	**0.187**	**0.063**	**17**
Western Basin	**0.287**	**0.064**	**23**

These data show stereo-selective enrichment of the *anti* isomer when compared to the technical DP profile. This holds true for all data except in Lake Erie where the f_{syn} is more similar to the technical mixture. In this study, only Lake Erie is upstream of the OxyChem plant which Hoh et al. suggested atmospheric deposition as a possible source to the lake. In their study air measurements in the Lake Erie basin show a similar

isomeric profile to the technical mixture and maybe related to a possible source from the manufacturing plant. It is interesting to note that the fractional abundance of the Niagara River sediments is significantly different from the commercial mixture. This is somewhat surprising when considering the proximity of the sampling site to the manufacturing plant. There is no significant change or trend in the f_{syn} abundance during the 22 year sampling period.

Very little experimental information exists on the physico-chemical properties of the DP stereoisomers. Current data primarily stems from the manufacturer's in-house laboratory results that were conducted during the 1970's and not commensurate with current Good Laboratory Practice (GLP), so that some of these tests conducted today may produce different results. The only available Log K_{OW} data was reported by OxyChem's laboratory in 1979 using a computer generated value, based on chemical structure-activity models. Only one Log K_{OW} value of 9.3 was given for both *syn*- and *anti*-DP stereoisomers.[21] However, the same document stated that the two isomers had different aqueous solubility at 207 ng L^{-1} and 572 ng L^{-1}, although no information was given as to which isomer exhibited which solubility. This would suggest that *syn*- and *anti*-DP possess differing physico-chemical properties and may be one of the factors contributing to the fractional abundance profile in the Niagara River suspended sediment. Similar profiles are also evident in the Lake Ontario non-depositional zones. The depositional zones in Lake Ontario showed a relative decrease in f_{syn} abundance to those in non-depositional areas 0.167 +/- 0.061 and 0.069 +/- 0.042, respectively. Whereas Lake Erie's shallow depth, particularly in the western basin, results in significant sediment

resuspension, Lake Ontario's greater depths allows less sediment for redistribution into the water column and, therefore, more representative of historical deposition.[8,13] However, assuming that the Niagara River is Lake Ontario's primary DP source and considering the river's relatively consistent fractional abundance profile since 1980 (f_{syn} = 0.099 +/- 0.042), then the depositional zone abundance profile could be the result of other mechanisms. One possibility is stereospecific microbial degradation. OxyChem's studies suggest that DP is susceptible to aerobic microbial degradation, but the report did not mention *syn*- or *anti*-DP specifically.[3] The difference in solubilities between *syn*- and *anti*-DP may suggest a difference in other physico-chemical properties such as log K_{OW} and log K_{OC}. If our assumption is true, then their tendency to preferentially sorb would be mediated by the differing organic content and general composition of suspended sediment from sediment in the depositional zones.

The mean f_{syn} abundance in Lake Ontario is less than that of Erie's and may reflect the similar fractional abundance profile exhibited in the Niagara River suspended sediments, which flows into Ontario. The overall fractional abundance profiles for Lake Erie surficial sediment are generally similar however; the two cores suggest a west to east increase in f_{syn} values. Interestingly, the highest f_{syn} value is measured closest to the reported source; the OxyChem plant .[2] There is no significant change in fractional abundance in relation to depth in all two Lake Erie cores suggesting little or no DP stereo specific decomposition related to anaerobic microbial activity.

DP Decomposition and Possible Dechlorinated Species in the Environment

When we analyzed the technical DP mixture in full scan, provided to us by Dr. Ron Hites, we observed two large peaks representing the *syn*- and *anti*-DP isomers. We postulated that a "batch" process, which uses starting agents of varying purity, would produce other chlorinated by-products in the mixture. In this case, it would be the impurities associated with the one mole 1,5-cyclooctadiene to two moles of hexachlorocyclopentadiene used in the production of the commercial DP, to which there are several reported impurities.[22] Other examples of impurity related by-products formed during the chemical manufacturing process are chemicals such as, chlorinated dibenzo-*p*-dioxin and polychlorinated naphthalenes produced during technical PCB production.[23] The technical DP product information suggests thermal decomposition begins at 285 ^{o}C [4]; however, no indications of any identified decomposition by-products are given. Therefore, all GC/MS operating temperatures were kept below this value, except the transfer line (290 ^{o}C) which, because it was located after the GC column, would not generate any dechlorinated species of differing retention times from the two main DP isomers. If any *in situ* dechlorination were to occur on the transfer line, the chromatographic *syn*- and *anti*-DP responses would only decrease. However, even though our instrument operating temperatures were below the suggested decomposition temperature (GC injector at 265 ^{o}C; DP eluted prior to the 285 ^{o}C maximum GC oven temperature program), the full scan analysis of raw, uncleaned samples resulted in a progressive decrease in *syn*-and *anti*-DP response within the run sequence, and the elution of new peaks. The corresponding *m/z* ion fragment clusters of the unknown peaks

related to [–Cl+H] and [-2Cl+2H] species giving rise to possible $[M]^-$ *m/z* ions of 613.7 and 579.8, respectively (Figure 5e, 5f) . Once the GC liner was replaced, the dechlorinated species were no longer evident suggesting that these compounds were produced and mediated by the "dirty" glass liner via *in situ* dechlorination mechanisms. This may potentially have a significant effect on accurate DP determinations if *in situ* liner dechlorination is occurring and not monitored. In light of the current information related to technical DP's stability and its apparent preponderance to GC liner dechlorination, an investigation to determine if these dechlorinated species existed in the open environment was conducted. Using a clean liner, sediment samples were analyzed for the dechlorinated species identified in the GC/MS analysis. Several compounds were tentatively identified with similar *m/z* ions and GC retention times as our dechlorinated compounds identified in the "dirty liner" injections. These unknowns were particularly prevalent in the Niagara River suspended sediment samples at Niagara-on-the-Lake, some higher in peak area than *syn*- and *anti*-DP (Figure 5d.).

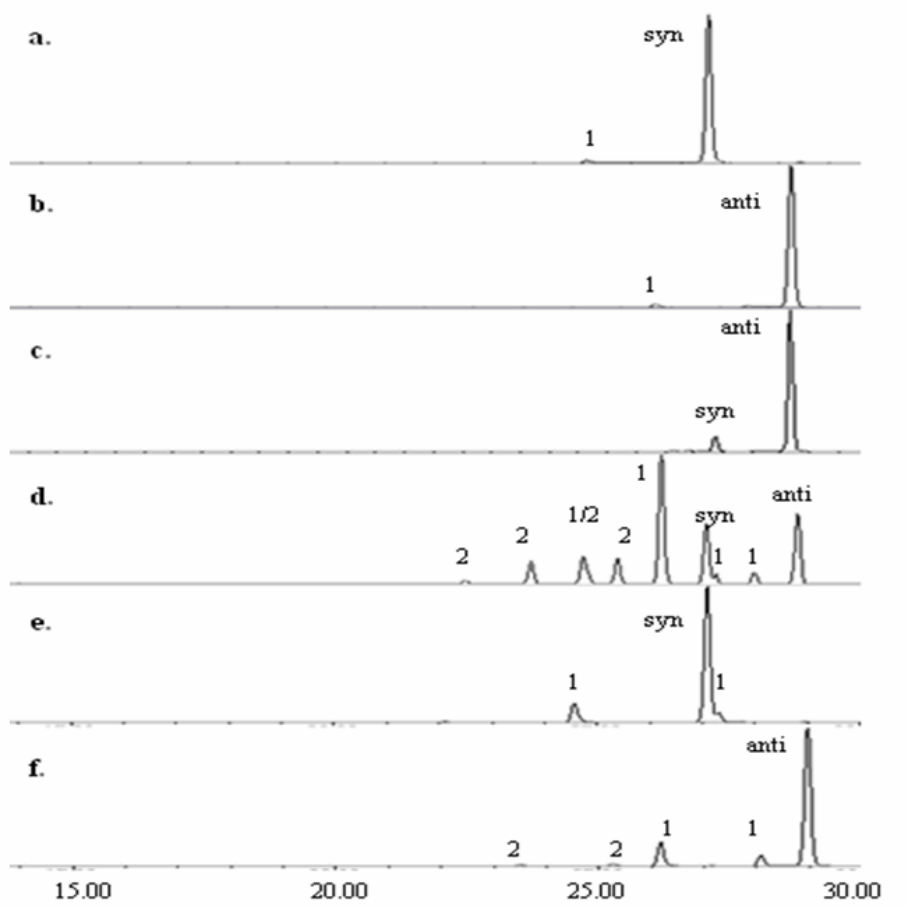

Figure 5. Total ion chromatograms of: a.) *syn*-DP; clean liner, b.) *anti*-DP; clean liner, c.) Lake Ontario sediment, d.) Niagara River sediment, e.) *syn*-DP; dirty liner, f.) *anti*-DP; dirty liner. "1" and "2" signify -1Cl and -2Cl dechlorination DP species, respectively.

The chromatogram exhibits the apparent existence of several -1Cl and -2Cl species. To further confirm these compounds, the extracts were analyzed by GC/TOF-MS to determine the possible elemental composition of the identified unknowns. Elemental composition analysis confirmed the unknown peaks as $C_{18}H_{13}Cl_{11}$ and $C_{18}H_{14}Cl_{10}$ within 3.7 ppm error. Initial analysis of suspended and lake-bottom sediments reveal the predominance of these compounds resided in the Niagara River sediment. To ensure the formation of the dechlorinated moieties were not induced by elevated injector temperatures, on-column GC/MS analyses confirmed the presence of these compounds in the extracts. None of these compounds were detected in Lake Erie surficial or core sediments, however, were detected in Lake Ontario. To help understand whether photodegradation may play a significant role, we initiated a simple UV exposure study which irradiated a 100 ng mL^{-1} isooctane solution of each DP isomer to UV light ($\lambda \geq 365$ nm) for a 30-day period. Our results showed a decrease in parent DP concentration of 10 % at 168 h and a further corresponding loss at 264 h and 504 h of 40 % and 65 %, respectively. In our study, *anti*-DP appeared to degrade more readily than the *syn*-DP stereoisomer.

Our experiments show that dechlorinated moieties, similar to DP's molecular composition, exist in the environmental compartments investigated in this study. DP's predecessor, mirex, was shown to uniquely degrade to photomirex via humic-mediated photo degradation.[24, 25] Although we have not conducted these similar studies, it may help to explain one possible degradation pathway and perhaps the differences measured in fractional abundances in the sediment when compared to the commercial mixture.

However, this does not explain why the fractional abundance of the sediment closest to the reported DP source is significantly different from the technical mixture.

Acknowledgements

The authors thank Gerry Ladwig for his analytical contribution to Niagara River sediments data, Dr. Kirk Green at McMaster University's Mass Spectroscopy laboratory for assistance with GC/TOFMS analysis, Gilles Arsenault of Wellington Laboratories for the analytical grade *syn*- and *anti*-DP stereoisomer standards and Ken Kuntz for provision of archived Niagara River sediments.

References

[1] Betts, K. S. A new flame retardant in the air. *Environ. Sci. Technol.* **2006** (40) 1090–1091.

[2] Hoh, E.; Zhu, L.; Hites, R.A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006** (40) 1184-1189.

[3] Unites States EPA Inventory Update Rule. http://www.epa.gov/cgi/iursrch3_2002.cgi.

[4] Occidental Chemical Corporation (OxyChem®), Dechlorane Plus® Manual, http://www.oxy.com/OXYCHEM/Products/dechlorane_plus/dechlorane_plus.htm.

[5] Weil, E. D.; Levchik, S. Commercial flame retardancy of polyurethanes. *J. Fire Sci.* **2004** (22) 251-263.

[6] Tomy, G.T; Pleskach, K.; Ismail, N.; Whittle, D.M.; Helm, P.A.; Sverko, E.; Zaruk, D.; Marvin, C.H. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* **2007** (41) 2249-2254.

[7] Mackay, D.; Bentxen, E. The role of the atmosphere in Great Lakes contamination. *Atmos. Environ.* **1997** (31) 4043-4047.

[8] Song, W.; Ford, J. C.; Li, A.; Sturchio, N. C.; Rockne, K. J.; Buckley, D. R.; Mills, W. J. Polybrominated diphenyl ethers in the sediments of the Great Lakes,. 3. Lakes Ontario and Erie. *Environ. Sci. Technol* **2005** (39) 5600-5605.

[9] Marvin, C. H.; Charlton, M. N.; Stern, G. A.; Braekevelt, E.; Reiner, E. J.; Painter, S. Spatial and temporal trends in sediment contamination in Lake Ontario. *J.Great Lakes Res.* **2003** (29) 317–331.

[10] Williams, D.J.; Neilson, M.A.T.; L'Italien, S.; Merriman, J.; Painter, S.; Kuntz, K.W.; El-Shaarawi, A.H. The Niagara River Upstream/Downstream Program 1986/7 – 1996/7: Concentrations, Loads, Trends. Environment Canada, Ecosystem Health Division Report 00-01/I. 2000.

[11] Li, A.; Rockne, K. J.; Struchio, N.; Song, W.; Ford, J. C.; Buckley, D. R.; Mills, W. J. Polydiphenyl diphenyl ethers in the sediments of the Great Lakes. 4. influencing factors, trends, and implications. *Environ. Sci. Technol* **2006** (40) 7528-7534.

[12] Zhu, L. Y.; Hites, R. A. Brominated flame retardants in sediment cores from Lakes Michigan and Erie and Ontario. *Environ. Sci. Technol.* **2005** (39) 3488-3494.

[13] Marvin, C. H.; Sverko, E.; Charlton, M. N.; Theissen, P. A.; Painter, S. Contaminants associated with suspended sediments in Lakes Erie and Ontario, 1997-2000. *J. Great Lakes Res.* **2004** (30) 277-286.

[14] Painter, S.; Marvin, C.; Rosa, F.; Reynoldson, T. B.; Charlton, M. N.; Fox, M.; Thiessen, L.; Estenik, J. F. Sediment contamination in Lake Erie: a 25-year retrospective analysis. *J. Great Lakes Res.* **2001** (27) 434-448.

[15] Delaware State Remedial Action Report http://www.dnrec.state.de.us/DNREC2000/Divisions/AWM/SIRB/Proposed_Plans/remedial.pdf

[16] Thomas, R. L. The distribution of mercury in the sediments of Lake Ontario. *Can. J. Earth Sci.* **1972** (9) 636-651.

[17] Comba, M. E.; Norstrom, R. J.; Macdonald, C. R.; Kaiser, K.L. A Lake Ontario_Gulf of St. Lawrence dynamic mass budget for mirex. *Environ. Sci. Technol* **1993** (27) 2198-2206.

[18] Pickett, R. L.; Bermick, S. Observed resultant circulation of Lake Ontario. *Limnol. Oceanogr.* **1997** (22) 1071-1076.

[19] Reiner, E.; Ladwig, G.; Marvin, C.; Sverko, E.; Helm, P.; Muir, D. Dechlorane Plus in the Niagara River: Temporal trends in archived suspended sediments from 1980 to 2002. Symposia papers presented before the division of the Environmental Chemistry American Chemical Society, San Francisco, CA. September, 2006.

[20] Marvin, C.; Williams, D.; Kuntz, K.; Klawuun, P.; Backus, S.; Kolic, T.; Lucaciu, C.; MacPherson, K.; Reiner, E. Temporal trends in polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like PCBs, and polybrominated diphenyl ethers in Niagara river suspended sediments. *Chemosphere* **2007** (67) 1808-1815.

[21] USEPA HPV voluntary robust summary. http://www.epa.gov/chemrtk/pubs/summaries/dechlorp/c15635tc.htm

[22] EPA, 1991a. Drinking water criteria document for hexachlorocyclopentadiene. Cincinnati, OH: US Environmental Protection Agency, Office of Water. ECAO-CIN-D007.

[23] Yamashita. N.; Kannan, K.; Imagawa, T.; Miyazaki, A.; Giesy, J. Concentrations and profiles of polychlorinated naphthalene congeners in eighteen technical polychlorinated biphenyl preprations. *Environ. Sci. Technol* **2000** (34) 4236-4241.

[24] Burns, S. E.; Hassett, J. P.; Rossi, M. V. Binding effects on humicmediated photoreaction: intrahumic dechlorination of mirex in water. *Environ. Sci. Technol* **1996** (30) 2934-2941.

[25] Burns, S. E.; Hassett, J. P.; Rossi, M. V. Mechanistic implications of the intrahumic dechlorination of mirex. *Environ. Sci. Technol* **1997** (31) 1365-1371.

CHAPTER 3

Compounds Structurally Related to Dechlorane Plus in Sediment and Biota from Lake Ontario (Canada)

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Extracts provided by Chris Marvin and Paul Helm were analysed by Donna Zaruk on the GC/MS and further hi-resolution mass spectrometric determinations were conducted by Li Shen and Karen MacPherson in Eric Reiner's laboratory. Robert McCrindle and

Gilles Arsenault synthesized the new compounds while Gregg Tomy provided editorial contributions. I discovered these new compounds during analysis of GC/MS chromatograms and was the principal investigator writing 90 % of this paper. This research was conducted under the supervision of Brian McCarry and published in the journal of Environmental Science and Technology (2010, 15 citations). The research was also hi-lited in the journal's feature news article.

ABSTRACT

The historical occurrence of Dechlorane Plus (DP) and detection of novel compounds structurally related to DP is described in a dated Lake Ontario sediment core. Our core was collected near the mouth of the Niagara River which is known to be a major source of DP to the lake. Maximum DP concentrations (920 ng g^{-1}, dry weight) were observed between 1976-1980; the highest reported to date. Following that time, we observed a dramatic decrease in DP concentration which coincided with the enactment of United States federal and state laws to mitigate free release of chemicals into the Niagara River and installation of an industrial wastewater treatment facility. During the course of our research, four new substances, structurally related to DP were also identified. These compounds were thought to arise from the Diels-Alder reactions resulting from impurities present in 1,5-cyclooctadiene, a feedstock used in production of DP. To confirm our hypothesis, Diels-Alder reactions were performed on the individual impurities. Using different stationary phase capillary gas chromatography columns and high resolution mass spectrometry we were able to positively identify some of these novel compounds in the core. Interestingly, we also were able to identify a monoadduct compound, formed by addition of one mole of hexachlorocyclopentadiene to two moles 1,3-cyclooctadiene, in lake trout. The concentration of this monoadduct was approximately two orders of magnitude greater than that of DP suggesting that it is more bioaccumulative.

INTRODUCTION

Flame retardant (FR) chemicals, which are designed to slow a flame's duration and propagation, have been applied to commercial products since the 19th century.[1] The apparent effectiveness of FRs has resulted in worldwide applications in various products including clothing, furniture, electronics and components for the transportation industry. Undoubtedly, the most successful class of FRs is the one based on bromine; the labile carbon-bromine bond easily avails itself during combustion, scavenging oxygen-containing radicals that ultimately suffocates the flame.[2] However, the widespread use has led to other unintended outcomes. For example, some of the congeners of polybrominated diphenyl ethers (PBDEs) are known to fulfill all three criteria of persistence, toxicity and bioaccumulation. This has led to their recent inclusion to the Stockholm Convention on Persistent Organic Pollutants.[3]

While brominated FRs continue to undergo further risk assessments, use and manufacture of other FRs continue to go unabated. An example is the highly chlorinated FR, Dechlorane Plus (DP, $C_{18}H_{12}Cl_{12}$). First synthesized in the late 1960s, DP has only recently been detected in biota, sediment and the atmosphere.[4] Technical DP contains two isomers *syn* and *anti*, which is used primarily in products such as cable coatings, plastic roofing materials and hard connectors in televisions. DP is currently unregulated for use and considered to be a high production volume (HPV) chemical, and so is subject to the United States Environmental Protection Agency's (USEPA) HPV challenge. It is also listed on Canada's Domestic Substances List.

Recent research has shown that both isomers can bioaccumulate and have the potential to biomagnify in some feeding relationships in aquatic food webs.[5] DP has also been measured in household dust.[6] This is important as human exposure to PBDEs is thought to occur primarily by inhalation of PBDEs sorbed to dust.[7] Muir et al. have also included DP in their top 50 priority compounds of environmental concern.[8]

While it is known that higher brominated congeners of PBDEs can debrominate to more toxic forms[9,10], our previous research has also shown that DP may be subject to dehalogenation as we detected dechlorinated analogues of DP in Niagara River suspended sediment.[11] However, source or environmental fate of these dechlorinated analogues has yet to be determined.

DP was recently included in a European Commission report as a possible candidate to replace deca-BDE in certain applications.[12] With tighter regulations placed on deca-BDE, it is increasingly important to understand the environmental fate and behaviour of DP and its derivatives.

In an effort to elucidate the historical occurrence of DP in Lake Ontario we analyzed a sediment core from the Niagara River Bar (NRB). The NRB is an area where sediment from the Niagara River deposits into Lake Ontario, downstream of and nearest the manufacturing facility. During the course of our research, compounds structurally related to DP were identified in the sediment. Using high resolution mass spectrometry we provide compelling evidence on the identity and potential source of these DP-like com-

pounds in sediment and also in lake trout (*Salvelinus namaycush*) from Lake Ontario. To our knowledge, this is the first report on these compounds occurring in the environment.

MATERIALS AND METHODS

Sample Collection and Dating

Mini box core samples were collected in Lake Ontario's NRB (43°20'198"N, 79°4'202"W) in 2007 (Figure 1). The core was divided into 1 cm slices down to a depth of 10 cm, beyond which 2 cm portions were collected down to 40 cm. Samples were shipped to Environment Canada's National Water Research Institute (NWRI) in WhirlPak bags, freeze-dried and stored (-20 °C) until extraction. Sedimentation rates were determined using the polonium distillation method as described elsewhere.[13] Based on the dating information, a sedimentation rate for the NRB was calculated to be 0.80 cm yr^{-1}. Lake trout (n = 4) were collected between 2000 and 2003. Fish were homogenized whole and stored at -20 °C until analysis.

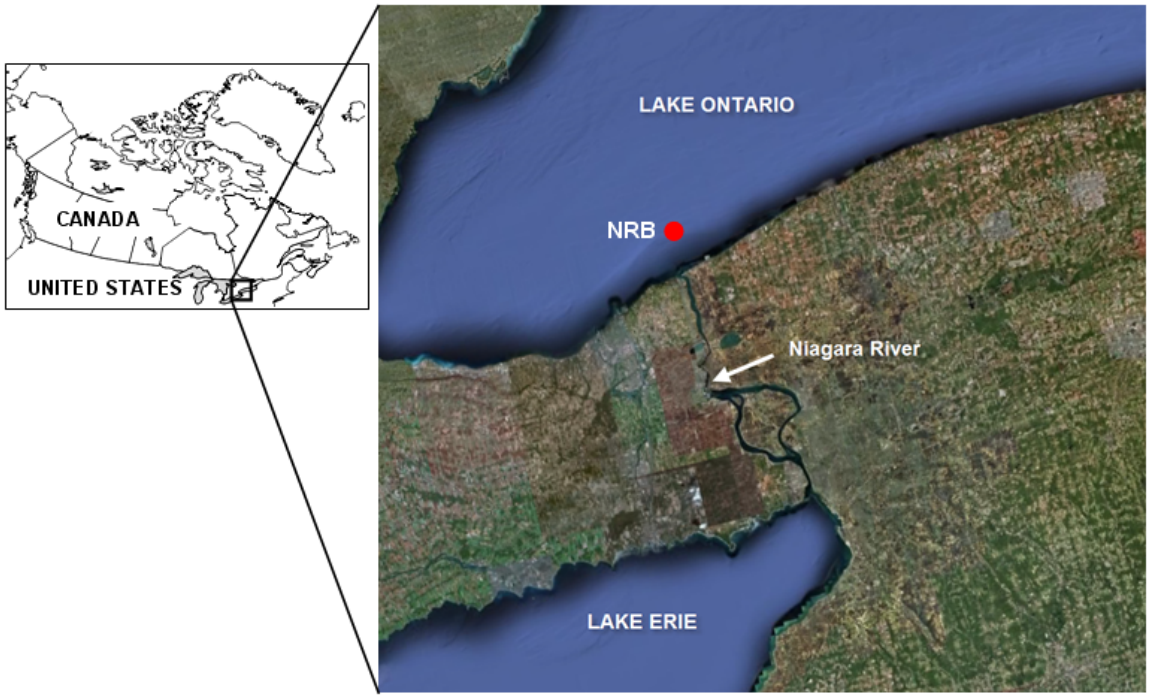


Figure 1. Location of the Niagara River Bar (NRB) core *ca*. 16 km from the mouth of the Niagara River.

Sample Extraction and Analysis

After the addition of recovery surrogates (CB30 and CB204, Accustandard, New Haven, CT), 5 g sediment samples were extracted with an automated pressurized liquid extraction unit (Dionex Corp., Mississauga, ON) using acetone:hexane, 1:1 (v/v). Extracts were purified with modified silica gel, fractionated into A and B using hexane and DCM:hexane, 1:1 (v/v), respectively. Biota were processed as described earlier by Tomy et al.[14] and shipped to NWRI for analysis.

Both sediment and biota extracts were injected into an Agilent (Mississauga, ON) 6890 GC, fitted with a 30 m DB-5 capillary column (0.25 μm film thickness x 0.25 mm i.d.; J&W Scientific, Folsom, CA). The GC was coupled to an Agilent 5975 mass selective detector in electron capture negative ionization mode (ECNI-LRMS) using methane as the moderating gas. One-microlitre injections were made in the pulsed splitless mode using an injector set isothermally at 265 ºC. The initial 80 ºC oven temperature held at 2 min, was ramped by 10 ºC min^{-1} to 285 ºC, and held for 5 min. Source and quadrupole temperatures were set to 150 ^{o}C and 106 ºC, respectively. The dominant peak in the identical molecular ion cluster of the *syn* and *anti* isomers (*m/z* 651.7) was used for quantitation while *m/z* 653.7 and 655.7 were confirming ions. An Agilent 6890 GC/ECD system measured the chlorinated biphenyl surrogates for sample extraction efficiencies during organochlorine pesticide analysis. All sediment and biota concentrations are given as dry weight and lipid weight, respectively.

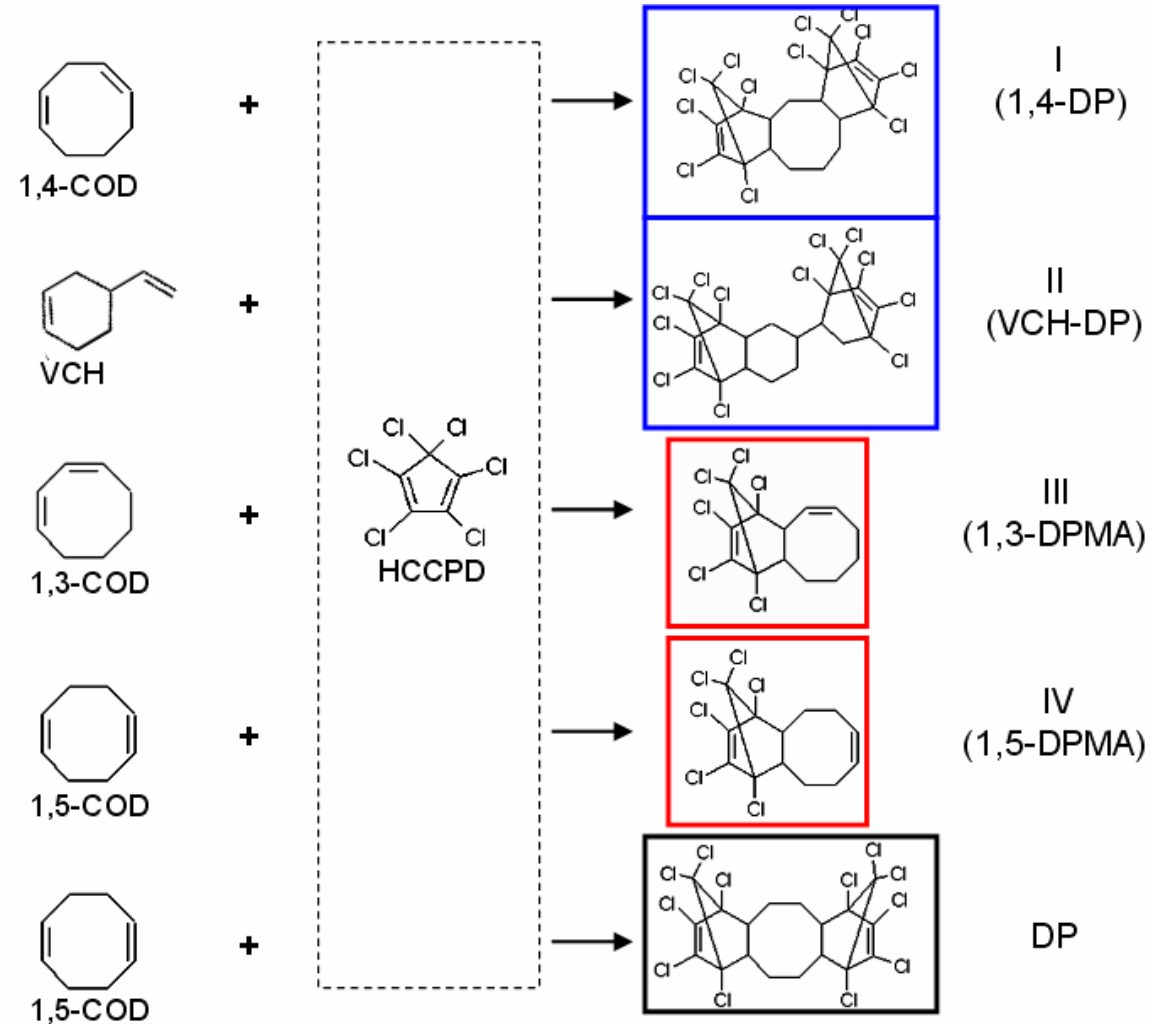
Confirmation of Structurally Related DP Compounds

The new compounds in this study were identified as I, II, III and IV (see Scheme 1). Determination of DP isobaric compounds, I and II, were conducted using gas chromatography high resolution mass spectrometry operated in the electron impact mode (GC/EI-HRMS) at the Ontario Ministry of Environment Laboratory Services Branch. One-microlitre injections were made using an Agilent 6890 GC in splitless mode (injector T = 265 ^{o}C) coupled to a Waters Autospec Premier HRMS (Manchester, UK).

The GC program was as follows: initial temperature of 100 ^{o}C and held for 1 min, ramped to 210 ^{o}C at 10 ^{o}C min^{-1}, followed by a ramp to 310 ^{o}C at 20 ^{o}C min^{-1} and held for 6 min. Ion source temperature was set at 280 ^{o}C, resolution was tuned to a resolving power greater than 10,000 monitoring for quantification and confirmatory *m/z* ions 651.7142 and 653.7112, respectively.

Analysis of the monoadduct compounds, III and IV, was done using a Kratos (Manchester, UK) triple sector HRMS at a resolving power of 10,000. Ion cluster monitored along with their theoretical abundances were: a) $[M]^-$: *m/z* 379.9041 (31.6 %), *m/z* 381.9011 (25.6 %), *m/z* 377.9070 (16.3 %) and *m/z* 383.8982 (11.1 %) and b) $[M\text{-}Cl+H]^-$: *m/z* 345.9430 (34.8 %), *m/z* 347.9400 (22.5 %), *m/z* 343.9460 (21.5 %) and *m/z* 349.9371 (7.3 %). The dwell time on each ion was 294.75 ms. Perfluorokerosene was used as the calibrant gas in ECNI mode and argon (UHP) was used as the moderating gas. The start and lock masses as set by the software were *m/z* 337.8346 and 380.9760, respectively. The dwell time on the lock mass was 50 ms.

Further confirmatory analysis of the compounds included chromatographic separations using an XLB phase column (J&W Scientific, Folsom, CA) with the same Agilent GC/ECNI-LRMS system and dimensions to the DB-5 column.



Scheme 1. Products resulting from a Diels-Alder reaction using 1,4-cyclooctadiene (1,4-COD), 4-vinylcyclohexene (VCH), and 1,3-cyclooctadiene (1,3-COD) with two moles of hexachlorocyclopentadiene (HCCPD). Products giving rise to compounds I, II and III; we term 1,4-DP, VCH-DP, and 1,3-DPMA, respectively. The reaction to produce compound IV (1,5-DPMA) used only one mole of HCCPD together with 1,5-cyclooctadiene (1,5-COD). Products in blue rectangles represent diadduct formation, whereas monoadduct formations are in red. The last reaction depicts 1,5-COD used to synthesize DP with two moles of HCCPD.

Quality Assurance/Quality Control

Surrogate recoveries in sediment for CB30 and CB204 were 81 ± 13 % and 104 ± 16 %, respectively (± 1 standard deviation). Extraction efficiency data for biota are detailed elsewhere.[14] One procedural blank was included for every 12 samples; neither DP isomers nor their related compounds were detected in laboratory blanks. To determine DP extraction efficiency, 50 ng of each isomer was spiked onto 5 g of Ottawa Sand (Fisher Scientific, Fair Lawn, NJ) accompanying every procedural blank. Mean recoveries during this study for *syn*- and *anti*-DP were 89 ± 11 % and 96 ± 9 %, respectively. A separate method spike study was conducted to determine recoveries of the monoadduct compounds, III and IV, due to the subsequent availability of analytical grade 1,5 – Dechlorane Plus monoadduct, (1,5-DPMA, Wellington Laboratories, Guelph, ON) to our original time of analysis. Mean recoveries of 84 ± 7 % were measured in replicate Ottawa Sand spikes (n = 7 @ 50 ng).

In this paper, concentrations have not been recovery corrected. Linear GC/MS dynamic range for *syn*- and *anti*-DP was 10 - 2000 pg on-column ($r^2 > 0.990$) for both isomers. Unless stated elsewhere, accepted isotopic ratios for compound identification were set at ± 15 % of those observed in the DP standard solution at the beginning of each run.

Concentrations of I and II, which are isobaric with DP, were assumed equi-responsive and calculated against *syn*-DP. Commercially available 1,5-DPMA, IV, was used to calculate the concentration of III.

RESULTS AND DISCUSSION

Profile of DP in NRB Sediment Core.

The NRB is located in Lake Ontario approximately 16 km from the mouth of the Niagara River where sediment from the river first collects (Figure 1). The core would therefore represent an historical account of chemicals originating from the Niagara River. Figure 2a shows the profile of DP in the NRB core detected first in *ca*. 1971 measuring 5.9 ng g^{-1}, and is consistent with others who reported on the appearance of DP in Lakes Erie and Michigan, USA, around that time.[4] The initial detection in the core also coincides with the restriction and eventual ban of Dechlorane (Mirex) which DP replaced.[15]

Qui et al.[16] measured a maximum DP concentration in a core from the central area of Lake Ontario that was approximately 3-fold lesser than in our NRB core. These comparative results are logical considering that particle-bound DP originating from the Niagara River would first be deposited in the area of the NRB. Subsequent resuspension and distribution throughout deep water depositional areas of the lake, coupled with mixing with other less-contaminated sediments, would result in a corresponding decrease in levels of accumulation in the major lake basins.

The period in which we observe our maximum DP concentration coincided with Hoh et al. who reported core maxima in Lakes Michigan and Erie between 1975-1980.[4] Their suggestion that the occurrence of DP was a result of atmospheric deposition released during manufacturing may point to an atmospheric driven influence in the Great Lakes. Indeed, OxyChem's submission to New York State's Department of Environmental Con-

servation includes the registration of a dust collector system intended to mitigate free release of DP particles into the air. [17] However, our previous research showed DP sediment concentrations 60-fold greater in Lake Ontario, downstream of the manufacturing facility, than in Lake Erie indicating direct input into the Niagara River.[11] Although source apportionment of DP into Lake Ontario related to atmospheric or direct input has not yet been established[16], another study measured distinctly lake-wide differences of f_{syn} values (the ratio of *syn*-DP to total DP) between Lake Erie and Lake Ontario implying primary sources influencing both lakes were different.[11] Therefore, the similarity in the period where DP was first detected in our Lake Ontario sediment core, and those from lakes reported by Hoh et al. suggest unintended concurrent release of DP to both water and air during the 1970's; a period in which perfunctory environmental control measures were likely employed.[18] This may help explain the steep increase of DP concentration in the NRB core from 1974-1976 (Figure 2a), perhaps a reflection of DP production. However, this remains speculative.

A similar steep decrease in DP concentration between 1979-1982 occurred during mitigation efforts enacted by US federal and state agencies to curb the free release of chemicals from manufacturing. This was largely the result of industrial chemicals discovered in a community along the Niagara River in the 1970's.[18]

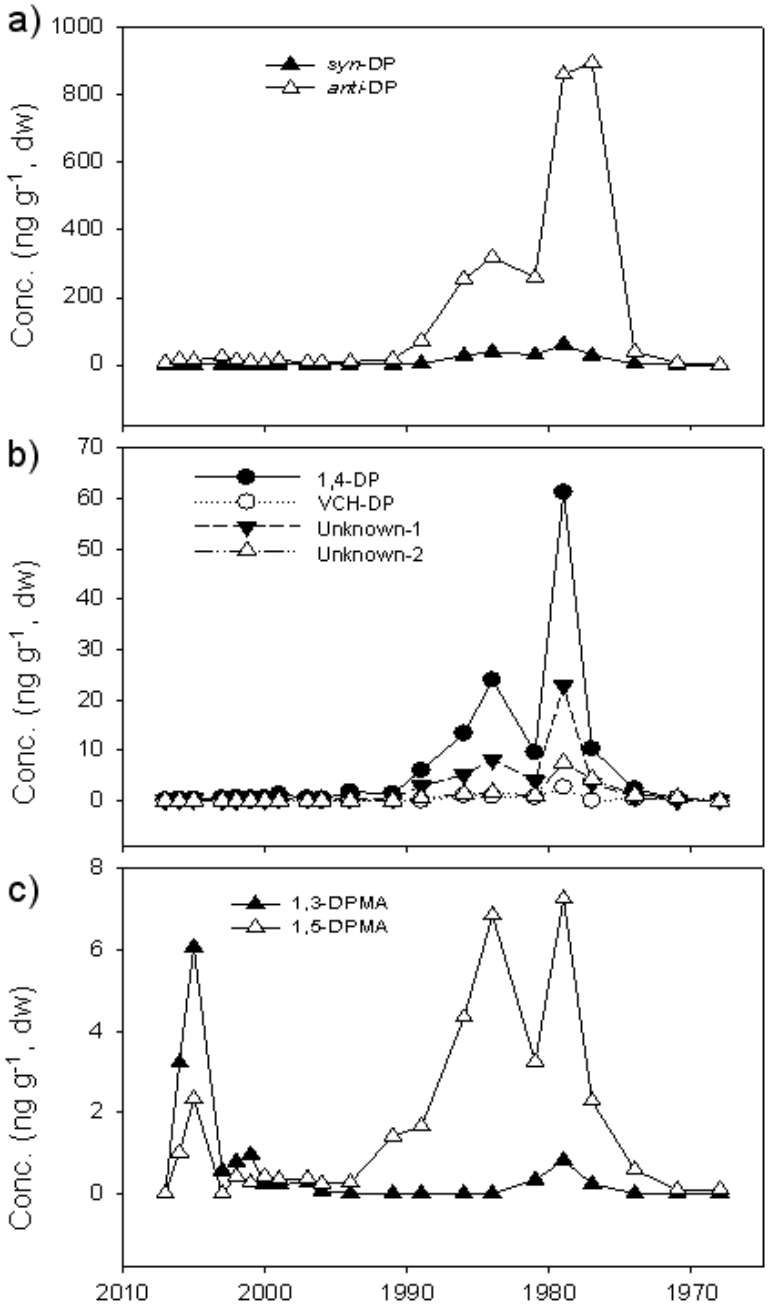


Figure 2. NRB core profiles representing, a.) *syn*- and *anti*-DP; b.) isobaric compounds likely related to DP and c.) monoadduct analogues of DP.

A second, but less dramatic decrease in DP concentration occurred between 1986-1990 which Ismail et al. also observed in Lake Ontario trout.[19] Interestingly, a wastewater treatment plant (WWTP) located along the Niagara River was approved by the USEPA in 1985 to receive and process industrial wastewater.[20] The WWTP's outfall pipe releasing treated wastewater into the Niagara River is regulated by the USEPA's Water Discharge Permit, which includes periodic testing of treated wastewater for targeted chemicals, including DP.[21] Monitoring of DP at the WWTP outfall would be consistent with OxyChem subjecting its DP manufacturing process wastewater to the treatment facility. However, this supposition is complicated by the fact that OxyChem also possesses outfall pipes for which the USEPA currently monitors DP implying that several entry points into the Niagara River may exist. OxyChem is reported to have increased its DP production capacity by 40 % in 1996.[22] If the added production capacity was indeed utilized, no subsequent increase in DP concentration was evident in the NRB core, suggesting that control measures used by the WWTP and/or OxyChem appear to be effective.

Detection of Structurally Related Substances to DP

Isobaric Compounds

DP is synthesized using the Diels-Alder reaction by adding hexachlorocyclopentadiene (HCCPD) to 1,5-cyclooctadiene (1,5-COD) at a 2:1 mole ratio, the latter of which is known to contain 1,3-cyclooctadiene (1,3-COD) and 4-vinylcyclohexene (VCH) as

impurities.[23,24] These impurities when undergoing the same Diels-Alder reaction results in products with the same molecular weight as DP (Scheme 1). Unintended compounds produced during chemical manufacturing from impurities in chemical feedstocks are well documented.[25] Technical polychlorinated biphenyl mixtures, for example, were known to contain minor amounts of polychlorinated naphthalenes stemming from impurities in the starting material.[26]

To examine whether a similar scenario existed for DP, we took technical DP donated to us by Dr. Ron Hites and analysed a diluted solution (~10 ng μL^{-1}) by GC/ECNI-LRMS. Four minor peaks were detected in the solution (Figure 3). GC/ECNI-LRMS chromatograms from the NRB showed the same peaks also confirmed by GC/EI-HRMS.

To test the hypothesis that these additional peaks may arise from 1,5-COD impurities, we purchased purified 1,3-COD and VCH (purity > 95 %, Sigma Aldrich, St. Louis, MO) and conducted separate Diels-Alder reactions in the presence of two moles HCCPD.

Analysis of the VCH reaction product by GC/ECNI-LRMS showed three large peaks (Figure 4), whereas the 1,3-COD did not. The latter observation is not surprising when

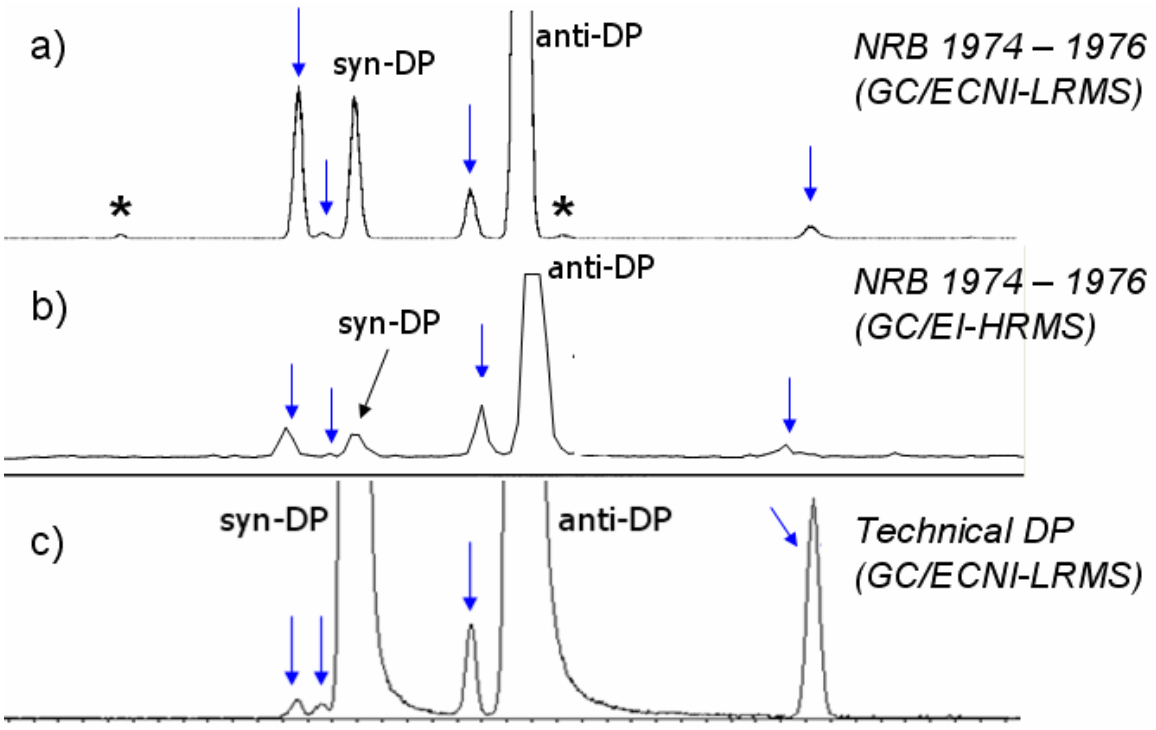


Figure 3. a.) An extracted ion chromatogram (*m/z* 651.7, 653.7) of the sediment core slice representing 1974-1976 using GC/ECNI-LRMS. Blue arrows represent peaks confirmed by HRMS whereas the peaks identified by an asterisk were not. b.) A GC/EI-HRMS ion chromatogram (resolving power > 10 000; *m/z* 651.7142, 653.7112) of the same sample. Differences in the retention time for compounds compared to the LRMS chromatogram are due to different GC temperature programs. c.) A GC/ECNI-LRMS extracted ion chromatogram magnified to depict the same four compounds in technical DP (*m/z* 651.7, 653.7).

considering the steric hindrance caused by the close proximity of π bonds [27] in 1,3-COD would result in an unfavourable diadduct structure.

In our VCH reaction product, a compound matched one of the unidentified peaks in the NRB core, compound II (Scheme 1 & Figure 4) however, a second compound (labeled '++') co-eluted with *syn*-DP. Analysis on a different phase column, XLB, resolved the co-elution. If this particular co-eluting VCH compound existed in the environment it would have obvious implications on the accurate measurement of *syn*-DP when using a DB-5 phase GC column, and any ability to determine source apportionment or environmental fate chemistries.

A 1975 patent claimed by Borg-Warner Corporation described the flame retardant properties of this Diels-Alder product using similar conditions to our VCH reaction, identified as "CNB" (Patent #3919356). However, we were unable to uncover any use or production information following this patent. Additionally, others have reported a *syn*-DP depletion in the environment rather than enhancement relative to *anti*-DP when compared to the commercial product. [4,5,11] This suggests that the VCH compound, which co-eluted with *syn*-DP, was not likely

significant or measurable in the environment. However, some have reported the predominance of *syn*- over the *anti*-DP isomer [6,28]; whether this is related to environmental fate mechanisms or contribution to the existence of CNB remains unclear.

In an effort to identify the three remaining unknown compounds in the NRB core, we turned our attention to another isomer of 1,5-COD, 1,4-cyclooctadiene (1,4-COD).

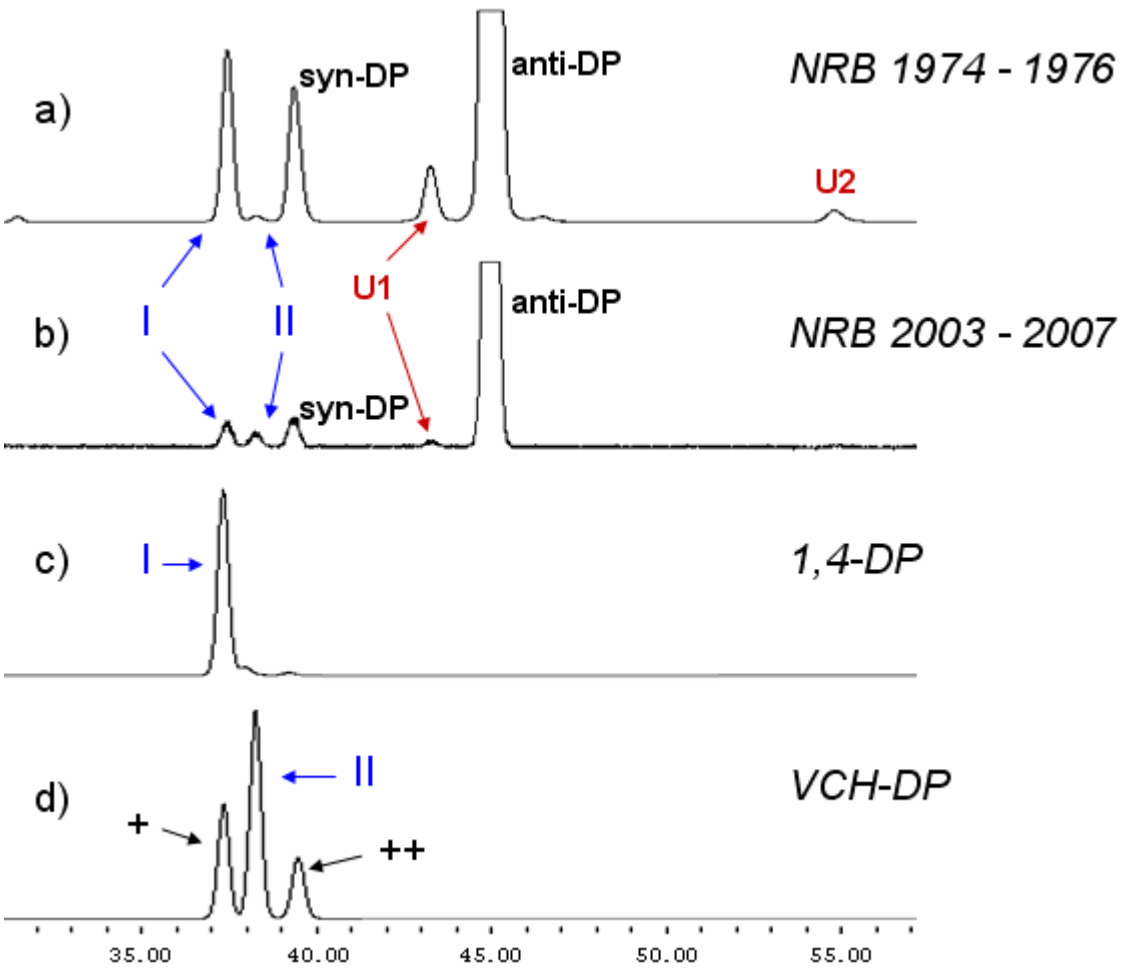


Figure 4. GC/ECNI-LRMS chromatograms (*m/z* 651.7, 653.7) representing, a.) sediment core 1974-1976; b.) sediment core 2003-2007; c.) Diels-Alder reaction products using 1,4-cyclooctadiene (1,4-COD); d.) Diels-Alder reaction products using 4-vinylcyclohexene (VCH). Compounds I and II are indicated in blue, unknowns U1 and U2 in red. Co-eluting compounds '+' with I, and '++' with *syn*-DP using a DB-5 GC phase column did not co-elute when employing an XLB phase column.

Although unable to find any evidence that 1,4-COD was an impurity in 1,5-COD, others have reported on its occurrence from the thermal isomerization of 1,5-COD (*29*). As commercial 1,4-COD was unavailable, a crude mixture was synthesized following the procedure detailed in the Supporting Information. The same Diels-Alder reaction using HCCPD was applied to the crude 1,4-COD mixture. GC/ECNI-LRMS analysis of the Diels-Alder product exhibited one predominant peak matching the retention time of the largest unknown compound in the NRB core profile, identified as compound I (Scheme 1 & Figure 4). The concentration, calculated by assuming similar instrumental response to *syn*-DP, resulted in a core maximum of 63 ng g^{-1} approaching one-tenth that of DP.

It is still unclear why I was found at concentrations greater than the other compounds in the NRB sediment core. Although one of the compounds in the VCH reaction product (labeled '+', Figure 4) did co-elute with I, we suspect its contribution to be minimal as II was the least in concentration of all the diadducts. While diadduct products from the 1,3-COD Diels-Alder reactions conducted during this research were not detected, we cannot rule out the possibility of their formation during commercial DP manufacture and whether these would co-elute with I.

The two remaining unknown compounds followed a similar core profile to the identified diadducts and DP, were therefore suspected to relate to the production of DP (Figure 2b). Research by two studies, reported on the thermal rearrangement of 1,2-divinylcyclobutane to form 1,5-COD [30, 31],a feedstock in the production of DP. It is understood that synthesis reactions rarely produce yields in 100 % quantities, leaving unreacted starting material in the final product. In this scenario, 1,2-divinylcyclobutane, if

present in 1,5-COD during the manufacture of DP, would create compounds possessing the same molecular weight as DP. Unfortunately, we were unable to locate a supplier of 1,2-divinylcyclobutane or synthesize it in the laboratory and therefore, could not determine whether this was a source for the two remaining unknown compounds in the NRB core.

Closer analysis of recent core slices (2003 - 2007) revealed the presence of I and II in similar peak intensity to *syn*-DP (Figure 4b). If created during DP production, it is surprising that these compounds are comparable in abundance to *syn*-DP while their relative ratio in technical DP (Figure 3c) measured less than 0.1 %. However, this suggests that these compounds which may originate as impurities in 1,5-COD, are related to the production of DP and are being produced today. None were detected in Lake Ontario trout.

Dechlorane Plus Monoadduct

Diadducts arising from Diels-Alder reactions are known to undergo a *retro* Diels-Alder process reverting the original compound to its monoadduct form.[32] DP, a diadduct itself, may be susceptible to this process lending then to the possibility of monoadduct formation. In an effort to determine if monoadduct compounds relating to DP are present in the environment, 1,5-COD was reacted with HCCPD at a mole ratio of 1:1 to favour monoadduct products. The resultant product, IV, (Scheme 1) was purified by several iso-

lation procedures at Wellington Laboratories. Analysis by GC/ECNI-LRMS produced a peak corresponding to the monoadduct ($[M]^-$ *m/z* 377.9, 379.9, 381.9).

Injection of the 1,3-COD Diels-Alder synthesis reaction mixture, which earlier gave unsuccessful diadduct yield, showed one large GC/MS peak producing similar mass isotope pattern to IV but resulting in a shorter retention time, tentatively identified as 1,3-DPMA (III, Scheme 1). Both isomers, III and IV were detected in the NRB core (Figure 2c). Interestingly, the deeper bimodal pattern exhibited by DP in our core was only mirrored by IV measuring a maximum of 7.3 ng g^{-1}, approximately 1 % of DP, and close to an order of magnitude greater than III. The predominating profile of IV over III was inverted during 1999 – 2000 in which III became 3-fold greater in concentration between 2003 – 2007 (6.1 ng g^{-1}); notably similar to that of DP (16 ng g^{-1}).

The difference in core profile of the monoadduct isomers would suggest a change in purity of 1,5-COD feedstock used in the manufacturing of DP over this period, or perhaps another source of III may exist, but this remains speculative. However, it is known that IV is used in the manufacture of a currently used chloro/bromo FR, hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO).[33]

Reaction mixtures produced in this study using VCH and 1,4-COD revealed the presence of several apparent monoadducts exhibiting similar $[M]^-$ isotope clusters as IV however, none of these compounds were detected in the NRB samples. Given the presence of the DP monoadduct (IV) in our core, it is surprising that neither of the monoadduct compounds relating to I and II were detected. This may suggest that they are less

stable in the environment or may exist at concentrations below our detection limits. No monoadduct compounds were detected in technical DP when analysed by GC/ECNI-LRMS.

Compound III was detected in Lake Ontario trout at an average concentration of 34 ± 43 ng g^{-1} lipid weight (n = 4). In comparison, smaller concentrations of DP were reported in a previous study by Tomy et al. [5] which analyzed the same trout showing a mean value of 0.21 ± 0.12 ng g^{-1} (lipid weight), similar to another study by Ismail et al.[19]

The greater concentration of III relative to DP is likely due to its smaller size and lower molecular weight and therefore likely more bioavailable. It is uncertain why compound IV was undetectable in trout. However, in our laboratory based exposure experiment with *syn*- and *anti*-DP we showed that the bioaccumulation tendencies can be quite different even for these structurally similar compounds[34]; perhaps this is the case for III and IV.

It is clear that unintended compounds originating from impurities in the 1,5-COD feedstock are being formed during industrial production of DP and released into the environment. Using HRMS and under controlled experimental conditions we were able to identify compounds similar in structure to DP, some of which appear to be produced during the industrial synthesis, in sediment and biota of Lake Ontario. Further research is needed to determine the relationship of these newly identified substances in the aquatic food web and their occurrence in other environmental compartments. This latter infor-

mation would be useful in assessing whether it is a local issue related to manufacturing or other contributing factors.

Acknowledgements

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References

[1] Gay Lussac, J. L. *Ann. Chim.* **1821**, *18*, 821-825.

[2] Alaee, M.; Arias, P.; Sjodin, A.; Bergman, A. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release *Environment International* **2003**, *29*, 683-689.

[3] Stockholm Convention media release on the COP4 meeting. http://chm.pops.int/Convention/Media/Pressreleases/COP4Geneva9May2009/tabid/542/language/en-US/Default.aspx (accessed August 12, 2009)

[4] Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40*, 1184-1189.

[5] Tomy, G. T.; Pleskach, K.; Ismail, N.; Whittle, D. M.; Helm, P. A.; Sverko, E.; Zaruk, D.; Marvin, C. H. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* **2007**, *41*, 2249-2254.

[6] Zhu, J.; Feng, Y. L.; Shoeib, M. Detection of Dechlorane Plus in residential indoor dust in the city of Ottawa, Canada. *Environ. Sci. Technol.* **2007**, *41*, 7694-7698.

[7] Zota, A. R.; Rudel, R. A.; Morello-Frosch, R. A.; Brody, J. G. Elevated house dust and serum concentrations of PBDEs in California: unintended consequences of furniture flammability standards. *Environ. Sci. Technol.* **2008**, *42*, 8158-8164.

[8] Muir, D. C. G.; Howard P. H.; Meylan W. Developing analytical methodology for PB&T substances – a systematic process for identification of important chemicals: An update. Final report to US EPA Great Lakes National Program Office. WSTD Contribution No. 09-045. Environment Canada, Waters Science & Technology Directorate, Burlington ON. 25 pp. + appendix.

[9] Stapleton, H. M.; Brazil, B.; Holbrook, D.; Mitchelmore, C. L.; Benedict, R.; Konstantinov, A.; Potter, D. In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile Rainbow Trout and Common Carp *Environ. Sci. Technol.* **2006**, *40*, 4653-4658.

[10] Soderstrom G,; Sellstrom U.; De Wit C. A.; Tysklind M. Photolytic debromination of decbromodiphenyl ether (BDE 209). *Environ. Sci. Technol.* **2004**, *38*, 127-132.

[11] Sverko, E.; Tomy, G. T.; Marvin, C. H.; Zaruk, D.; Reiner, E.; Helm, P. A.; Hill, B.; McCarry, B. E. Dechlorane Plus levels in sediment of the lower Great Lakes *Environ. Sci. Technol.* **2007**, *42*, 361-366.

[12] The European Commission report on potential alternatives to deca-BDE. http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE.pdf (accessed August 12, 2009).

[13] Eakins, J. D.; Morrison, R. T. A new procedure for the determination of lead-210 in lake and marine sediments. *Int. J. Appl. Radiat. Isotopes.* **1978**, *29*, 531-536.

[14] Tomy, G. T.; Palace, V. P.; Halldorson, T.; Braekevelt, E.; Danell, R.; Wautier, K.; Evans, B.; Brinkworth, L.; Fisk, A. T. Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile Lake Trout (*Salvelinus namaycush*) *Environ. Sci. Technol.* **2004**, *38*, 1496-1504.

[15] Kaiser, K. L. E. Pesticide report: the rise and fall of mirex. *Environ. Sci. Technol.* **1978**, *12*, 520-528.

[16] Qui ; Marvin, C. H.; Hites, R. A. Dechlorane Plus and other flame retardants in a sediment core from Lake Ontario *Environ. Sci. Technol.* **2007**, *41*, 6014-6019.

[17] Report of applications for the renewal of State Pollution Discharge Elimination System permits to the New York Department of Environmental Conservation. http://www.dec.ny.gov/enb2001/20011226/Reg9.html (accessed August 12, 2009).

[18] Engelhaulpt, E. Happy birthday, Love Canal *Environ. Sci. Technol.* **2008**, *42*, 8179-8186.

[19] Ismail, N.; Gewurtz, S. B.; Pleskach, K.; Whittle, D. M.; Helm, P. A.; Marvin, C. H.; Tomy, G. T. Brominated and chlorinated flame retardants in Lake Ontario, Canada, lake trout (salvelinus namaycush) between 1979 and 2004 and possible influences of food-web changes. *Environ. Toxicol. Chem.* **2009**, *28*, 910-920.

[20] The Niagara Falls Water Board Wastewater Facility Information. http://www.nfwb.org/wastewater/html/approval.htm (accessed August 12, 2009).

[21] USEPA discharge records for the Niagara Falls Water Board Wastewater Facility http://oaspub.epa.gov/enviro/multisys2.get_list?FACILITY_UIN=110000541227 (accessed August 12, 2009).

[22] Elsevier Science, Editor: Shelton, J. *Additives for Polymers* **1996**, March Issue, pp 8.

[23] Zerpner, D.; Holtrup, W.; Streck,R Specific inhibition of metathesis reactions by 1,3-COD. *J. Mol. Catal.* **1986**, *36*, 153-157.

[24] Nubel, P. O.; Yokelson, H. B.; Luyman, C. A.; Bouslog, W. G.; Behrends, R. T.; Runge, K. D. Preparation of an ester-terminated telechelic polybutadiene by a two-step olefin metathesis process *J. Mol. Cat.* **1997**, *115*, 43-50.

[25] Masunaga, S.; Takasuga, T.; Nakanishi, J. Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations. *Chemosphere* **2001**, *44*, 873-885.

[26] Yamashita, N.; Kannan, K.; Imagawa, T.; Miyazaki, A.; Giesy, J. P. Concentrations and profiles of polychlorinated naphthalene congeners in eighteen technical polychlorinated biphenyl preparations *Environ. Sci. Technol.* **2000**, *34*, 4236-4241.

[27] Pellissier, H. Asymmetric hetero-Diels-Alder reactions of carbonyl compounds *Tetrahedron* **2009**, *65*, 2839-2877.

[28] Ren, N.; Sverko, E.; Li, Y. F.; Zhang, Z.; Harner, T.; Wang, D.; Wan, X.; McCarry, B. E. Levels and isomer profiles of Dechlorane Plus in Chinese air *Environ. Sci. Technol*. **2008**, *42*, 6476-6480.

[29] Duca, D.; La Manna, G.; Deganello, G. Kinetic study of 1,5-cyclooctadiene hydro-isomerization on Pd/Pumice catalysts *Catal. Lett.* **1998**, *52*, 73-79.

[30] Zora, M. NICS Evaluation for Cope Rearrangment of cis-1,2-divinylcyclopropane and cis-1,2-divinylcyclobutane *J. Mol. Struct. (Theochem)* **2003**, *625*, 251.

[31] Caramella P.; Quadrelli, P.; Toma, L.; Romano, S.; Khuong K. S.; Northrop, B.; Houk, K. N. The three corrugated surfaces of 1,4-divinyltetramethylene diradical intermediates and their connections to 1,2-divinylcyclobutane, 4-vinylcyclohexene, 1,5-cyclooctadiene, and two butadienes *J. Org. Chem.* **2005**, *70*, 2994-3008.

[32] Wijnen, J. W.; Engberts, J. B. F. N. Retro-Diels-Alder reaction in aqueous solution: toward a better understanding of organic reactivity in water *J. Org. Chem*. **1997**, *62*, 2039-2044.

[33] Zhu, J.; Hou, Y.; Feng, Y.; Shoeib, M.; Harner, T. Identification and determination of hexachlorocyclopentadiene-dibromocyclooctane (HCDBCO) in residential indoor air and dust: a previously unreported halogenated flame retardant in the environment *Environ. Sci. Technol*. **2008**, *42*, 386-391.

[34] Tomy, G. T.; Thomas, C. R.; Zidane, T. M.; Murison, K. E.; Pleskach, K.; Hare, J.; Arsenault, G.; Marvin, C. H.; Sverko, E. Examination of isomer specific bioaccumulation parameters and potential in vivo hepatic metabolites of syn- and anti-Dechlorane Plus isomers in juvenile rainbow trout (oncorhynchus mykiss) *Environ. Sci. Technol*. **2008**, *42*, 5562-5567.

CHAPTER 4

Fate of Dechlorane Plus Mono Adducts in a Lake Ontario (Canada) Food Web and Biotransformation by Lake Trout (*Salveinus namaycush*) Liver Microsomes

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I conceived and conducted this research with suggestions from Gregg Tomy and Vince Palace. Alan McAlees and Robert McCrindle synthesized the new compounds. I wrote 80 % of the paper under the supervision of Brian McCarry. This manuscript was submitted to Environmental Science and Technology for peer review.

ABSTRACT

Dechlorane Plus monoadducts (DPMA), 1,3-DPMA and 1,5-DPMA were measured the food web of Lake Ontario (Canada). Only 1,3-DPMA was detected throughout the food web with concentrations ranging between 0.12 – 199 ng g^{-1} lipid weight. We theorized that the unsterically hindered double bond in 1,5-DPMA allowed for greater enzyme attack and, therefore, more readily metabolized out of the organism. *In vitro* lake trout liver microsomal exposures to the individual DPMA isomers showed that the depletion rate constant for 1,3- and 1,5-DPMA were 0.344 and 0.839 h^{-1}, respectively, with corresponding $t_{1/2}$'s of 2.02 ± 0.50 and 0.83 ± 0.18 h. This study supports the lack of 1,5-DPMA presence in the food web. Our attempts to identify the biotransformation products were unsuccessful.

INTRODUCTION

Production and release of unintended chemical impurities in commercial products are well documented and can arise because many industrial-scale syntheses typical employ starting materials of relatively low purity. Once synthesized, these unintended by-products can enter the environment in much the same manner as other anthropogenic chemicals and if they are persistent, bioaccumulative and toxic can lead to deleterious effects.[1-5]

Dechlorane Plus (DP), is a high production volume chlorinated chemical that is applied to products such as plastic cable coatings, plastic connectors in televisions and computers, and rubber roofing tiles.[1] Industrial synthesis involves the Diels-Alder

reaction of hexachlorocyclopentadiene (HCCPD) and 1,5-cyclooctadiene (1,5-COD) at a 2:1 mole ratio. Product formation results in the HCCPD diadduct isomers: *syn*- and *anti*-DP. Our recent work identified several impurities (including DP monoadducts) in a Lake Ontario sediment core located at the Niagara River Bar (NRB), downstream of the Niagara Falls DP manufacturing plant.[2] Monoadduct formation may occur through various mechanisms such as a *retro* Diels-Alder reaction, or possibly as unintended byproducts during the manufacture of DP. Two such DP monoadducts, 1,5- and 1,3-Dechlorane Plus MonoAdduct (1,5-DPMA and 1,3-DPMA, respectively) were positively identified in the NRB sediment core.

(a) **(b)**

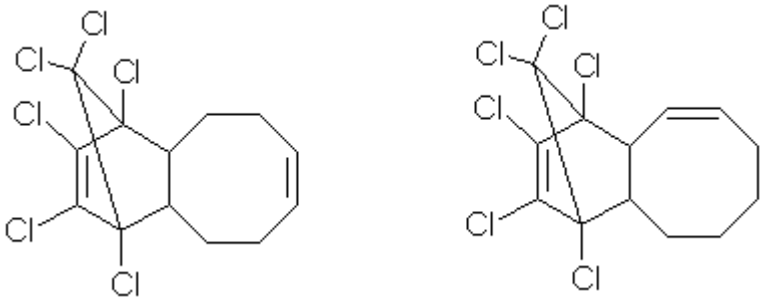

Figure 1. Structures of Dechlorane Plus monoadducts: (a) 1,5-DPMA (1,10,11,12,13,13-hexachlorotricyclo[8.2.1.02.9] trideca 5,11-diene); (b) 1,3-DPMA (1,10,11,12,13,13-hexachlorotricyclo[8.2.1.02.9] trideca 3,11-diene).

This is interesting as the presence of 1,5-DPMA could likely be attributed to the incomplete reaction of the starting materials during the synthesis of DP but did not explain the existence of 1,3-DPMA. Moreover, while the 1,5-DPMA NRB sediment core profile was similar to that of DP, the 1,3-DPMA profile was not. The profile of 1,3-DPMA showed increasing concentration during the more recent (surficial) layers and was *ca*. three times greater than 1,5-DPMA. This suggested a secondary source to the environment, unrelated to the production of DP. Furthermore, a recent investigation by our group also showed that only 1,3-DPMA was measureable in Lake Ontario's lake trout (*Salvelinus namaycush*), the lake's apex food web predator.[2]

To better understand the fate and metabolism of 1,3- and 1,5-DPMA in lake trout, an *in vitro* liver microsomal exposure study was conducted with hopes that it would help explain why only 1,3-DPMA was detected in the Lake Ontario lake trout. Based on our understanding of hepatic phase I chemistry we hypothesize that hydroxy and ketone DPMA analogues would be the major products formed. Other possible phase I transformation products *viz* dihydroxy and epoxide DPMA were also monitoring by selecting likely *m/z* ions ascribed to the $[M]^-$ and $[M\text{-}Cl+H]^-$ ion cluster. Further, we analyzed an archived Lake Ontario pelagic food chain to examine the extent of trophic transfer of both DPMA isomers. To our knowledge, this is the first report on the bioaccumulation of these compounds in a food web.

MATERIALS AND METHODS

Liver Microsomes

Lake trout liver tissues were prepared as described by Palace et al.[3] Liver microsomes (25 μL; total protein = 0.35 ± 0.01 mg) were added to a polypropylene microcentrifuge tube containing 890 μL of 0.05 M Tris-HCl buffer (pH = 7.0, with 0.1 M NaCl) and 100 μL of buffer containing 1 mg mL^{-1} reduced nicotinamide adenine dinucleotide phosphate (NADPH) (Sigma-Aldrich, Oakville, ON). Half of the seventy-two tubes prepared in this manner were spiked with 375 pmoles (in 10 μL of acetone) of 1,3-DPMA while the remaining half received 1,5-DPMA (Wellington Laboratories Incorporated, Guelph, ON). The tubes were incubated in a shaking water bath at 8 ± 1 ^{o}C and in the dark to exclude the possibility of photo degradation. The incubation temperature was chosen so as to mimic the preferred habitat for lake trout. Reactions were terminated with 500 μL ice-cold MeOH (Caledon, Georgetown, ON) at hour periods 0, 0.25, 0.5, 1, 2, 4 and 16 (three replicates for each of the seven reaction times). Additional incubations of 1,3-DPMA and 1,5-DPMA were performed to evaluate the effect of varying substrate concentrations on transformation rates. These experiments used identical conditions to those noted above except that a range of 1,3-DPMA (2.6, 4.0 26.9, 94.3 and 116 μM) and 1,5 DPMA (1.3, 3.1, 13.3, 104 and 196 μM) concentrations were included and all assays were terminated after a 16 h incubation period.

After termination, samples from both sets of experiments were centrifuged (10,000 rpm) for 10 min, the supernatant was transferred to a 15 mL borosilicate

centrifuge tube where 50 ng of 2,3,3',4',5-pentachloro-4-biphenylol and Mirex (Accustandard, New Haven, CT) were added to determine extraction efficiency. Following the addition of 4 mL dichloromethane:hexane (1:1 v/v), the mixture was vortexed for 2 min, centrifuged for 15 min at 4000 rpm and the solvent transferred to a clean 15 mL centrifuge tube; this process was further repeated twice. The extracts were concentrated to a final volume of 1 mL for the analysis of 1,3- and 1,5-DPMA. Samples were further concentrated to 100 μL and re-injected for the detection of targeted metabolites.

Food Web

Biota samples were collected between 2000 and 2003. Components of the food web include a composite sample of plankton (n=1*, composite of three samples*), diporeia (n=1*, composite of three samples*), and individual samples of mysis (n=1) sculpin (n=3), alewife (n=2), smelt (n=2) and trout (n=4). All were homogenized with dry ice and extracted using pressurized fluid extraction (Dionex, Sunnyvale, CA), lipid removal was conducted by gel permeation chromatography, and extracts were further purified using florisil as detailed by Tomy et al.[4] Stable isotope analysis of nitrogen, reported elsewhere[5], was previously determined to define trophic levels.

Instrument Analysis

Extracts were injected into an Agilent (Mississauga, ON) 6890 GC, fitted with a 30 m DB-5 capillary column (0.25 μm film thickness x 0.25 mm i.d.; J&W Scientific, Folsom, CA). The GC was coupled to an Agilent 5975 mass selective detector low resolution mass spectrometer in electron capture negative ionization mode (ECNI-LRMS) using methane as the moderating gas. One-microlitre injections were made in the pulsed splitless mode using an injector set isothermally at 265 ºC. The initial 80 ºC oven temperature held at 2 min, was ramped by 10 ºC min^{-1} to 285 ºC, and held for 5 min. Source and quadrupole temperatures were set to 150 ºC and 106 ºC, respectively. The dominant *m/z* ion in the identical $[M\text{-}Cl+H]^-$ ion cluster of the DPMA isomers (*m/z* 345.9) was used for quantitation while *m/z* 347.9 and 343.9 were confirming ions. Ketone (DPMA=*O*), hydroxy (DPMA-*OH*) and epoxide (DPMA-*O*) analogues of DPMA were monitored by using *m/z* 393.9/395.9/397.9/399.9 while the diol (DPMA-*diol*) was measured using *m/z* 411.9, 413.9 and 415.9.

GC/HRMS

Analysis of the 1,3- and 1,5-DPMA and proposed DPMA-metabolites was done using a Kratos (Manchester, UK) HRMS of EBE geometry at a resolving power of 10,000 run in selected ion monitoring mode and using electron capture negative ionization. For 1,3- and 1,5-DPMA, the $[M\text{-}Cl+H]^-$ ion cluster was monitored: corresponding ions monitored along with their theoretical abundances were: *m/z*

345.9430, (31.6 %), *m/z* 347.9400 (25.6 %) and *m/z* 343.9460 (16.3 %). For the DPMA=*O* and DPMA-*OH* standard, only the molecular ion gave abundant ions in the ECNI mass spectra. As such, we monitored the four most abundant ions in the molecular ion cluster of the three metabolites: for DPMA=*O* this corresponded to *m/z* 395.8990 (31.6 %), 397.8960 (25.6 %) and 393.9019 (16.3 %). The theoretical abundances of the molecular ions of DPMA-*OH* and DPMA-*diol* were identical to that of DPMA=*O* and the respective parent ions monitored were: *m/z* 413.9095/415.9066/411.9125 and 397.9146/399.9117/395.9176. The dwell time on each ion was 64.13 ms. Perfluorokerosene was used as the calibrant gas in electron capture negative ion (ECNI) mode and argon (UHP) was used as the moderating gas. The start and lock masses as set by the software were *m/z* 337.8346 and 342.9792, respectively. The dwell time on the lock mass was 100 ms

All food web concentrations are reported on a lipid weight basis.

Quality Assurance/Quality Control

No DPMAs or their targeted analogues were detected in laboratory blanks (*n*=3). Laboratory blank spike (*n*=3) recoveries for 1,3-DPMA, 1,5-DPMA, DPMA=*O* and DPMA-*OH* were 88 ± 17 %, 96 ± 22 %, 103 ± 12 % and 74 ± 16 %, respectively; while combined mean recovery for the surrogates in samples and QA/QC was 79 ± 14 %. Quantitation of food web and liver microsome samples were based on a three-point calibration curve ($r^2 > 0.995$) using external standard calibration. Method detection limits

for 1,3-DPMA, 1,5-DPMA, DPMA=*O* and DPMA-*OH* were based on a 5:1 S/N ratio and were 5, 5, 0.06 and 0.8 pg injected, respectively.

RESULTS AND DISCUSSION

Food web concentrations of 1,3- and 1,5-DPMA

Only the 1,3-DPMA isomer was detected throughout the food web. Table 1 shows the measured concentrations in biota from Lake Ontario. The rank order of the median concentrations of 1,3-DPMA was inversely related to trophic level (TL) of the animals, *i.e.*, plankton > diporeia > sculpin > smelt > alewife > trout. Concentrations of 1,3-DPMA in plankton 199 ng g^{-1} were much greater than the median concentration in lake trout (0.31 ng g^{-1}). Measured amounts of 1,3-DPMA in diporeia was *ca*. 3 times less than those in plankton. In smelt, median concentration of 1,3-DPMA was *ca*. 4 times smaller than that in sculpin (24.3 ng g^{-1}). Undetectable amounts of 1,3-DPMA (and 1,5-DPMA) were observed in alewife and mysis samples.

Table 1. Concentration (ng g^{-1} lipid) of 1,3-DPMA in components of a Lake Ontario pelagic food web[*].

Sample	*n*	Concentration
Plankton	1[**]	199
Diporeia	1[**]	56.1
Alewife	1[***]	3.40
Sculpin	3	16.4, 24.3, 101
Smelt	2	5.9, 7.8
Trout	4	0.50, 0.12, 0.22. 0.41

[*]undetectable amounts of 1,3-DPMA were observed in Mysis (n=1)

[**]these are composite (n=3) samples

[***]detected in 1 out of 2 samples

Detection of 1,5-DPMA in the Lake Ontario food web was sporadic and mostly in the lower TL organisms. Non-detectable amounts of 1,5-DPMA in higher TL organisms strongly suggest that 1,5-DPMA is more readily eliminated/metabolized than 1,3-DPMA or that the former is less bioavailable. Because the position of the double bond in 1,5-DPMA is less sterically hindered we hypothesize that it is more susceptible to CYP P_{450} attack relative to 1,3-DPMA (Figure 1).

While 1,3-DPMA was readily detected in the Lake Ontario food web, Figure 2 clearly shows that 1,3-DPMA is being diluted with increasing TL. One likely reason is that 1,3-DPMA is being eliminated either in parent form or as metabolites more quickly than it is being stored in higher TL organisms. Admittedly, a caveat of the data plot is the limited number of samples especially those occupying the smaller TLs. However,

individual biomagnification factors are all smaller than one for every predator to prey feeding relationship. Taken together, these two lines of evidence strongly suggest that 1,3-DPMA is being biodiluted with increasing TL in the animals studied from Lake Ontario.

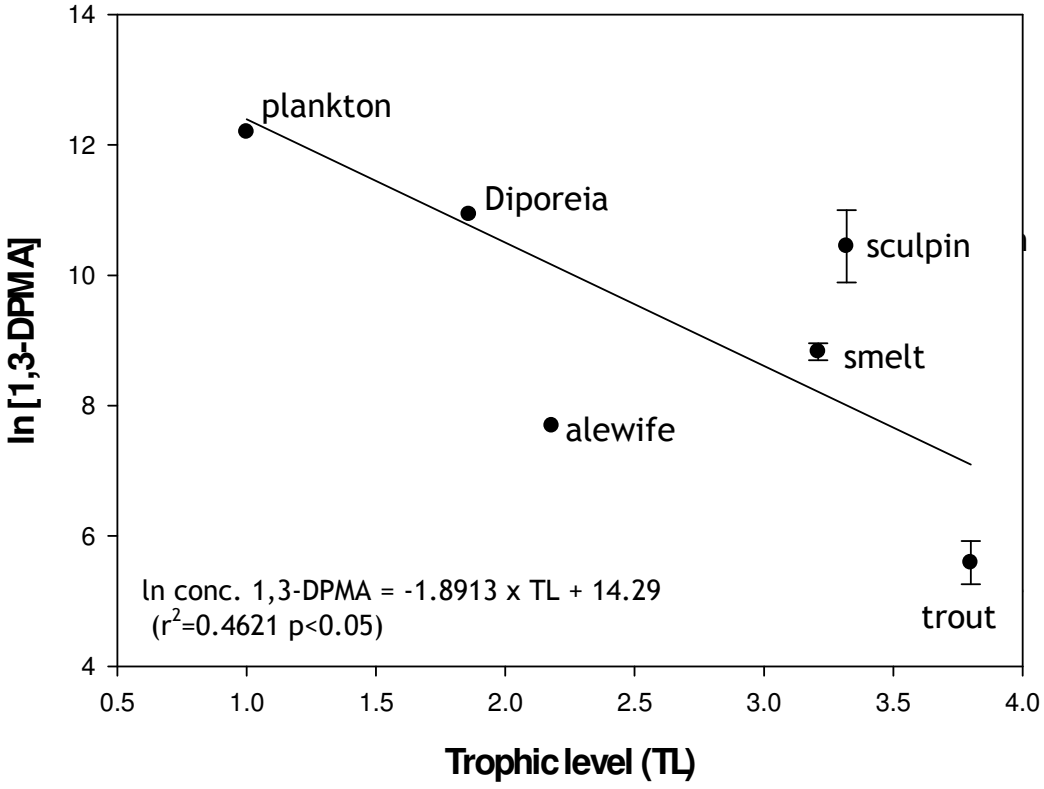

Figure 2. Plot of 1,3-DPMA concentrations (ng g^{-1} lipid) versus trophic level for Lake Ontario aquatic food web.

To test our hypothesis that DPMA isomers are being metabolized by top TL organisms and that the 1,5 isomer is more prone to metabolism we turned our attention to *in vitro* exposure experiments using trout liver microsomes.

DPMA microsome kinetics

The results of our liver microsomal study are shown in Figure 3. The depletion curves for both 1,3- and 1,5-DPMA are similar; both compounds were depleted rapidly within the first 4 h of the incubation experiment. After that time, there was minimal depletion. The *in vitro* bioassay supports our hypothesis that, based on our observations of trophic dilution with the Lake Ontario aquatic food web, 1,3-DPMA is being eliminated/metabolized more quickly than it is being stored in lipids. Furthermore, the depletion of 1,5-DPMA was more rapid than 1,3-DPMA. By plotting the natural log transformed concentration against incubation time we established that the depletion of both isomers obeyed first order kinetics. The depletion rate constant for 1,3- and 1,5-DPMA were 0.3438 and 0.8386 h^{-1}, respectively, with corresponding $t_{1/2}$'s of 2.02 ± 0.50 and 0.83 ± 0.18 h.

While the release and bioaccumulation potential of 1,3- and 1.5-DPMA may be different, the results of our *in vitro* study clearly show that because the $t_{1/2}$ of 1,5-DPMA is *ca*. 2.5 times less than that of 1,3-DPMA it is being depleted more quickly in trout. This is consistent with our inability to detect 1,5-DPMA throughout the aquatic food web and supports our hypothesis that the greater steric hindrance on the free double bond in 1,3-

DPMA, experienced by the neighbouring chlorines, reduces the accessibility for CYP P_{450} metabolism to occur.

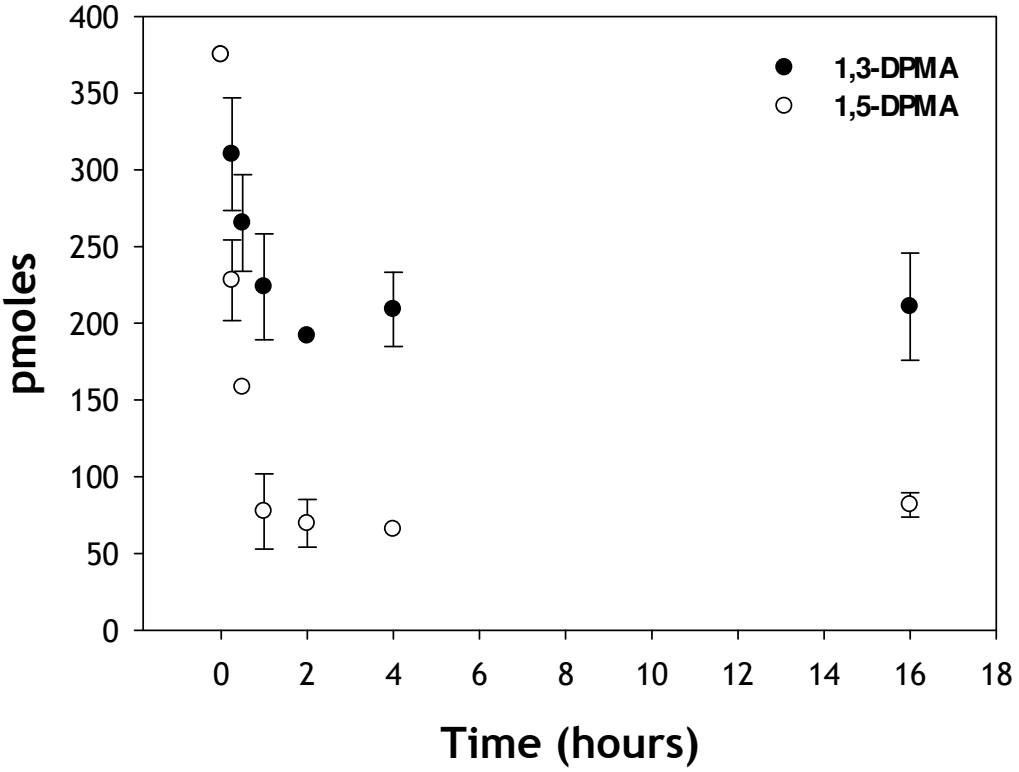

Figure 3. Depletion curve for 1,3-DPMA (closed circle) and 1,5-DPMA (open circle) incubated with rainbow trout hepatic microsomes. Each point represents the arithmetic mean ± standard error. Total amounts for both 1,3- and 1,5-DPMA at time 0 were 375 pmoles.

Results from our transformation kinetics experiments shown in Figures 4 and 5 further supports that 1,5-DPMA may not be present in biota in appreciable amounts because it is more rapidly metabolized than 1,3-DPMA. Lineweaver–Burk plots (1/velocity vs. 1/[substrate]) yielded $r^2 > 0.9$ and kinetic analysis revealed $K_M = 4.17 \times 10^{-3}$ μM and $V_{max} = 44.6$ nm/min/mg protein for 1,3 DPMA and $K_m = 2.59 \times 10^{-3}$ μM and $V_{max} = 986.8$ nm/min/mg protein for 1,5 DPMA.

Biotransformation of both 1,3-DPMA and 1,5-DPMA was biologically mediated, as no transformation of either substrate was detected in parallel assays where microsomes were replaced with buffer. Aromatic substrates are most often metabolized by cytochrome P_{450}, or phase I, oxidation reactions involving epoxide formation or hydroxylation. The location at which oxidation is initiated on a substrate is dependent on reactivity and accessibility of the carbon atoms within the structure.[6] While the double bonds of 1,3-DPMA and 1,5-DPMA are likely to have similar reactivity, accessibility would be greater for the 1,5-DPMA making this substrate more amenable to metabolism. In terms of oxidation reactions, metabolism of both substrates is favourable considering the reported K_M's for estradiol hydroxylation (~0.7 μM)[7], catechol and hydroquinone formation from phenol (~10-15 μM)[8] and hydroxylation of nitrosonornicotine (~0.7 – 69 μM)[9] by hepatic enzyme systems.

Determination of metabolite products

Because the DPMA isomers were readily metabolized in the microsomal study, we focused on likely Phase I biotransformation products. Phase I metabolic processes are normally ascribed to producing oxygenated species, specifically hydroxy, ketone, epoxide or dihydroxy forms. Purified solutions of hydroxy and ketone 1,5-DPMA (DPMA-*OH* and DPMA=*O*, respectively, (Figure 6a, 6b) were synthesized and used to detect the proposed metabolites in the

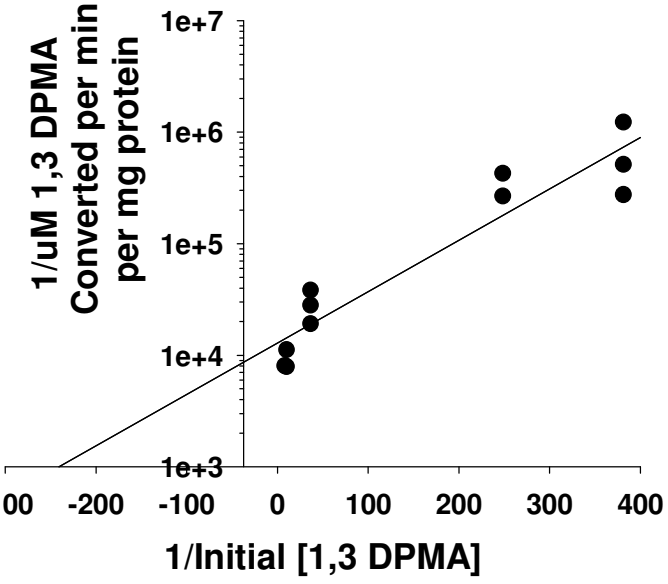

Figure 4. Lineweaver–Burk plot of transformation of 1,3-DPMA in trout liver.

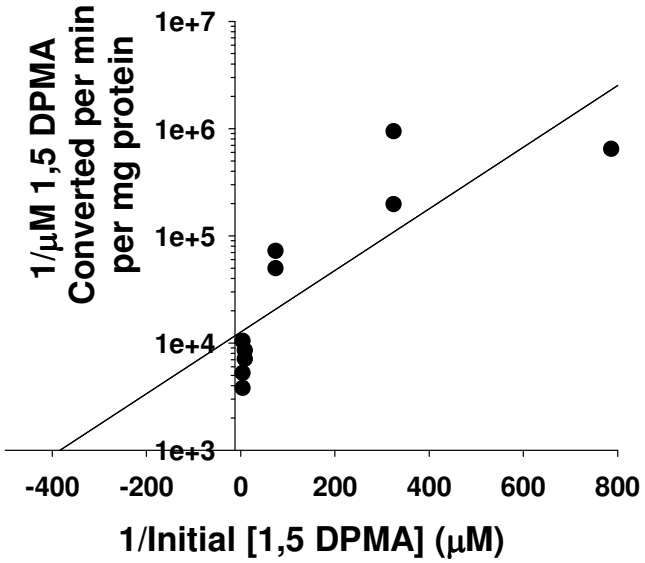

Figure 5. Lineweaver–Burk plot of transformation of 1,5-DPMA in trout liver.

microsomal extracts. Despite our best efforts, we were unable to detect the compounds in any of the samples. Further qualitative GC/MS analysis for the epoxide and dihydroxy DPMA forms (Figure 6c, 6d) also did not successfully identify any likely candidate peaks. Reasons for this remain unclear but perhaps it could be an analytical detection issue.

In summary, our food web study showed that the 1,3-isomer was readily detectable while the 1,5-isomer was detected sporadically and only in lower TL organisms. Our *in vitro* experiments also confirmed that while both isomers are readily depleted by trout liver microsomes the 1,5-isomer is depleted *ca.* 2.5 times faster than the 1,3-isomer which is consistent with the results from our food web study. It remains puzzling why we were unable to detect any of our proposed metabolites.

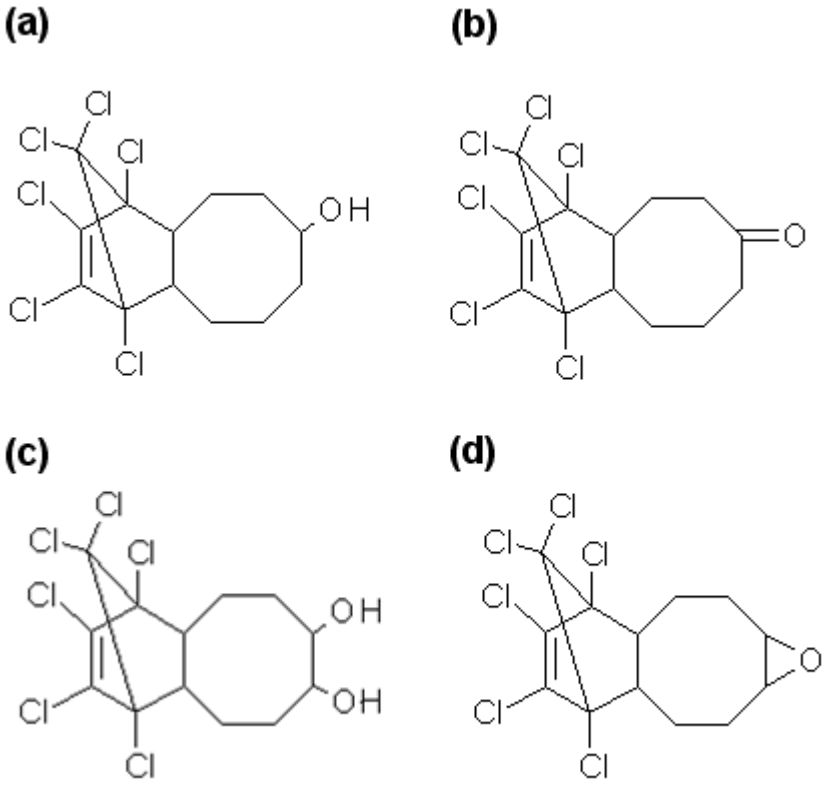

Figure 6. The proposed DPMA biotransformation products (a) hydroxy, (b) ketone, (c) diol and (d) epoxide.

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References

[1] Haglund, P.; Jakobsson, E.; Athanasiadou, M.; Bergman, Å. Determination of polychlorinated naphthalenes in polychlorinated biphenyl products via capillary gas chromatography-mass spectrometry after separation by gel permeation chromatography. Journal of Chromatography 634, 79-86. 1993.

[2] Yamashita, N.; Kannan, K.; Imagawa, T.; Miyazaki, A.; Giesy, J. P. Concentrations and profiles of polychlorinated naphthalene congeners in eighteen technical polychlorinated biphenyl preparations. Environmental Science and Technology 34[19], 4236-4241. 2000.

[3] Johnson, E. S.; Parsons, W.; Weinberg, C. R.; Shore, D. L.; Mathews, J.; Patterson, D. G., Jr.; Needham, L. L. Current serum levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin in phenoxy acid herbicide applicators and characterization of historical levels. *J. Natl. Cancer Inst.* 1992, *84* (21), 1648-1653.

[4] Masunaga, S.; Takasuga, T.; Nakanishi, J. Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations. *Chemosphere* 2001, *44* (4), 873-885.

[5] Phuong, N. T.; Hung, B. S.; Schecter, A.; Vu, D. Q. Dioxin levels in adipose tissues of hospitalized women living in the south of Vietnam in 1984-89 with a brief review of their clinical histories. *Women Health* 1990, *16* (1), 79-93.

[6] Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* 2006, *40*, 1184-1189.

[7] Sverko, E.; Reiner, E.; Tomy, G. T.; McCrindle, R.; Shen, L.; Arsenault, G.; Zaruk, D.; MacPherson, K.; Marvin, C. H.; Helm, P. A.; McCarry, B. E. Compounds structurally related to Dechlorane Plus in sediment and biota from Lake Ontario (Canada). *Environ. Sci. Technol.* 2010, *44* (2), 574-579.

[8] Palace, V. P.; Baron, C. L.; Klaverkamp, J. F. An assessment of ah-inducible phase I and phase II enzymatic activities and oxidative stress indices in adult lake trout (salvelinus namaycush) from lake ontario and lake superior. Aquat.Toxicol. 42, 149-168. 1998.

[9] Tomy, G. T.; Tittlemier, S. A.; Palace, V. P.; Budakowski, W. R.; Braekevelt, E.; Brinkworth, L.; Friesen, K. J. Biotransformation of N-Ethyl Perfluorooctane Sulfonamide (N-EtPFOSA) by Rainbow Trout

(*Onchorhynchus mykiss)* Liver Microsomes. *Environ. Sci. Technol.* 2004, *38*, 758-762.

[10] Tomy, G. T.; Budakowski, W. R.; Halldorson, T. H. J.; Whittle, D. M.; Keir, M. J.; MacInnis, G.; Alaee, M. Biomagnification of a- and g-hexabromocyclododecane (HBCD) isomers in a Lake Ontario food web. *Environ. Sci. Technol.* 2004, *38*, 2298-2303.

[11] Klopman, G.; Tu, M.; Fan, B. T. Prediction of the metabolism of polycyclic aromatic hydrocarbons. Theoretical Chemical Accounts 102, 33-38. 1999.

[12] Hayes, C. L.; Spink, D. C.; Spink, B. C.; Cao, J. Q.; Walker, N. J.; Sutter, T. R. 17 beta-estradiol hydroxylation catalyzed by human cytochrome P450 1B1. *Proc. Natl. Acad. Sci. U. S. A* 1996, *93* (18), 9776-9781.

[13] Kolanczyk, R. C.; Schmieder, P. K. Rate and capacity of hepatic microsomal ring-hydroxylation of phenol to hydroquinone and catechol in rainbow trout (Oncorhynchus mykiss). *Toxicology* 2002, *176* (1-2), 77-90.

[14] Wong, H. L.; Murphy, S. E.; Hecht, S. S. Cytochrome P450 2A-catalyzed metabolic activation of structurally similar carcinogenic nitrosamines: N'-nitrosonornicotine enantiomers, N-nitrosopiperidine, and N-nitrosopyrrolidine. *Chem. Res. Toxicol.* 2005, *18* (1), 61-69.

CHAPTER 5

Levels and Isomer Profiles of Dechlorane Plus in Chinese Air

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Nanqi Ren is the Director of the State Key Laboratory in Harbin – first authorship is customary. Zhi Zhang, Degao Wang and Xinnan Wan conducted the analysis under the supervision of Yi-Fan and me. I also trained the three individuals conducting the analysis when visiting the laboratories in 2007. Tom Harner provided editorial contributions. I

led the research and wrote 90 % of the paper while supervised by Brian McCarry. This was published in Environmental Science and Technology (2008) currently cited 32 times.

ABSTRACT

The highly chlorinated flame retardant, Dechlorane Plus (DP), was measured in air across 97 urban and rural sites in China. DP was detected in 51 of these sites with a mean air concentration in urban centers (15.6 ± 15.1 pg m^{-3}) approximately five times greater than those measured in rural areas (3.5 ± 5.6 pg m^{-3}). These DP levels were likely attributable to local sources rather than trans-boundary influences. Elevated urban levels were measured along the southeastern coast and in south-central China; the highest concentration was observed in the city of Kunming (66 pg m^{-3}). Few of the urban samples (7 %) and a majority of the rural samples (62 %) were below the method detection limit, notably areas in rural central and northeastern China. The mean fractional abundance of the syn-DP isomer (f_{syn}) in all samples was 0.33 ± 0.10, values indistinguishable from that of a commercial mixture (f_{syn} = 0.35). This paper represents the first report on DP levels in Chinese air, together with isomeric ratio profiles from urban and rural sites.

INTRODUCTION

Persistent organic pollutants (POPs) are chemicals which bioaccumulate, may be toxic to humans or wildlife and degrade slowly in the environment. The Stockholm Convention [1] was initiated to restrict and regulate these chemicals with the intention to reduce their potential deleterious effects. To effectively monitor and establish levels of POPs in the environment, the Stockholm Convention included air as one of the main

environmental compartments in which these compounds are measured. One of the recent approaches used to determine POP air levels is the global atmospheric passive sampling (GAPS) study utilizing polyurethane foam. Passive air samplers (PAS) are useful as a cost effective means to measure airborne contaminants, especially in areas where electricity is unavailable.

The first global-scale deployment of PASs was reported by Pozo et al.[2] Results were used to determine local and transboundary influences from sources including compounds such as polybrominated diphenyl ethers (PBDEs), which are a chemical class known as brominated flame retardants (BFRs). The fate and occurrence of BFRs in the environment have been a primary focus for scientists during the past decade.[3-5] Furthermore, the Stockholm Convention considers PBDEs as a candidate for inclusion to its list of target compounds. Notably, the penta- and octa-BDE formulations have been discontinued through legislative restrictions due to concerns related to their toxicity and bioaccumulative properties.[6,7] While policy makers consider further restrictions on these currently used BFRs, Dechlorane Plus (DP), a chlorinated flame retardant ($C_{18}H_{12}Cl_{12}$) manufactured for over 40 years has only recently been reported in the environment.[8] Annual production of DP is estimated to be as high as ten million pounds. This formulation is used primarily in products such as cable coatings, plastic roofing materials and hard connectors in computers and televisions.[9] The United States Environmental Protection Agency (EPA) has classified this flame retardant additive as a High Production Volume (HPV) chemical. As such, the manufacturer (OxyChem, Niagara Falls, NY) is obliged to conduct certain toxicological and chemical tests, reporting the

results in the form of a Robust Summary.[10] OxyChem's submission suggested that DP had little to no toxicity. However, the report suggested sediment bearing organisms may be affected by DP due to its adsorptive properties. DP is also on the Canadian Domestic Substances List but not ranked highly in terms of risk for bioaccumulation because of its high molecular mass (654 Da) and high log K_{OW} (9.3). However, recent research by Tomy et al.[11] demonstrated the biomagnification properties of DP for certain trophic relationships in food webs within Lake Winnipeg and Lake Ontario, Canada. Based on these data, the bioaccumulation potential of DP may need to be re-evaluated.

DP is sold worldwide, including Europe and the Far East. In a European Union (EU) report, annual importation of DP into the EU was estimated to be 2,200 tons.[12] Existing data on global ambient environmental concentrations of DP is sparse; current information stems primarily from studies located in North America. Recently, measurements of DP in tree bark provided the first data on DP levels in the Asian and European continents.[13] In an effort to further determine DP concentrations beyond the North American continent, a study was initiated at the International Joint Research Centre for Persistent Toxic Substances (IJRCPTS) centered at the Harbin Institute of Technology, Harbin, to analyze samples collected using a network of PASs deployed across China. In this paper we present DP levels in ambient air, together with isomeric composition in urban and rural areas of China.

MATERIALS AND METHODS

Sample Collection

PASs using polyurethane foam (PUF) disks were deployed in 97 sites across China for approximately three months between mid-July and mid-October, 2005. PUF disks were pre-cleaned by soxhlet extraction for 24 h (acetone:hexane, 1:1 v/v) at the IJRCPTS laboratories located at the Harbin Institute of Technology and at Dalian Maritime University, China. The cleaned disks were transported to sampling locations using sealed, solvent-rinsed (acetone) amber glass jars with Teflon-lined caps. At the end of the deployment period, the PUF disks were resealed in their original jars, and returned to the IJRCPTS laboratories where they were stored at -20 ^{o}C until extraction.

Details of the passive air samplers employed in this study are described elsewhere.[14,15] Briefly, the PUF disks measured 15 cm in diameter by 1.45 cm thick, giving a surface area of 420 cm^2, a total mass of 5.12 g and a volume of 256 cm^3 (density 0.0200 g cm^{-3}). The planar surface area of the PUF disks measured approximately 30 % less compared to PUF disks used by Klanova et al.[18] Because sampling rate is proportional to planar surface area, the effective sampling rate was reduced by 30 % of the value reported by Klanova et al., to 0.5 m^3 d^{-1}. The PUF disks were placed in passive samplers, a stainless steel chamber which protects the sampling media from precipitation, UV sunlight, and direct particle deposition. The chamber also reduces the dependence of sampling rate on wind speed, resulting in a sampling rate that is equally weighted with time over the sampling period.[14]

Sampling chambers were pre-washed and rinsed with acetone prior to installation of the passive sampling media. All work was performed using clean gloves and PUF disks were handled using acetone-rinsed tongs. Fourteen field blanks were collected at different sampling sites across China in which no DP was detected.

Sample Extraction and Analysis

The PUF samples were extracted and analyzed according to the methods established by the Hazardous Air Pollutants Laboratory and the National Laboratory for Environmental Testing, Water Science and Technology Branch, Environment Canada.[14,16] Briefly, the PUF disks were soxhlet extracted for 24 h using acetone:hexane (1:1 v/v). Extracts were purified by silica chromatography (1.2 cm i.d.) which contained fully-activated silica gel (5.0 g) topped with 1.5 g of anhydrous sodium sulfate. Following a sequential rinse of 25 mL with dichloromethane (DCM) and 25 mL of hexane, the 1.0 mL sample extract was purified by eluting 30 mL of DCM:hexane (1:1 v/v). The eluant was solvent exchanged into isooctane and concentrated to 300 μL under a gentle stream of nitrogen gas. PCB congeners 30 and 204 were added as internal standards (Accustandard, New Haven, CT, USA). Analytical grade solutions of the *syn*-DP and *anti*-DP isomers were purchased from Wellington Laboratories (Guelph, ON, Canada) and diluted in high purity isooctane (> 98 %, Caledon Inc., Caledon, ON, Canada). Details of sample analysis are presented elsewhere.[11] Briefly, DP measurements were determined by gas chromatography-mass spectrometry analysis under negative ion chemical ionization conditions, using methane, by an Agilent 6890

gas chromatograph and an Agilent 5973N mass selective detector. Splitless injections of 1 μL were made into an injector set isothermally at 265 ºC. The initial oven temperature was set isothermally at 80 ºC for a 2 min, ramped 10 ºC min^{-1} to 285 ºC, and held for 5 min. A 30 m DB-5ms column (J&W Scientific, Folsom, CA, 0.25 mm internal diameter and 0.25 μm film thickness) was operated with a helium carrier gas flow of 1 mL min^{-1}. The instrument was operated in selected ion monitoring mode with the *m/z* 653.8 ion used for quantification and *m/z* 649.8 and 651.8 ions used for confirmation.

Quality Assurance/Quality Control

All samples were spiked with a surrogate recovery standard (CB155, Accustandard Inc., New Haven, CT) prior to extraction; mean recoveries were 83 ± 10 % (± 1 SD). Recoveries of PCBs were further assessed by spiking PUF disks (*n*=9) with the calibration solution. Mean recoveries for all PCBs ranged from 90 to 135 % with a mean of 103 %. No recovery correction was applied to the samples. To address the possible difference in extraction efficiencies between DP and the lesser chlorinated CB155 surrogate, fortified recovery studies were conducted at concentrations ranging from 0.5–50 ng mL^{-1}. One-way ANOVA analysis indicated no difference between the recoveries of CB155 and the DP isomers over this concentration range. Therefore, recovery of the surrogate was deemed suitable as an indicator of DP sample recovery (Table 1). Linear dynamic range of the GCMS instrument was between 10 pg and 1200 pg on column (r^2 > 0.990) for both DP isomers. Instrument performance was monitored using quality control standards after every six samples. The ratio of the quantitation and confirmation ions in

samples was within 15 % of measured standard values in all cases. Method detection limits were determined by calculating the standard deviation of replicate standard solutions injected at 5.0 pg μL^{-1} on the instrument (n = 10). The resulting standard deviation was normalized to the method's final volume and the average sampling period of 90 days. This standard deviation was then applied to a one-sided student's t-test at the 95 % confidence interval, which gave rise to MDLs of 0.86 and 0.88 pg m^{-3} for the *syn*- and *anti*-DP isomers, respectively. Procedural blanks were added at a rate of one for every 10 samples. *Anti*-DP was detected in one laboratory blank at a level near the detection limit. Samples were not blank corrected.

Table 1. Mean **e**xtraction recoveries (± 1 SD) at low (0.5 ng mL^{-1}), medium (5.0 ng mL^{-1}) and high (50 ng mL^{-1}) at each spiking level (n = 3).

	Low	Mid	High
syn-DP	89 ± 12	78 ± 8	91 ± 9
anti-DP	76 ± 9	81 ± 6	85 ± 8
CB155	79 ± 8	83 ± 7	93 ± 4

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Data Calculation

In samples where DP was not detected, one-half the method detection limit (0.4 pg m^{-3}) was used to determine mean calculations. When calculating f_{syn} values, five data points were excluded because only one isomer was detected.

RESULTS AND DISCUSSION

Spatial Total DP Concentrations

The use of PASs has been applied to studies which measure chemicals existing primarily in the vapor phase; recent research has indicated that these samplers also collect fine particulates that enter the sampling chamber because they behave much like gas-phase chemicals.[18] Chemicals possessing log K_{OA} values greater than ~12 are predicted to reside largely in a particulate-bound form.[19] Using US EPA's EPIWIN (v 3.12) modeling program, the log K_{OA} for DP was estimated to be 14. Therefore, it is proposed that DP levels measured in the PUF samplers must be associated primarily with particles. Furthermore, Hoh et al.[8] found 99 % of the atmospheric DP composition resided in the particulate phase. Klanova et al.[18] investigated particulate-phase sampling rates for PUF disk passive air samplers by comparing 42 paired concurrent high volume and passive samples collected over a three-year period. They reported that particle phase sampling rates were consistent over numerous sampling intervals and were approximately one-tenth of the gas phase sampling rates. The sampled particles were mainly associated with fine and ultrafine particles and because of their small size, are capable of migrating into

the passive sampling chamber and collected much like gas-phase molecules. Although further research is needed to fully develop and test the PASs for particle associated chemicals, PAS techniques are believed to enable estimates of the "true concentration", for mainly gas-phase compounds, within a factor of 2 to 3.[20] This degree of accuracy is sufficient for comparison purposes with other atmospheric contaminants and needs to be confirmed for chemicals that are mainly particle-bound as other meteorological factors may come into play.

Dechlorane Plus was detected in extracts from 51 of the 97 sampling sites; this data set consisted of samples from 24 urban sites and 27 rural sites. Air concentrations were determined from the amount of DP collected on the PUF disk divided by the effective air volume sampled. This volume is simply the deployment time (typically ~90 days) times the particle-phase sampling rate of 0.5 $m^3 d^{-1}$ [18] or equivalent to ~45 m^3. Total DP concentrations observed

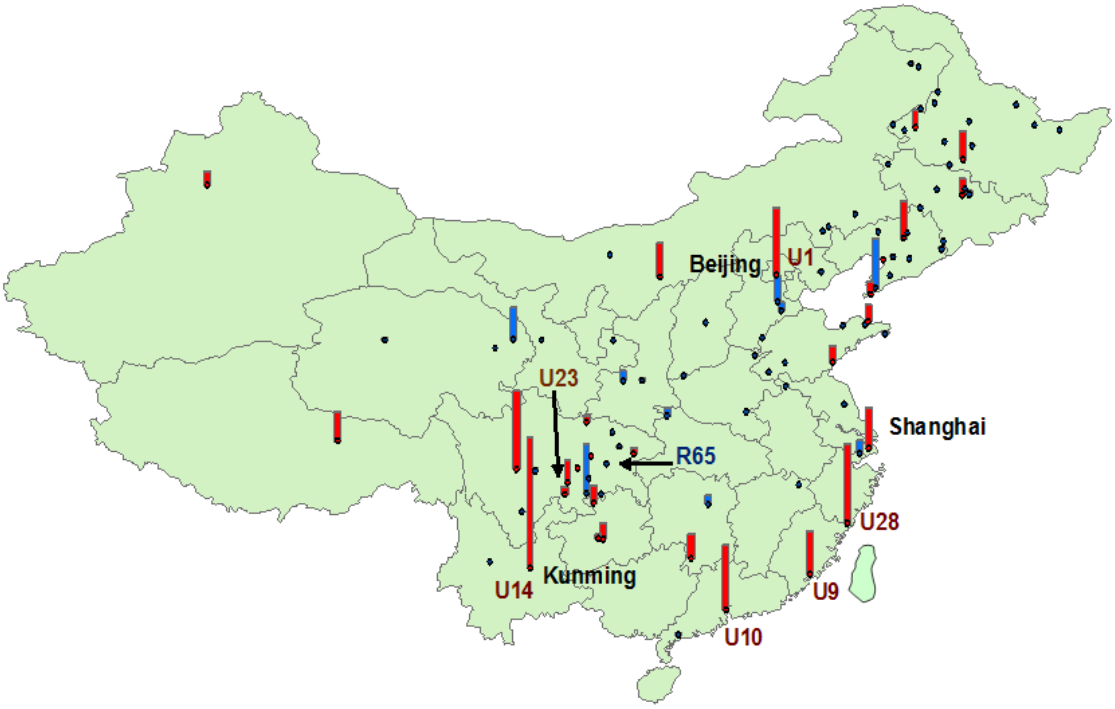

Figure 1. Red and blue bars represent total DP concentrations in air sampled at 97 urban and rural sites, respectively, across China. Dots represent non-detects. Key: largest bar, U14 = 66 pg m^{-3}.

during this study ranged from not detected (< 0.8 pg m^{-3}) to a maximum of 66 pg m^{-3} (Figure 1); the latter value was measured in the city of Kunming in Yunnan province. This is somewhat surprising as Kunming is not particularly noted for its manufacturing sector, but rather a tourist destination. A previous study measuring air concentrations of PBDE's in China did not find elevated levels of this flame retardant in Kunming[21], however, the highest soil concentration of PCB in another study was found to be in this city.[17] The elevated level of PCBs in Kunming may indicate an historic or current local

industrial influence, which may help to explain the DP air concentration. The mean DP concentration for urban sites was higher than that of rural sites, 15.6 ± 15.1 pg m^{-3} and 3.5 ± 5.6 pg m^{-3}, respectively (p = 0.001). The higher DP concentration in urban areas relative to rural areas suggests that local sources rather than trans-boundary influences are primarily responsible for the observed DP levels. Areas where DP was not detected were primarily limited to rural regions in central and northeastern China (Figure 1). Of the 46 sites where we did not detect DP, 44 were rural corresponding to only 38 % of the 71 rural sites where DP was measured. On the other hand, DP was observed at 93 %, or 24 of the 26, urban sites.

A study in the North American Great Lakes region measured air concentrations of DP in several urban and rural areas using active air sampling techniques. The vapor and particulate components were collected separately for 24 h, every 12th day from April to December, 2004.[8] The reported range of DP during this period was 0.04 – 490 pg m^{-3} with the highest concentration found at a rural site close to a DP manufacturing plant. The two urban sites, Chicago and Cleveland, had mean values similar to those measured in this study, 3.2 ± 4.1 pg m^{-3} and 23.4 ± 44.7 pg m^{-3}, respectively.[8] Episodic maxima that are captured by high volume samplers are smoothed by passive samplers that integrate over a three month period and provide a time-weighted concentration over the sampling period.[24]

Although DP is sold in China, little information exists on the reasons for its importation or uses within the country. However, previous studies have associated high DP air concentrations with manufacturing sources typical of urban/industrial regions.[8] In

this study there were 12 cities where the population exceeded 1 million. When the airborne DP concentration in these cities was plotted against the population, a good correlation (Figure 2, $r^2 = 0.57$, $p < 0.05$) was obtained. The data for the city of Kunming was excluded from this plot due to its very high value which is likely attributed to a nearby and specific source of DP.

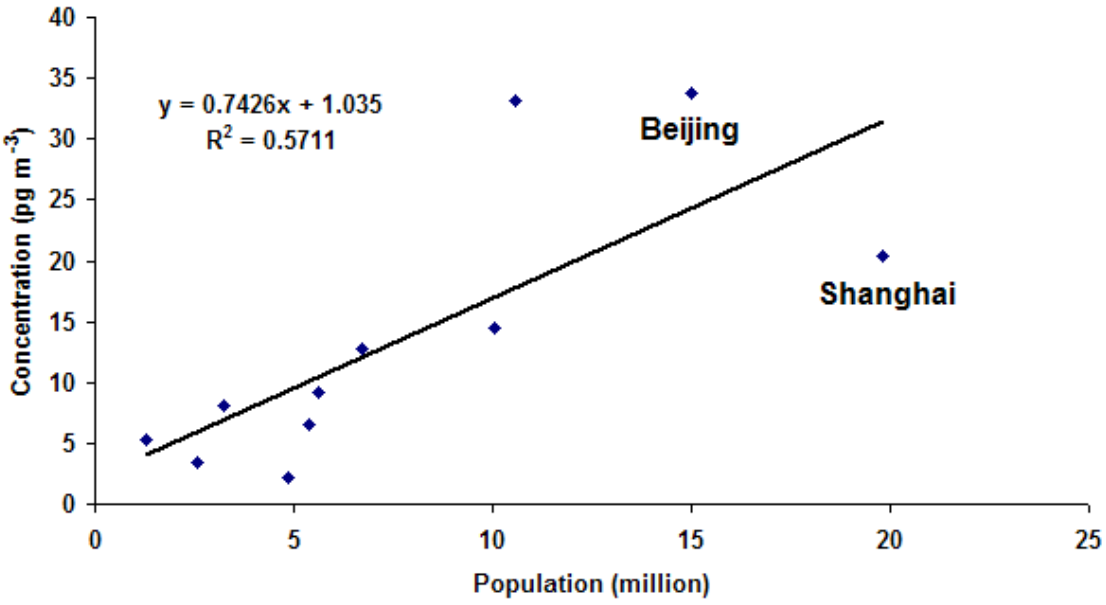

Figure 2. Correlation of total air DP concentrations plotted against the population in urban centers in China with populations greater than 1 million people.

Another potential source of DP is the practice of open burning of e-waste (electronic waste) cables and other electronic components located in various, unspecified

locations. This may help explain the elevated levels in some of our rural sites. The practice is not restricted to China and has been reported in other Asian countries and some parts of Europe.[25,26] Local sources of airborne e-waste contaminants were reported in Guiyu, China where electronic components are dismantled (chipped and melted) to collect and resell the reclaimed metals.[23] Worker exposure to chemicals during this processing is also a concern.[22] Based on OxyChem's product information, DP's thermal stability has an operational maximum of 280 ^{o}C. Above 350 ^{o}C, thermal decomposition products are reported to occur;[27] however, since no information is available on the identification of these decomposition products, we were unable to scan for them in the samples.

Fractional Abundance of Dechlorane Plus Isomers in China

The mean f_{syn} value, measured as the concentration of *syn*-DP divided by total DP, for the entire data set (Figure 3) was 0.33 ± 0.10, very close to the value reported for OxyChem's technical DP mixture (f_{syn} = 0.35).[11] The distribution of f_{syn} values was reasonably narrow showing similar urban and rural f_{syn} profiles (urban: 0.32 ± 0.08, n = 24; rural: 0.34 ± 0.11, n = 22). Two sites in central China, an urban site, U23 (f_{syn} = 0.56, Figure 3) and a proximate rural site, R65 (f_{syn} = 0.67) had f_{syn} values that exceeded the mean by 2 standard deviations. This may indicate specific sources at these sites that differ from the typical source observed in China. Overall, no significant correlation of f_{syn} values to DP concentration or population was evident. However, the city of

Kunming, measuring the highest level of DP, exhibited an f_{syn} value (0.26) relatively close to that of the North American commercial product.

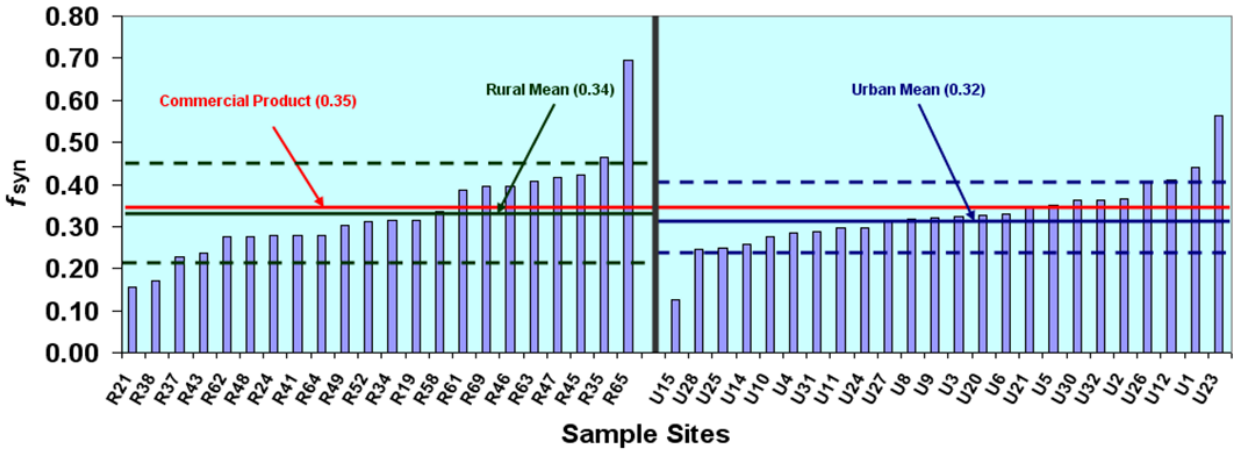

Figure 3. The f_{syn} values for all samples which contained DP (collected across China between July and October, 2005) are plotted in order of increasing f_{syn} value; the solid line indicates the mean value of all samples; the dashed lines indicate one standard deviation. Sample sites preceded by "U" represent urban sites while those preceded by "R" represent rural sites.

Previous air measurements in the Great Lakes[8] also demonstrated relatively constant f_{syn} values, similar to the OxyChem technical formulation. This result is in contrast to the depletion of syn-DP relative to the anti-DP isomer observed in sedimentary environments. For instance, Sverko et al. [28] reported a f_{syn} value of 0.069 in Lake Ontario

surficial sediment. The pathways/processes that alter f_{syn} values in sediment are still unknown. This is an area for further investigation as these signatures may be useful for tracking the movement and source-receptor relationships for DP.

Implications

This study has demonstrated the prevalence of DP in air across China, particularly in urban areas. Although the results implicate urban activities as the main emission source of DP, there is little information on the specific uses of DP in China and the technical formulations that are used. This latter information is necessary to better assess emission of DP and potential for human exposure. There is also the question of whether the processing of e-waste may represent an important contribution to atmospheric DP in some regions of China.

The isomeric composition of DP presents a unique opportunity to track the movement and processing of this chemical. Research is needed to investigate the degradation pathways of DP in various environmental media. Related to this is the need for more information on basic physical-chemical properties and multi-media partitioning of the two DP isomers.

Acknowledgements

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References

[1] *Stockholm Convention on Persistent Organic Pollutants (POPs)*; Interim Secretariat for the Stockholm Convention, United Nations Environmental Programme (UNEP) Chemicals: Geneva, Switzerland, Oct 2001. http://www.pops.int.

[2] Pozo, K.; Harner, T.; Wania, F.; Muir, D. C. G.; Jones, K.C.; Barrie, L. A. Toward a Global Network for Persistent Organic Pollutants in Air: Results from the GAPS Study. *Environ. Sci. Technol.* **2006**, *40*, 4867-4873.

[3] Rahman, F.; Langford, K. H.; Scrimshaw, M. D.; Lester, J. N. Polybrominated diphenyl ether (PBDE) flame retardants. *Sci. Total Environ.* **2001**, *275,* 1-17.

[4] Alaee, M.; Wenning, R. J. The significance of brominated flame retardants in the environment: current understanding, issues and challenges. *Chemosphere* **2002**, *46,* 579-582.

[5] DeWit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46*, 583-624.

[6] Tomy, G. T.; Palace, V. P.; Halldorson, T.; Braekevelt, E.; Danell, R.; Wautier, K.; Evans, B.; Brinkworth, L.; Fisk, A. T. Bioaccumulation, Biotransformation, and Biochemical Effects of Brominated Diphenyl Ethers in Juvenile Lake Trout (*Salvelinus namaycush*). *Environ. Sci. Technol.* **2004**, *38,* 1496-1504.

[7] Boon, J. P.; Lewis, W. E.; Tjoen-A-Choy, M. R.; Allchin, C. R.; Law, R. J.; deBoer, J.; ten Hallers-Tjabbed, C. C.; Zegers, B. N. Levels of Polybrominated Diphenyl Ether (PBDE) Flame Retardants in Animals Representing Different Trophic Levels of the North Sea Food Web. *Environ. Sci. Technol.* **2002**, *36,* 4025-4032.

[8] Hoh, E.; Zhu, L.; Hites, R.A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40*, 1184-1189.

[9] Betts, K. S. A new flame retardant in the air. *Environ. Sci. Technol.* **2006**, *40*, 1090-1091.

[10] USEPA HPV voluntary robust summary. (Accessed January 9, 2008) http://www.epa.gov/chemrtk/pubs/summaries/dechlorp/c15635tc.htm

[11] Tomy, G.T; Pleskach, K.; Ismail, N.; Whittle, D.M.; Helm, P.A.; Sverko, E.; Zaruk, D.; Marvin, C.H. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* **2007**, *41*, 2249-2254.

[12] The European Union's Hexachlorocyclopentadiene Risk Assessment Report http://ecb.jrc.it/documents/ExistingChemicals/RISK_ASSESSMENT/DRAFT/R401_0512_env.pdf (Accessed January 9, 2008)

[13] Qui, X.; Hites, R. A. Dechlorane Plus and Other Flame Retardants in Tree Bark from the Northeastern United States. *Environ. Sci. Technol.* **2008**. *42*, 31-36.

[14] Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4142-4151.

[15] Pozo, K.; Harner, T.; Shoeib, M.; Urrutia, R.; Barra, R.; Parra, O.; Focardi, S. Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environ. Sci. Technol.* **2004**, *38,* 6529-6537.

[16] Su, Y.; Hung, H.; Sverko, E.; Fellin, P.; Li, H. Multi-year measurements of polybrominated diphenyl ethers (PBDEs) in the Arctic atmosphere. *Atmos. Environ.* **2007**, *41*, 8725-8735.

[17] Ren, N.; Que, M.; Li, Y.; Liu, Y.; Wan, X.; Xu, W.; Sverko, E.; Ma, X. Polychlorinated biphenyls in chinese surface soils. *Environ. Sci. Technol.* **2007**, *41*, 3871-3876.

[18] Klanova, J.; Cupr, P.; Kohoutek, J.; Harner, T. Assessing the Influence of Meteorological Parameters on the Performance of Polyurethane Foam-Based Passive Air Samplers. *Environ. Sci. Technol.* **2008**, *42*, 550-555.

[19] Bidleman, T. F. and Harner, T. Sorption to aerosols In: D. Mackay and R. S. Boethling (eds.), Property Estimation Methods for Chemicals: Handbook of Environmental and Health Sciences, **2000**, Lewis Publishers, Boca Raton, Florida, 33431, U.S.A.

[20] Harner, T.; Bartkow, M.; Holoubek, I.; Klanova, J.; Wania, F.; Gioia, R.; Moeckel, C.; Sweetman, A. J.; Jones, K. C. Passive Air Sampling for Persistent Organic Pollutants: Introductory Remarks to the Special Issue.

Environ. Pollut. **2006**, *144*, 361-364.

[21] Jaward, F. M.; Zhang G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C. Passive Air Sampling of Polychlorinated Biphenyls, Organochlorine Compounds, and Polybrominated Diphenyl Ethers Across Asia. *Environ. Sci. Technol.* **2005,** *39*, 8638-8645.

[22] Bi, X.; Thomas, G. O.; Jones, K. C.; Qu, W.; Sheng, G.; Martin, F. L.; Fu, J. Exposure of Electronics Dismantling Workers to Polybrominated Diphenyl Ethers, Polychlorinated Biphenyls, and Organochlorine Pesticides in South China. *Environ. Sci. Technol.* **2007**, *41*, 5647-5653.

[23] Li, H.; Yu, L.; Sheng, G.; Fu, J.; Peng, P. Severe PCDD/F and PBDD/F Pollution in Air around an Electronic Waste Dismantling Area in China. *Environ. Sci. Technol.* **2007**, *41*, 5641-5646.

[24] Gouin, T.; Harner, T.; Blanchard, P.; Mackay, D. Passive and active samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes basin. *Environ. Sci. Technol.* **2005**, *39*, 9115-9122.

[25] The European Union's Report on cable burning. http://ec.europa.eu/environment/dioxin/pdf/stage1/metalreclamation.pdf (Accessed January 9, 2008)

[26] Steiner, S. Risk Assessment of E-waste burning in Delhi, India. (Thesis) Umweltwissenschaften Eidgenossosche Technische Hochschule Zurich, Zurich 2004.

[27] Occidental Chemical Corporation (OxyChem®), Dechlorane Plus® Manual, (Accessed January 9, 2008)

http://www.oxy.com/OXYCHEM/Products/dechlorane_plus/dechlorane_plus.htm.

[28] Sverko, E.; Tomy, G. T.; Marvin C. H.; Zaruk, D.; Reiner, E.; Helm, P.; Hill, B.; McCarry, B. E. Dechlorane Plus Levels in Sediment of the Lower Great Lakes. *Environ. Sci. Technol.* **2008**, *42,* 361-366.

CHAPTER 6

Implications of Dechlorane Plus and Dechloranes in the Global Atmospheric Passive Sampling (GAPS) Study as Global Contaminants

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GAPS extracts were provided by Tom Harner (logistical support provided by Sum Chi Lee); both contributing to the paper. I wrote 80 % of the paper under the supervision of Brian McCarry. This manuscript is currently under review at the journal of Environmental Science and Technology.

ABSTRACT

The recent detection of chlorinated flame retardants (FR) in the environment, namely Dechlorane Plus (DP), the related dechlorination compounds and other Dechlorane flame retardant have garnered much interest. Several studies have shown the prevalence of these FRs in sediment, soil, biota and the atmosphere; however, these studies were focused on local or regional distributions of these chemicals. The current study represents atmospheric concentrations from seven continents over a period of one year. Divided into three-month sampling periods, we were able to measure seasonal variations of these FRs. The maximum total DP concentration during the study was detected in Delhi, India (226 pg m^{-3}) while the overall proportion of these greater concentrations were centered over the Indo-Asian region. No dechloro-DP compounds were detected suggesting UV photolytic degradation is not a significant process.

Only Dec602 was detected during our study suggesting its production and use may be more prevalent than Dec603 and Dec604. The Dec602 primarily occurred in the Indo-Asian and Middle-Eastern continents would indicate a source, or sources, within this region.

This is the first measurement of these FRs on a global scale.

INTRODUCTION

Flame retardant (FR) chemicals are applied to a wide variety of consumer products. Their apparent effectiveness has spawned the creation of a wide variety of chemical substances to suit various commercial product needs. Brominated-containing FRs far out number all other halogenated analogues put together; both in production volume and variety of products. An example is the very popular, high production volume FR formulation: polybrominated diphenyl ether (PBDE). Shown to be a global contaminant and toxic to humans and wildlife, this formulation is now restricted or regulated for use.[10]

While brominated FRs continue to undergo further scrutiny, a chlorinated FR (Dechlorane Plus, DP), also considered by the U.S. EPA as a high production volume (HPV) chemical product, is unrestricted for use. Although already classified by the U.S. EPA as a HPV chemical, the European Commission identified DP as a replacement candidate for the brominated FR, deca-BDE, adding to the prospect of an increase in DP's production volume. Even though DP was manufactured for over 50 years, the first measurements in the environment were reported in 2006.1 Not surprisingly, much of the initial research focused on the occurrence of DP in biotic and abiotic environments were located within the area surrounding the manufacturing plant (OxyChem); namely, the North American Great Lakes.[1,11-13] These reported on greater concentrations of DP nearest the manufacturing plant.

Several papers further revealed the presence of the chlorinated flame retardant in Germany, Italy, Spain, China and Korea.[13-20] Although originally thought to be produced only in Niagara Falls, NY, a DP manufacturing plant was recently identified in China.[18] The evidence of DP's persistent nature was given by its presence in the atmosphere and water along an Atlantic Ocean transect spanning Greenland to the Antarctic.[21]

Dechlorinated moieties of DP were also identified in various media[11,19,20,22-24] providing truth to the concept that DP can dehalogenate in the environment.

Recently, a series of Dechloranes (Dec602, Dec603 and Dec604) have been reported in the environment.[25] Like DP, they are chlorinated flame retardants; however, knowledge of their production volumes and uses are less well known. To date, measurements of the newly detected FRs are limited to the North American Great Lakes and China.[25,26]

To help construct the terrestrial occurrence of DP and Dechloranes on a global scale we turned our attention to the Global Atmospheric Passive Sampling (GAPS) study, which monitors airborne contaminants in more than 40 sites in seven continents.[27] Initially conceived to assess the effectiveness of the Stockholm Convention in controlling targeted persistent organic pollutants (POPS) in the atmosphere, the GAPS sampling network also serves as a broad-range depiction for other various anthropogenic chemicals.

We present global atmospheric spatial and seasonal total DP concentrations, its isomers and the newly detected Dechloranes collected over the span of one year.

MATERIALS AND METHODS

Sampling

A detailed description is explained by others.[16-19] Briefly, pre-cleaned passive polyurethane foam (PUF) disk samplers were deployed from April 2005 through to March 2006. PUF disks were collected and replenished every three months, providing a quarterly 'seasonal' perspective of atmospheric concentrations. Field blanks were deployed once at each site. Upon completion, PUF disks were collected and shipped in a solvent-rinsed one-litre amber jar.

The design of this study was to determine spatial and temporal distribution of DP and related compounds for a period of one year, therefore not all GAPS sites were included due to their infrequent sampling rate. Location of sites are shown in Figure 1.

Figure 1. Location of sample sites used in this study.

Extraction and Analysis

Prior to extraction, PUF disks were spiked with surrogate recovery standard consisting of ^{13}C-CB105 (CIL, Andover, MA). Samples were Soxhlet extracted using petroleum ether for 24 h. The combined extracts were concentrated, solvent exchanged into isooctane (> 98 %, Caledon Inc., Caledon, ON) and concentrated down to a final volume of 500 μL. From this, an aliquot was removed and further purified using 0.5 g of fully activated silica and concentrated down to a final volume of 50 μL. One-microlitre injections were made into an Agilent (Mississauga, ON, Canada) 5980 gas chromatograph (GC) coupled to an Agilent 5973 mass spectrometer (MS) operated in

electron capture chemical ionization mode using methane as a moderating gas. The GC was fitted with a 30 m DB-5 capillary column (0.25 μm film thickness x 0.25 mm i.d.; J & W Scientific, Folsom, CA) using helium as the carrier gas. The initial oven temperature was set at 80 ^{o}C with a 2 min hold time, ramped at 10 ^{o}C/min to 285 ^{o}C and held for 15 min. Source and quadrupole temperatures were set to 150 and 106 ^{o}C, respectively. DP was detected by monitoring for *m/z* 649.8, 651.8 and 653.8 while the dechlorinated moieties, Cl_{11}-DP(-Cl+H) and Cl_{10}-DP(-2Cl+2H) were monitored by using *m/z* ions 615.7/617.7/619.7 and 581.8/583.8/585.8, respectively. Detection of Dec 602, 603 and 604 was conducted by monitoring *m/z* 613.6/611.6/615.6, 637.6/635.6/639.6 and 541.6/543.6/463.7, respectively.

Analytical solutions of *syn*- and *anti*-DP, *anti*Cl_{11}-DP and *anti*Cl_{10}-DP were purchased from Wellington Laboratories (Guelph, ON) while Dec 602, 603 and 604 were purchased from Toronto Research Chemical Inc (Toronto, ON).

Quality Assurance/Quality Control

Procedural blanks and laboratory spikes were added at a rate of one for every 12 samples. No compounds were detected in the blanks. Combined arithmetic mean recovery for the targeted analytes was 89 ± 18 %. Sample surrogate recovery for ^{13}C-CB105 was 94 ± 15 % measured during separate organochlorine pesticide analysis. To address the possible differences in extraction efficiency between the targeted Dechlorane compounds in this study and the lesser chlorinated CB105 surrogate, fortified recovery

studies were conducted at concentrations ranging from 0.5 – 50 ng mL^{-1}. One-way ANOVA analysis indicated there was no difference in recoveries between the Dechlorane compounds and CB105.

Table 1. Mean **e**xtraction recoveries (± 1 SD) at low (0.5 ng mL^{-1}), medium (5.0 ng mL^{-1}) and high (50 ng mL^{-1}) at each spiking level (n = 3).

	Low	Mid	High
syn-DP	**102 ± 13**	**94 ± 19**	**89 ± 8**
anti-DP	**92 ± 18**	**88 ± 9**	**95 ± 12**
Dec602	**77 ± 9**	**87 ± 7**	**91 ± 10**
Dec603	**101 ± 11**	**96 ± 14**	**103 ± 18**
Dec604	**79 ± 7**	**102 ± 11**	**81 ± 14**
CB105	**82 ± 12**	**97 ± 15**	**93 ± 10**

(Table 1) and was therefore deemed a suitable surrogate. Only *syn*- and *anti*-DP were detected in the field blanks. Concentrations were less than 10 % to those in corresponding samples; values were therefore not blank corrected.

Linear dynamic range for gas chromatograph mass spectrometry analysis was 0.25 – 500 pg injected (r^2 > 0.990). Instrument performance was monitored using a quality control standard every six injections to account for retention time and sensitivity

drift. Target and confirmation ions for compounds identified in samples were within 15 % to those measured in the analytical standard during the analysis.

Method detection limits (MDL) were based on replicate injections (n = 10) of a 0.25 pg μL^{-1} solution. The resulting standard deviation was applied to a one-sided student's t-test at a 95 % confidence interval. This was normalized to the final extract volume and an average sampling period of 90 days giving rise to MDLs for the DP and DP-related compounds ranging from 0.052 to 0.11 pg m^{-1}.

Deriving Air Concentrations

The details on the method used to calculate concentration were described previously.[16,27,28] Briefly, the effective sampling rate (R,) for high molecular weight compounds (high log K_{OA}) that are entirely particle bound has been estimated to be 0.5 m^3 day^{-1}. The PUF disks are suspended in a stainless steel chamber that reduces sampling artefacts associated with precipitation, wind and direct sunlight.

RESULTS AND DISCUSSION

Dechlorane Plus

DP was detected in 82 % of samples and at every GAPS site, at least once, with concentrations (pg m^{-3}) ranging from below detection limit (0.052) to 226, giving a mean of 9.2 (Figure 2). The high detection rate of DP in the atmosphere is supported by the

observations from Möller et al. who reported the presence of DP in all air samples along an Atlantic Ocean transect from Greenland to the Antarctic.[21] The greatest concentrations measured along the western waterways of Europe (maximum 1.6 pg m^{-3}) were attributed to the commercial use of DP-containing products in urban areas. This was also noted by Ren et al. who reported a linear relationship between DP concentrations in the Chinese atmosphere and population.[16] Although this relationship with human activity was generally true in this study, a noted striking feature was the predominance of DP concentrations in the Indo-Asian urban, rural and agricultural sites. This is curious, as others have reported greater concentrations of DP within the vicinity of DP manufacturing plants.[17,18,29] One possible reason is the existence of other manufacturing plants operating in this region; however, this remains speculative. Another possibility is the recycling of e-waste.

The United Nations Environment Programme (UNEP) estimates 50 – 80 % of the e-waste collected for recycling from developed nations are imported to China, India, Pakistan, Vietnam and the Philippines.[30] According to UNEP, e-waste has become the fastest growing waste stream in the industrialized world. A recycling technique commonly used in these countries is open-pit burning[31] where the plastic coatings are burned to reveal the valuable metal. Some of these e-waste recycling centers can employ up to 100,000 workers, such as in Guiyu, China.[31] There are numerous papers describing the liberation of FRs into the environment from these facilities and most recently, on DP.[19,20,32-36]

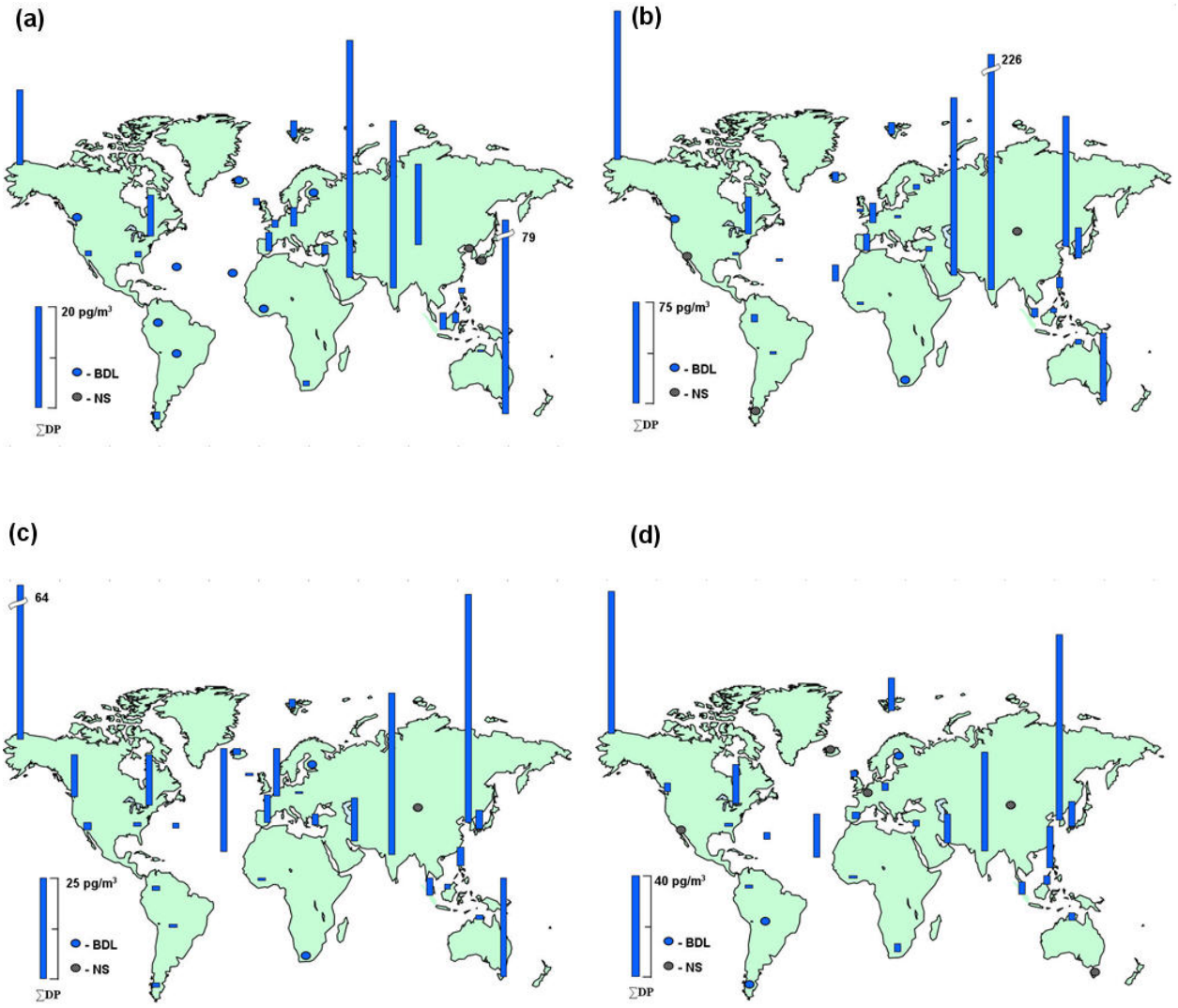

Figure 2. Air concentrations (pg m^{-3}) of total DP in 2005, (a) March – June; (b) June – September; (c) September – December; and (d) December – March (2006). BDL indicates values below the detection limit of 0.1 pg m^{-3} while NS represents locations where samples were not collected.

Lee et al.[37] presented worldwide atmospheric levels of a discontinued FR, polychlorinated naphthalene (PCNs), which certain congeners can also form during combustion. The spatial distribution was similar to that of DP in this study, the maximum concentrations primarily located in the Indo-Asian and Middle-Eastern regions. Further analysis of these sample sites showed the PCN profiles were dominated by combustion related congeners. Countries such as China did not adopt polychlorinated biphenyls as flame retardants, the replacement for PCNs, as readily as western countries ostensibly continuing to use PCNs for this purpose.

Further research is needed to determine whether e-waste facilities indeed are the source for DP, and/or other FRs in this region.

While Africa is reported to be a destination for e-waste from the developed world,38 elevated concentrations of DP were not observed. This may be attributed to the limited sampling locations in Africa (De Aar and Kalahari) which may not capture DP atmospheric concentrations from these sources.

DP levels at the Global Atmospheric Watch (GAW) site in Cape Grim, Tasmania dominated the southern hemispheric profile. This is surprising as it is considered a background site with a low population density. Previous GAPS studies at this site that measured current-use pesticides and PBDEs reflected the background nature of the site with very low air concentrations of these target compounds.[27] Air parcel back trajectories were calculated using the Canadian Meteorological Centre (CMC) trajectory model for each of the periods during this study. Three-day back trajectories were produced at an

elevation of 10 m every 6 h resulting in "spaghetti" plots (Figure 3). All periods showed air currents stemmed primarily from the Atlantic Ocean and Antarctic vectors with a minority originating from Australia. Möller et al. measured the lowest atmospheric concentrations of DP along an Atlantic Ocean transect in this region. While this would point to Australia as the potential source, it should be noted that DP measurements reported by Möller et al. were of an instantaneous nature and therefore, do not capture DP concentrations over time. Nevertheless, obvious sources of DP from the Atlantic Ocean and Antarctica are not known and seem unlikely. Although the prospect

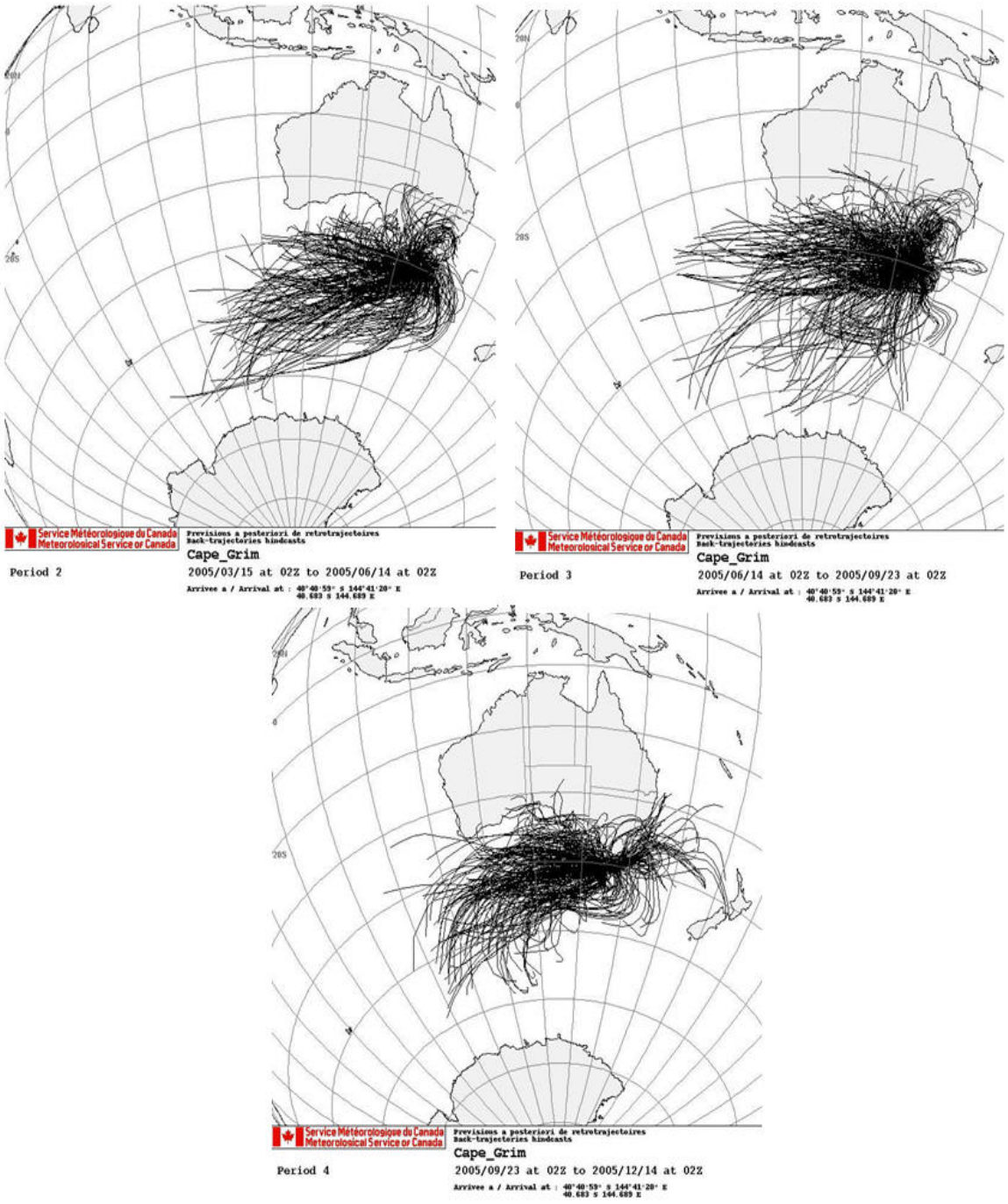

Figure 3. Back trajectory "spaghetti" plots at Cape Grim for Periods 2 (top left), 3 (top right) and 4 (bottom).

of local contamination at Cape Grim may be a consideration, no potential sources were identified.

With the exception of Cape Grim, DP concentrations in the southern hemisphere are lower than those in the northern hemisphere, with a mean of 1.1 and 16.2 pg m^{-3}, respectively ($p < 0.05$). Although higher concentrations of anthropogenic air contaminants are typically associated with more populated/industrialized regions, higher concentrations of DP in the northern hemisphere may be attributed to a greater proportion of urban GAPS sites here versus the southern hemisphere.

In the northern hemisphere, a surprising feature is the DP concentrations measured at the polar site of Barrow, AK. As with Cape Grim, this site is located in a relatively unpopulated area. However, unlike Cape Grim, the Arctic is known as a reservoir for long-range transport of contaminants from the Indo-Asian continent. To further support this knowledge, we conducted similar back trajectory analysis as done at the Cape Grim site but using 6-day, instead of 3-day, back trajectories to better capture longer distant sources (Figure 4). Although the prevailing wind patterns in this region are known to be south westerly, back trajectory model estimates suggest that air sources primarily originated from the Beaufort Sea. This may suggest that the levels in Barrow are stemming from local influences.

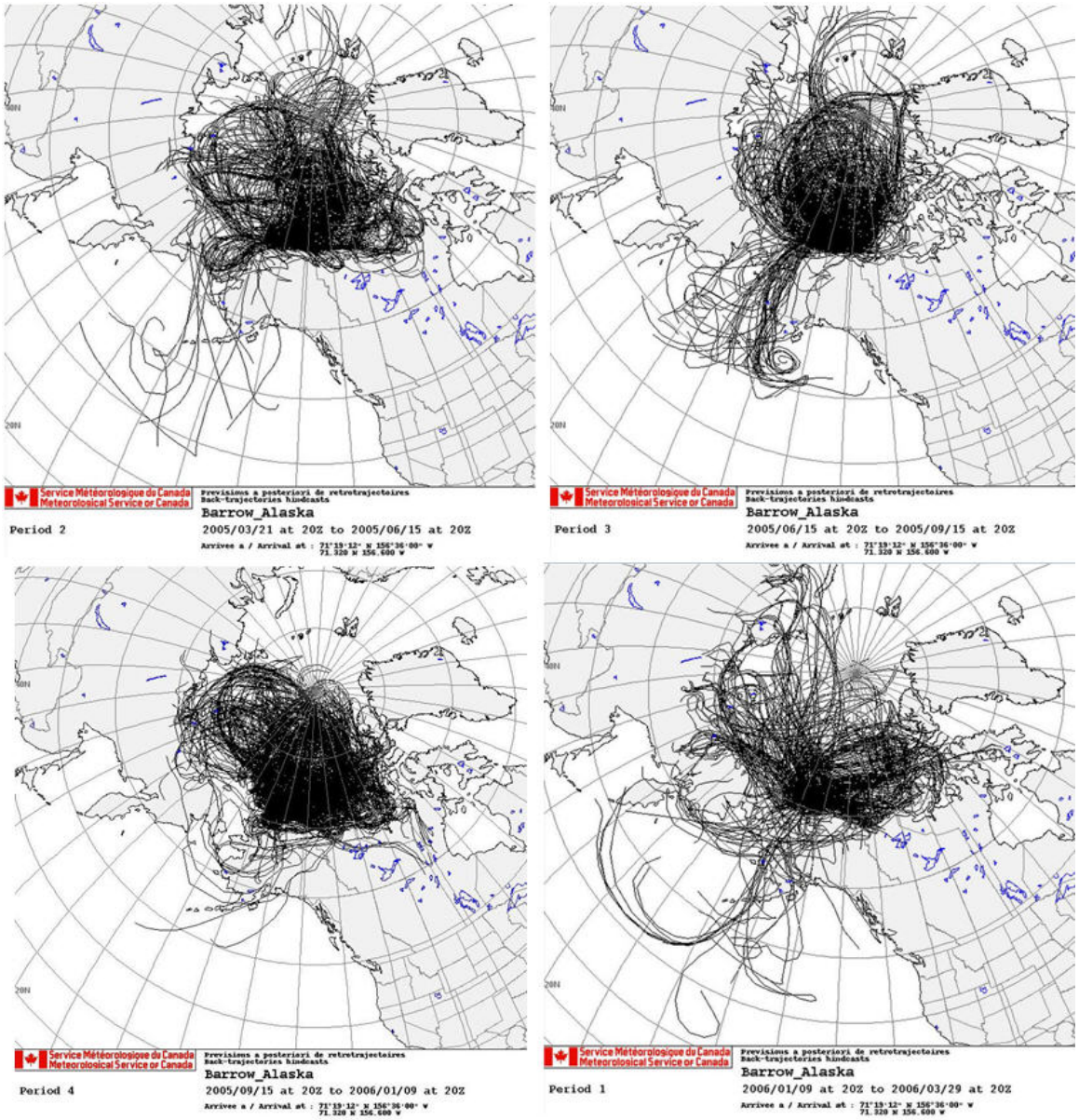

Figure 4. Back trajectory "spaghetti" plots at Barrow in 2005 for Periods 2 (top left), 3 (top right), 4 (bottom left) and 1 (2006, bottom right).

There appears to be no temporal relationship with DP concentrations. This is not surprising as DP is largely particle-bound and not susceptible to vapour phase partitioning, even in warmer temperatures.

Syn- and anti-DP isomer ratios

Caution should be employed when comparing DP isomer ratios in the environment due to both analytical instrument artefacts and unknown fate processes. For example, the general f_{syn} profiles in Lake Ontario bottom sediment, downstream of OxyChem, were distinctly different from the commercial mixture while in Lake Erie, upstream of the manufacturer, the profiles were similar. Additionally, a previous study showed that *syn*- and *anti*-DP were susceptible to *in situ* GC liner dechlorination; each at different rates.[11] If the *m/z* ions are not monitored for these dechloro-DP moieties, accuracy of f_{syn} measurements would remain uncertain. Therefore, comparison of f_{syn} values from those who did not monitor for dechloro-DP compounds in their analytical instrumental analysis, should be noted.

Figure 5 shows the significant variation of f_{syn} values during this study. While the sampling sites nearest the two known manufacturing plants, OxyChem and Anpon, show similar f_{syn} values to the technical mixtures, others appear to either enhance or deplete *anti*-DP. A lower concentration of *anti*-DP was shown in Europe while certain remote regions, such as Barrow and Cape Grim, gave a reduced f_{syn} values compared to the

technical mixtures. The long-range transport of DP to these remote regions would represent older aerosols perhaps suggesting isomer specific enhancement of *anti*-DP over

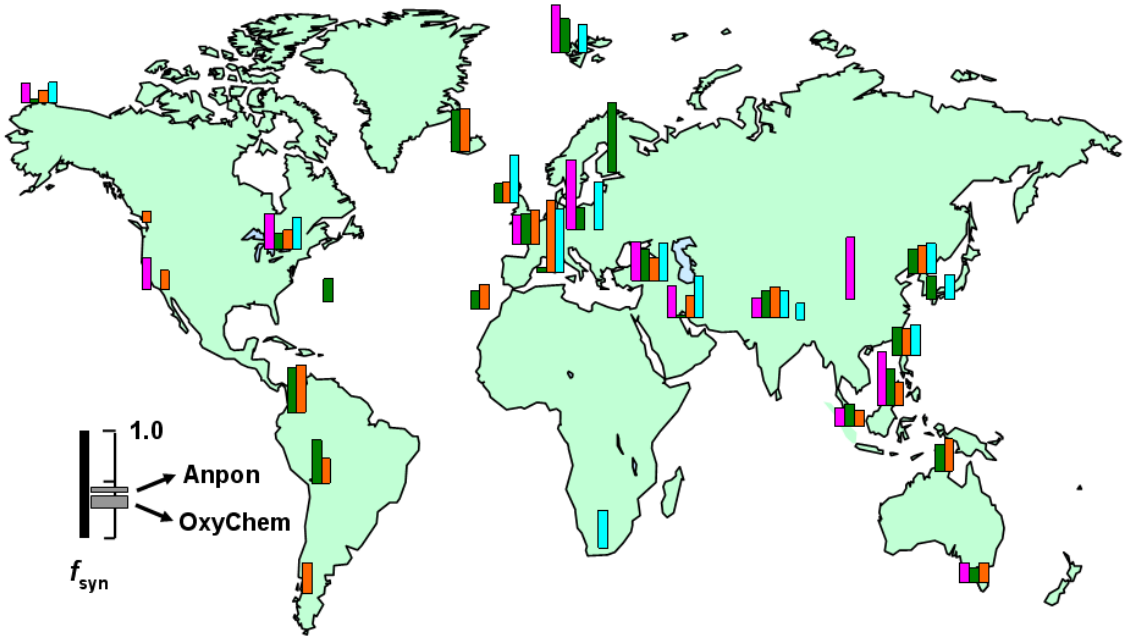

Figure 5. This represents the fraction of *syn*-DP (f_{syn}) to total DP concentration. The four sampling periods are identified as bars in: pink (March – June 2005); green (June – September 2005); orange (September – December 2005) and blue (December – March 2006). The solid black bar in the legend represents an f_{syn} value of 1.0 while the two grey lateral bars signify values associated with commercial mixtures from the currently known manufactures of DP. Results are only included if both isomers were detected.

the *syn* isomer. However, there is considerable uncertainty to this process as no experimental data exist to confirm this. Further investigation is required to determine fate of the DP isomers during long-range atmospheric transport.

Dechlorinated DP compounds

Previous studies detected dechlorinated DP moieties in various matrices including water,[12] sediment,[11] human hair and serum,[11,23] biota[22] and house dust,[24] suggesting there may be several mechanisms for their formation. However, no dechloro-DPs were measured in our air study implying dechlorination of DP in the atmosphere may not be likely. This was also observed by Möller et al. in a recent study of concurrent air and water measurements; detecting dechloro-DP compounds only in water.[21] Previous laboratory studies exposing DP solutions to UV light reported on the formation of several dechloro-DP compounds[11,39] suggesting DP was susceptible to photolytic degradation; however, Raff and Hites proposed that chemicals sorbed to carbonaceous aerosols were not vulnerable to photolytic degradation due to the shielding effect.[40] DP, possessing a log K_{OA} of 14 and shown to be almost entirely bound to particles,[1,16] would likely experience this effect.

Although trace amounts (< 1 % DP concentrations) of dechloro-DP compounds were detected in Chinese air, it was ascribed to pyrolytic processes from a nearby e-waste recycling facility rather than photolytic degradation.[33] These e-waste facilities would

therefore present a source for dechloro-DP compounds and should be considered when detecting these compounds in the atmosphere.

Dechloranes

Shen et al. first reported on the occurrence of Dec602, Dec603 and Dec604 in sediment and biota of the Laurentian Great Lakes in 2010[25] of which, Dec602 predominated. Dec602 was subsequently detected in Chinese sediment and soil[18,26] and biota in Spain.[14] While there exists a lack of information on the production volumes and uses for these Dechloranes, Dec602 and Dec604 are included in Canada's Nondomestic Substances List implying these are in commercial use today.

During our study only Dec602 was detected (Figure 6) with the maximum concentration located in Delhi, India (22 pg m^{-3}). Although not detected in all four sampling periods, Dec602 was present primarily in the Indo-Asian and Middle-Eastern regions. Interestingly, the only North American occurrence was detected in Toronto, located nearest the DP manufacturing plant in Niagara Falls, NY.

While it is not possible to comprehensively assess the impact of these initial data on atmospheric Dec602 concentrations, the prevalent occurrence of Dec602 appears to exist in the environment warranting further investigation.

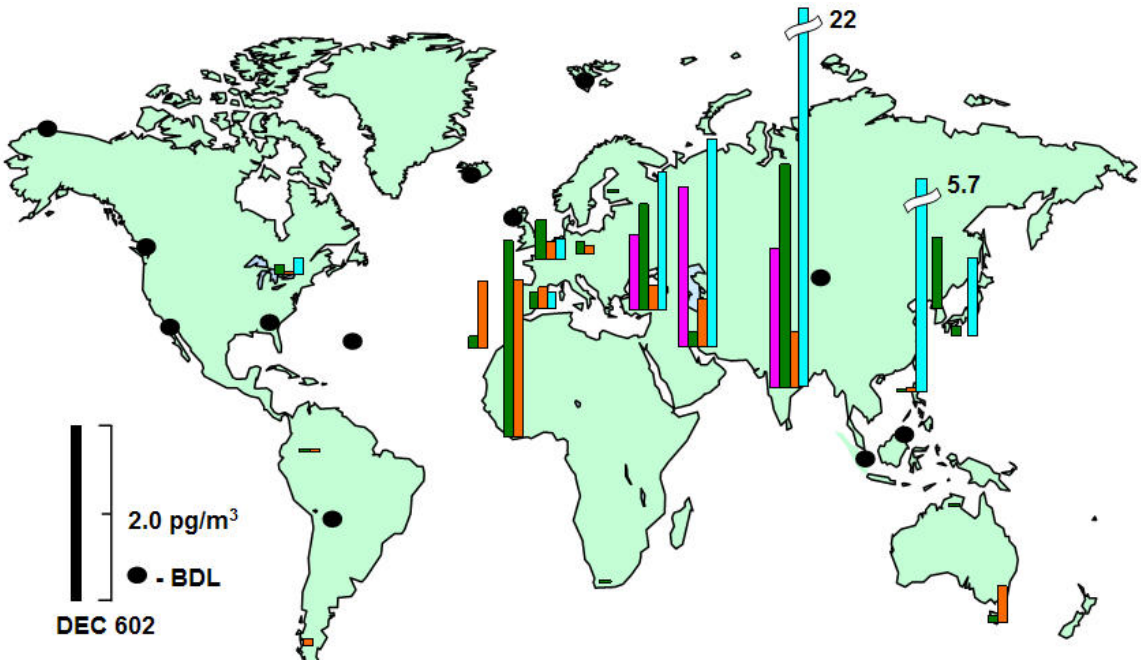

Figure 6. Atmospheric concentrations (pg m^{-3}) of Dec602. The four sampling periods are identified as bars in: pink (March – June 2005); green (June – September 2005); orange (September – December 2005) and blue (December – March 2006). BDL indicates values below the detection limit of 0.08 pg m^{-3}.

Implications

Although DP and Dechloranes are predominantly measured in the northern hemisphere, these FRs are shown to be a worldwide contaminant. One of the three Stockholm Convention's tenants (PB&T) identifying chemicals of interest based on persistence in the environment; identifying chemicals in areas far from their source(s). While DP was

shown to bioaccumulate, little to no toxicity studies have been conducted thus far. Even if DP proves relatively low in toxicity, it's worldwide presence requires further monitoring for increasing trends in concentration, especially in light of DP's candidacy for replacement of the brominated HPV, deca-BDE.

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References

[1] European Chemicals Bureau http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE.pdf (accessed July 10, 2011), Internet Communication 2007.

[2] Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006,** *40*, 1184-1189.

[3] Sverko, E.; Tomy, G. T.; Marvin, C. H.; Zaruk, D.; Reiner, E.; Helm, P. A.; Hill, B.; McCarry, B. E. Dechlorane Plus levels in sediment of the lower Great Lakes. *Environ. Sci. Technol.* **2008,** *42* (2), 361-366.

[4] Tomy, G. T.; Pleskach, K.; Ismail, N.; Whittle, D. M.; Helm, P. A.; Sverko, E.; Zaruk, D.; Marvin, C. H. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* **2007,** *41*, 2249-2254.

[5] Qiu, X.; Hites, R. A. Dechlorane plus and other flame retardants in tree bark from the northeastern United States. *Environ. Sci. Technol.* **2008,** *42* (1), 31-36.

[6] Guerra, P.; Fernie, K.; Jimenez, B.; Pacepavicius, G.; Shen, L.; Reiner, E.; Eljarrat, E.; Barcelo, D.; Alaee, M. Dechlorane Plus and Related Compounds in Peregrine Falcon (Falco peregrinus) Eggs from Canada and Spain. *Environ. Sci. Technol.* **2011**.

[7] Ma, W. L.; Liu, L. Y.; Qi, H.; Sun, D. Z.; Shen, J. M.; Wang, D. G.; Li, Y. F. Dechlorane plus in multimedia in northeastern Chinese urban region. *Environ. Int.* **2011,** *37* (1), 66-70.

[8] Ren, N.; Sverko, E.; Li, Y. F.; Zhang, Z.; Harner, T.; Wang, D.; Wan, X.; McCarry, B. E. Levels and isomer profiles of dechlorane plus in Chinese air. *Environ. Sci. Technol.* **2008,** *42* (17), 6476-6480.

[9] Wang, B.; Iino, F.; Huang, J.; Lu, Y.; Yu, G.; Morita, M. Dechlorane Plus pollution and inventory in soil of Huai'an City, China. *Chemosphere* **2010,** *80* (11), 1285-1290.

[10] Wang, D. G.; Yang, M.; Qi, H.; Sverko, E.; Ma, W. L.; Li, Y. F.; Alaee, M.; Reiner, E. J.; Shen, L. An Asia-specific source of dechlorane plus: concentra-

tion, isomer profiles, and other related compounds. *Environ. Sci. Technol.* **2010,** *44* (17), 6608-6613.

[11] Yu, Z.; Lu, S.; Gao, S.; Wang, J.; Li, H.; Zeng, X.; Sheng, G.; Fu, J. Levels and isomer profiles of Dechlorane Plus in the surface soils from e-waste recycling areas and industrial areas in South China. *Environ. Pollut.* **2010,** *158* (9), 2920-2925.

[12] Zheng, J.; Wang, J.; Luo, X. J.; Tian, M.; He, L. Y.; Yuan, J. G.; Mai, B. X.; Yang, Z. Y. Dechlorane Plus in human hair from an e-waste recycling area in South China: comparison with dust. *Environ. Sci. Technol.* **2010,** *44* (24), 9298-9303.

[13] Moller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Large-scale distribution of dechlorane plus in air and seawater from the Arctic to Antarctica. *Environ. Sci. Technol.* **2010,** *44* (23), 8977-8982.

[14] Munoz-Arnanz, J.; Saez, M.; Hiraldo, F.; Baos, R.; Pacepavicius, G.; Alaee, M.; Jimenez, B. Dechlorane plus and possible degradation products in white stork eggs from Spain. *Environ. Int.* **2011**.

[15] Ren, G.; Yu, Z.; Ma, S.; Li, H.; Peng, P.; Sheng, G.; Fu, J. Determination of Dechlorane Plus in serum from electronics dismantling workers in South China. *Environ. Sci. Technol.* **2009,** *43* (24), 9453-9457.

[16] Zhu, J.; Feng, Y. L.; Shoeib, M. Detection of dechlorane plus in residential indoor dust in the city of Ottawa, Canada. *Environ. Sci. Technol.* **2007,** *41* (22), 7694-7698.

[17] Shen, L.; Reiner, E. J.; Macpherson, K. A.; Kolic, T. M.; Sverko, E.; Helm, P. A.; Bhavsar, S. P.; Brindle, I. D.; Marvin, C. H. Identification and screening analysis of halogenated norbornene flame retardants in the Laurentian Great Lakes: Dechloranes 602, 603, and 604. *Environ. Sci. Technol.* **2010,** *44* (2), 760-766.

[18] Jia, H.; Sun, Y.; Liu, X.; Yang, M.; Wang, D.; Qi, H.; Shen, L.; Sverko, E.; Reiner, E. J.; Li, Y. F. Concentration and bioaccumulation of dechlorane compounds in coastal environment of northern China. *Environ. Sci. Technol.* **2011,** *45* (7), 2613-2618.

[19] Pozo, K.; Harner, T.; Wania, F.; Muir, D. C.; Jones, K. C.; Barrie, L. A. Toward a global network for persistent organic pollutants in air: results from the GAPS study. *Environ. Sci. Technol.* **2006,** *40* (16), 4867-4873.

[20] Klanova, J.; Eupr, P.; Kohoutek, J.; Harner, T. Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. *Environ. Sci. Technol.* **2008,** *42* (2), 550-555.

[21] Qiu, X.; Marvin, C. H.; Hites, R. A. Dechlorane plus and other flame retardants in a sediment core from Lake Ontario. *Environ. Sci. Technol.* **2007,** *41* (17), 6014-6019.

[22] UNEP DEWA/GRID-Europe E-waste, the hidden side of IT equipment's manufacturing and use.Chapter 5 - Early Warning on Emerging Environmental Trends.http://www.grid.unep.ch (accessed July 10, 2011), Internet Communication 2005.

[23] Wong, M. H.; Wu, S. C.; Deng, W. J.; Yu, X. Z.; Luo, Q.; Leung, A. O.; Wong, C. S.; Luksemburg, W. J.; Wong, A. S. Export of toxic chemicals - a review of the case of uncontrolled electronic-waste recycling. *Environ. Pollut.* **2007,** *149* (2), 131-140.

[24] Chen, S. J.; Tian, M.; Wang, J.; Shi, T.; Luo, Y.; Luo, X. J.; Mai, B. X. Dechlorane Plus (DP) in air and plants at an electronic waste (e-waste) site in South China. *Environ. Pollut.* **2011,** *159* (5), 1290-1296.

[25] Tian, M.; Chen, S. J.; Wang, J.; Shi, T.; Luo, X. J.; Mai, B. X. Atmospheric deposition of halogenated flame retardants at urban, e-waste, and rural locations in southern china. *Environ. Sci. Technol.* **2011,** *45* (11), 4696-4701.

[26] Wang, J.; Tian, M.; Chen, S. J.; Zheng, J.; Luo, X. J.; An, T. C.; Mai, B. X. Dechlorane plus in house dust from E-waste recycling and urban areas in South China: Sources, degradation, and human exposure. *Environ. Toxicol. Chem.* **2011**.

[27] Zhang, X. L.; Luo, X. J.; Liu, H. Y.; Yu, L. H.; Chen, S. J.; Mai, B. X. Bioaccumulation of several brominated flame retardants and dechlorane plus in waterbirds from an e-waste recycling region in South China: associated with trophic level and diet sources. *Environ. Sci. Technol.* **2011,** *45* (2), 400-405.

[28] Zhang, Y.; Luo, X. J.; Wu, J. P.; Liu, J.; Wang, J.; Chen, S. J.; Mai, B. X. Contaminant pattern and bioaccumulation of legacy and emerging organhalogen pollutants in the aquatic biota from an e-waste recycling region in South China. *Environ. Toxicol. Chem.* **2010,** *29* (4), 852-859.

[29] Lee, S. C.; Harner, T.; Pozo, K.; Shoeib, M.; Wania, F.; Muir, D. C.; Barrie, L. A.; Jones, K. C. Polychlorinated naphthalenes in the Global Atmospheric Passive sampling (GAPS) study. *Environ. Sci. Technol.* **2007,** *41* (8), 2680-2687.

[30] Ni, H. G.; Zeng, E. Y. Law enforcement and global collaboration are the keys to containing e-waste tsunami in China. *Environ. Sci. Technol.* **2009,** *43* (11), 3991-3994.

[31] Wang, J.; Tian, M.; Chen, S. J.; Zheng, J.; Luo, X. J.; An, T. C.; Mai, B. X. Dechlorane plus in house dust from E-waste recycling and urban areas in South China: Sources, degradation, and human exposure. *Environ. Toxicol. Chem.* **2011**.

[32] Raff, J. D.; Hites, R. A. Deposition versus photochemical removal of PBDEs from Lake Superior air. *Environ. Sci. Technol.* **2007,** *41* (19), 6725-6731.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE RESEARCH AND CONCLUSIONS

It seems clear that Dechlorane Plus is globally ubiquitous; however, due to a lack of monitoring data, similar conclusions cannot yet be made about the DP analogues. DP is present in remote regions far from manufacturing facilities. DP and some of its analogues are bioaccumulative and persistent in certain environmental media; however, while persistence and bioaccumulation have been sufficiently demonstrated for DP (in particular), reliable toxicity data and further research evaluating the potential for significant adverse effects are needed before these chemicals can be considered for Annex D evaluation under the United Nations Stockholm Convention on Persistent Organic Pollutants. It is suggested that future work in the following areas is required:

- Laboratory biota-sediment accumulation factor measurements to quantify the transfer and availability of DP and its analogs from sediments (both aged and spiked) to representative benthic organisms.
- Use of passive samplers to estimate dissolved-phase concentrations of DP and its analogs in sediment pore water and in the overlying water column.
- Dietary bioaccumulation studies of DP analogs to obtain key bioaccumulation parameters such as dietary assimilation efficiency, BMF, and depuration half-lives that could then be used to estimate biotransformation half-lives. This information could reduce uncertainty in parameterizing and applying food web models for exposure and risk estimates for lower and upper trophic level

organisms.

- Environmental degradation studies of DP and its analogs to determine medium-specific half-lives.
- More environmental measurements of DP and its analogs are needed, particularly in Europe; it is important to fully establish the environmental distribution of these chemicals.
- Acute and chronic toxicity studies on DP and its analogs are needed; however, due to the low water solubilities of these compounds, toxicity tests for aquatic species will require dietary-based dosing strategies.

APPENDIX A

ANALYTICAL CONSIDERATIONS FOR DP ANALYSIS

GC/MS Artefacts

As mentioned in the previous chapters, DP isomers can preferentially degrade in the GC liner complicating the determination of f_{syn} values and, in extreme cases, the accurate measurement of DP concentrations. Degradation largely occurs when extracts containing a complex matrix (i.e., unpurified and/or containing high boiling point compounds) deposit on the liner creating active sites for this to occur. This process can progress gradually over the course of a sequence or catastrophically within the injection of a few samples. Once this occurs, the GC liner must be replaced and extracts reinjected.

To monitor for GC liner degradation, dechlorination DP moieties should be included in the analytical run by adding *m/z* ions associated with [-Cl+H] and [-2Cl+2H] (noted in previous Chapters). This is achieved by including a DP standard solution after every five samples. Dechloro-DP compounds will normally be detected in sensitive GC/MS instruments at < 5 % of total DP – this can be considered as normal as long as this remains consistent within a sequence. Increasing, or varying amounts of dechloro-DP compounds in the continued injection of DP standard solutions indicates a dynamic, unstable condition. Once the area counts of the dechoro-DP compounds are > 10 % of

total DP, the injector should be replaced and the subsequent samples in the sequence should be reinjected.

Matrix type usually determines whether *in situ* GC liner dechlorination will occur. Biota samples, such as fish, benthic and terrestrial organisms, typically do not require frequent replacement of GC liners. However, those matrices thought to contain high levels of humic acids (soil, sediment, 'dirty' urban air), require frequent liner replacement.

Determination of f_{syn}

Determination of f_{syn} values should be based on isomeric concentrations rather than absolute GC/MS area counts. Those based on area counts do not account for response differences between syn- and anti-DP when using different source temperatures. Fragmentation of each isomer in this envrionment is different and therefore, the absolute response for each M- ion cluster monitored for both DP isomers is different. This can only be normalized if f_{syn} values are based on isomeric ratios derived by concentration rather than relative area counts.

Sample Extract Clean up

Purification of a sample extract normally includes an elution process through some modified adsorbent to remove interfering constituents. Previous studies have

included a two-fraction clean up whereby DP resides in the latter, polar, fraction (Fr-B); however, verification steps are made to ensure both DP isomers completely elute into Fr-B. This is done by conducting laboratory recovery spikes and periodic inclusion of FR-A sample extracts in the sequence to account for matrix anomalies affecting DP fractionation.

APPENDIX B

Number: **SOP 03-3751**

Title: **STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF CHLOROBENZENES, ORGANOCHLORINE PESTICIDES, TOTAL POLYCHLORINATED BIPHENYLS AND POLYNUCLEAR AROMATIC HYDROCARBONS IN SEDIMENT USING ULTRASONIC EXTRACTION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE AND MASS SELECTIVE DETECTORS**

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Background Information

Chlorinated aromatic hydrocarbons, or chlorobenzenes (CBs), are discharged into soil and sediment through chemical waste dump leachate, manufacturing effluent and solvent applications. As the result of runoff from the soil surface or movement through soil into underground water systems, these hydrophillic compounds may also contaminate water.

The organochlorine pesticides (OCs) are chlorinated derivatives of alicyclic hydrocarbons. They are primarily released into the environment as insecticides. The

OCs include aldrin, dieldrin, heptachlor, chlordane, and DDT, which are classified as epigenic carcinogens. The application of pesticides results in the direct pollution of soil. Pesticide residues may exist in plant products because pesticides in soil can be adsorbed into plant roots and transported to the whole plant body.

Polychlorinated biphenyls (PCBs), which are also carcinogenic, have been used extensively in industry as flame retardants, high pressure lubricants, water- proofing compounds, casting wax, adhesives, asphalt, and as dielectric, hydraulic and grinding fluids.

Poly-nuclear aromatic hydrocarbons (PAHs) are the largest known class of chemical carcinogens. They are formed by combustion reactions and petroleum processing. PAHs also occur naturally; they are produced by biosynthesis, natural combustion, and the long-term degradation of biological material. The hydrophobic, lipophilic nature of PAHs results in their strong adsorption to sediment and soil particles. The higher molecular weight PAHs are especially persistent and tend to bio-accumulate in aquatic organisms.

This method provides the analytical and supporting methodology necessary for the extraction, quantitative determination and confirmation of chlorobenzenes, organochlorine pesticides, total polychlorinated biphenyls, and polynuclear aromatic hydrocarbons from 20 grams of wet sediment or 10 grams of freeze-dried sediment at the nanogram per gram (ng/g) level and is deemed fit for intended use.

The method detection limit (MDL) is the lowest concentration of analyte in

sediment that a method can detect reliably and which is statistically different from the response obtained from a blank carried through the complete method, including extraction and pre-treatment of the sample.

The coefficient of determination (r^2) is a measure of the closeness of fit of a scatter graph to its regression line. This method has been tested for linearity and has been demonstrated to be applicable over the working range.

Scope and Application

This method applies to the qualitative and quantitative determination of chloro-benzenes, organochlorine pesticides, polynuclear aromatic hydrocarbons, and total poly-chlorinated biphenyls (Aroclor 1242, Aroclor 1254 and Aroclor 1260) from 20 grams of wet sediment or 10 grams of freeze-dried sediment using ultrasonic extraction, back extraction, deactivated silica gel cleanup and analysis by gas liquid chromatography with electron capture and mass selective detectors.

Summary of Method

A 20 gram wet sediment sample or a 10 gram freeze-dried sediment sample is ultrasonically extracted using a 1:1 mixture of acetone and hexane. The concentrated extract is partitioned with water and back-extracted with dichloromethane. The combined extract is concentrated, cleaned up and fractionated on a 3% (w/w) deactivated silica gel column. It is then re-concentrated to a final volume of 10 mL prior to analysis. Dual

column capillary gas liquid chromatography with electron capture detectors is used for PCBs, CBs and OCs, and single column capillary gas liquid chromatography with a mass selective detector is used for PAHs.

Interferences

Common interferences originate from contaminated solvents, reagents and glass-ware. All solvents must be checked for background levels of interferences by concentrating a known volume of the solvent and analysing the extract by GC/ECD. Interferences from reagents and glassware can be checked by analysing a method blank with each set of 12 samples. The method blank consists of 300 mL of 1:1 acetone in hexane, which has been carried through the analytical process. Positive values detected on both columns and for which the source of contamination cannot be determined must be subtracted from the samples.

Co-extracted non-target organic compounds from the sediment samples are potential interferences. The silica gel column cleanup for this method usually removes such interferences.

Apparatus, Equipment and Materials

For CB, OC and PCB analysis

Gas liquid chromatograph (HP 5890 or equivalent) equipped with split/split-less dual

capillary column injection port, two electron capture detectors and automatic sampler (HP 7673A).

Chromatographic Conditions for CB and OC Analysis (GC/ECD):

Columns:	GC capillary, 30 m x 0.25 mm ID, 25 micron film thickness, fused silica DB-1 (confirmation column) and DB-5 (primary column)
Injection Port:	Split/split-less, purge valve on after 30 seconds
Injection Port Temperature:	250 ^{o}C
Injection Volume:	3 μL
Auto-injector:	HP 7673A
Detector:	Electron capture (Ni^{63})
Detector Temperature:	350 ^{o}C
Carrier Gas:	Hydrogen (ultra-high purity)
Make Up Gas:	Nitrogen @ 60 mL/minute
Column Head Pressure:	15 psi
Initial Column Temperature:	80 ^{o}C; hold for 2 minutes
Programming Rate :	4 ^{o}C /min to 260 ^{o}C and hold for 8 minutes

For PAH Analysis

Gas liquid chromatograph (HP-5890 or equivalent) equipped with split/split-less injection port, mass selective detector-5971A and automatic sampler (HP 7673A).

Chromatographic Conditions for PAHs Analysis (GC/MSD):

Column:	GC capillary, 30 m x 0.25 mm ID, 25 micron film thickness, fused silica, HP-5MS (or equivalent)
Injection Port:	Split/split-less, purge valve on after 30 seconds
Injection Port Temperature:	265^{o}C
Injection Volume:	2 μL
Column Head Pressure:	11 psi
Carrier Gas:	Helium (ultra high purity)
Initial Column Temperature:	80 ^{o}C; hold for 3 minutes
Programming Rate 1:	60 ^{o}C /minute to 180 ^{o}C
Programming Rate 2:	30 ^{o}C /minute to 280 ^{o}C
Final Time:	22 minutes
Detector:	Mass selective
Transfer Line Temperature:	320 ^{o}C
Acquisition Mode:	Selected Ion Monitoring (SIM)

Quality Assurance/Quality Control

Surrogates

Surrogates are used in this method to monitor recovery and method performance. Two different standards have been incorporated into the method.

The field surrogate standard for sediment and biota contains 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene and BHC. This spike is added by the analyst to the sediment just before ultrasonic extraction. The recovery of these compounds is calculated to monitor extraction efficiency.

The **CB/OC Lab Surrogates Spiking Standard** contains 1,3-dibromobenzene and endrin ketone. This spike is added by the analyst to every sample and quality control sample prior to the extraction. It monitors the recovery of the method.

The **PAH Lab Surrogates Spiking Standard** contains naphthalene-D8, fluorene-D8, pyrene-D10 and perylene -D12. This spike is added by the analyst to every sample and quality control sample prior to the second concentration. It monitors the recovery at this stage of the method.

Calibration Stability: Within a run, the responses for the analytes in each of the Continuing Calibration standards(CC1..CC3) should fall within 30% of the initial calibration standards (S2 for OCs, S3 for PAHs in the analytical tray pattern shown in **Table 3-3751:5**). If any standard is found to have response values outside of this limit, it should be rejected, the instrument should be recalibrated and the analysis repeated from that point. The performance check standard is also assessed at the beginning and end of each tray pattern to determine instrument stability. Document the non-conformance and the corrective action taken on the audit trail sheet.

Control Charts: Keep ongoing control charts for accuracy, precision, contamination and recovery. Calculate control limits and prepare control charts as described in **Chapter 1** of the **NLET Manual of Analytical Methods, Volume 3**.

Accuracy: X - (Shewhart) Charts for OCs-Fraction A (1,2,4-trichlorobenzene, hexachlorobenzene and mirex); OCs-Fraction B (BHC, dieldrin and p,p' DDT); PAHs-Fraction A & B (1,2,3,4-tetrahydronaphthalene, phenanthrene and benzo(*g,h,i*)perylene): With each batch of 12 samples, analyse 2 spiked method blanks. After the analysis, plot the concentrations for each of the 3 compounds onto separate control charts. The data should fall within the established control limits**.** If the plot indicates the data to be out of control, refer to corrective actions.

Precision: **X** - (Shewhart) Difference Charts for OCs-Fraction A (1,2,4-tribromobenzene, hexachlorobenzene and mirex); OCs-Fraction B (BHC, dieldrin and p,p'-DDT); PAHs-Fraction A&B (1,2,3,4-tetrahydronaphthalene, phenanthrene and benzo(*g,h,i*)perylene): Analyze 2 spiked method blanks, used as references, with each batch of 12 samples and determine the difference between the two for the compounds listed. Plot the difference onto separate control charts. The differences in concentrations should fall within the established control limits. If the plot indicates the data to be out of control, refer to corrective actions.

Contamination: Zero C Line Charts for OCs-Fraction A (1,2,4-trichlorobenzene, hexachlorobenzene and mirex); OCs-Fraction B (BHC, dieldrin and p,p'-DDT); PAHs-

Fraction A&B (1,2,3,4-tetrahydronaphthalene, phenanthrene and benzo(*g,h,i*)perylene): Analyse 1 method blank with each batch of 12 samples to monitor contamination and background interference. After the analysis, plot the values for each of the compounds onto separate control charts. The concentrations obtained should fall within the established control limits. If the plot indicates the data to be out of control, refer to corrective actions.

Recovery: X-(Shewhart) % Recovery Chart for 1,3-dibromobenzene and endrin ketone (surrogate sample spike, to monitor all laboratory procedures): After the analysis, plot the percent (%) recovery of 1,3-dibromobenzene and endrin ketone from each of the samples onto a separate control chart. The recovery should fall within the established control limits. If the plot indicates the data to be out of control, refer to corrective actions**.**

Corrective Actions: If the control and warning limits on a control chart are set at 3 S_d (standard deviation) and 2 $S_{d,}$ respectively, it is expected that 1 out of 20 and 1 out of 100 data points will exceed the warning and control limits, respectively. On careful examination of the control charts, the following guide will indicate to the analyst when to intervene and take appropriate actions to correct the problems.

Control Limit: If one data point exceeds the control limit, determine the source of the problem and correct if possible. If not, confer with the Supervising Chemist about flagging the data in the final report. Document the non-conformance and the corrective action taken in the QC file containing the control charts.

Warning Limit: If two out of three successive data points exceed the warning limits, analyse another sample. If the next data point is within the warning limits, continue the analysis; otherwise, investigate the problem and notify the Supervising Chemist. Document the non-conformance and the corrective action taken in the QC file.

Preparation and Procedure

An analytical run will normally consist of 12 samples, 1 method blank and 1 spiked method blank and 1 duplicate spike method blank. The method blank is prepared by processing 300 mL of 1:1 acetone in hexane through the analytical procedure. The spiked method blank and duplicate is prepared by spiking 1 mL each of the CB/OC Method Spiking Standard solution**,** PAH Method Spiking Standard solution and PCB Method Spiking Standard solution into 300mL of 1:1 acetone in hexane.

Extraction

Retrieve the samples from the appropriate storage facility. Wet sediment must first be thawed, and then its moisture content must be determined. Dry sediment can be extracted immediately.

After thawing the wet sediment, mix thoroughly with a metal spatula to obtain homogeneity. Weigh out an aliquot of the sample into a tared aluminium dish. Record

the weight of the wet sediment on the % moisture calculation sheet. Heat overnight in an oven maintained at 105 ^{o}C to dry the sample and determine the moisture content.

Weigh out 20 g of wet sediment sample into a 250 mL stainless steel beaker.

Weigh out 10 g of dry sediment into a 250 mL stainless steel beaker and add 30-40% of Type I water. Mix thoroughly to make a slurry.

Add 1 mL of the OC/CB field surrogate spike standard and PAH laboratory surrogate to each sample, mix thoroughly, cover the beaker with aluminium foil, and let stand twenty minutes.

Add 100 mL 1:1 of acetone in hexane to the sediment sample. Secure the beaker in an ice bath and sonify for three minutes at 50% duty cycle and output control set at eight. Allow a few minutes for the slurry to settle.

Note: Since sonification generates heat, an ice bath is used to reduce the loss of volatile analytes.

Decant the supernatant from the sediment extract into an Allihn funnel containing 5 cm of celite, prewashed with 25 mL of pet ether, followed by 25 mL of 1:1 acetone in hexane and fitted onto a 1000 mL round bottom flask.

After the third extraction, pour all of the sediment into the funnel and rinse the beaker twice with 25 mL of 1:1 acetone in hexane. Pour the rinsings into the funnel and apply gentle vacuum suction until the celite is dry.

Thoroughly rinse the sonfier probe with (1:1) acetone in hexane between samples

to avoid cross contamination of samples.

Concentrate the extract to approximately 200 mL on the vacuum- controlled rotary evaporator.

Back Extraction:

Transfer the extract to a clean 1 L separatory funnel. Rinse the round bottom flask three times with 5 mL of hexane and add the rinsings to the separatory funnel. Add 100 mL of Type I water to the funnel. Shake this mixture vigorously for two minutes and allow the two phases to separate. If an emulsion occurs, add 5 mL of saturated sodium sulphate solution and swirl to disperse the emulsion.

Drain the aqueous (bottom) layer into a 500 mL separatory funnel. Do not discard the solvent layer (acetone in hexane extract) in the 1 L separatory funnel.

Add 100 mL of dichloromethane to the aqueous layer and shake vigorously for two minutes. Allow the two layers to separate. Drain the organic (bottom) layer into the 1 L separatory funnel containing the acetone in hexane extract.

Repeat the extraction twice more, using 50 mL of dichloromethane each time.

Filter the combined extracts in the 1 L separatory funnel into an Allihn funnel containing 5 cm anhydrous sodium sulphate, prewashed with 20 mL dichloromethane and fitted onto a clean 1000 mL round bottom flask.

Rinse the sodium sulphate cake three times with 25 mL dichloromethane. Apply gentle vacuum suction until the sodium sulphate cake is dry.

Add 10 mL of iso-octane and 1 mL of OC/CB laboratory surrogate spiking standard to the extract.Concentrate the extract to approximately 3 mL, using the vacuum- controlled rotary evaporator.

Quantitatively transfer the extracts from round bottom flasks to graduated centrifuge tubes, using rinsings of 2 x 3 mL iso-octane.

To ensure that there are no traces of dichloromethane remaining in extract, add 5 mL of iso-octane, vortex and evaporate to 3 mL.

Silica Gel Column Cleanup:

Pack a glass chromatography column (12 mm x 350 mm) by inserting a plug of clean si-lanized glass wool at the bottom of the column. Then, while tapping it gently, add 2.5 cm of anhydrous sodium sulphate, 8 cm of 3% deactivated silica gel and another 2.5 cm of anhydrous sodium sulphate.

Pre-wash the packed column with 25 mL of hexane. Discard this rinsing and put a 100 mL round bottom flask under the column.

Transfer the concentrate onto the top of the column using a clean disposable pipette. Rinse the graduated centrifuge tube with 2 mL of hexane and apply to the column after the extract sinks to the top layer of sodium sulphate. Rinse the tube two more times with

2 mL of hexane. Elute the column with 40 mL of hexane. This is labelled Fraction A and contains PCBs, CBs, OCAs and some PAHS.

Elute the column with 60 mL of 1:1 hexane in dichloromethane and collect the eluent in another 100 mL round bottom flask. This is labelled Fraction B and contains OCBs and most of the PAHs.

Note: If samples are required for PAH analysis only, fraction A and B are collected together in 250 mL round bottom flask.

Add 10 mL of iso-octane to Fractions A and B. Concentrate both fractions to approximately 3 mL, using the vacuum-controlled rotary evaporator.

Quantitatively transfer the extracts from the round bottom flasks to graduated centrifuge tubes, by rinsing of 2 x 3 mL iso-octane, and make the volume up to 10 mL. Mix the extracts thoroughly, using a vortex mixer.

Concentrate Fraction B under nitrogen to 5 mL, using the Turbovap LV Evaporator. To ensure that there are no traces of dichloromethane left in the sample, add 5 mL of iso-octane, vortex and evaporate back down to 3 mL. Adjust the final volume to 10 mL with iso-octane.

Sulfur may be present in the Fraction A sediment extract. It causes interference during gas chromatographic analysis and therefore must be removed. Transfer 1 mL of the extract from the centrifuge tube into a 2 mL disposable glass vial and add 2-3 drops of mercury.

Using a single capillary GC/MSD set to the conditions, analyse a (1:1) mixture of Fraction A and Fraction B for the polynuclear aromatic hydrocarbons. Prepare this mixture by measuring 45 μL of each fraction with a syringe into a vial containing a glass insert. Add 10 μL of the PAH Internal Standard to each glass insert. Cap the vial and mix thoroughly using a vortex mixer.

GC/MSD (Single Capillary) Calibration:

Instrument Tune Criteria: The performance of the GC/MSD is checked by carrying out an Autotune. The autotune is carried out using perfluorotributylamine (PFTBA) as the celebrant. A hard copy of the resulting spectrum scan of PFTBA and ion profile scan should be filed for future reference. A visual comparison of the absolute abundances of masses 69, 219, and 502 and the electron multiplier voltage to the previous autotune values is made and is checked for trends. These trends can serve as guidelines for scheduling maintenance and for the diagnosis of malfunctions.

Instrument Performance Check: Inject an instrument performance check standard (lowest level standard)**.** This standard is used to evaluate detector and chromatographic response. Chromatograms should exhibit well-defined peak shape and detector response for each analyte. An example of an acceptable chromatogram is stored in the GC/MSD Instrument Quality Control Manual under Tuning. If values fall outside of these limits, maintenance may be necessary (e.g., change the septum, insert and/or cut columns).

Instrument Calibration: Calibration standards are used to quantify target analyte concentrations**.** The calibration standards (S1-S6) are injected at the start of the sequence. Continuing calibration standards (CC1..CC3) are injected at the intervals shown in the analytical tray pattern. The response factors for all standards must be within 30% of the initial calibration standard (S3), or the analysis must be repeated from the point of calibration failure.

Instrument External Standard Check: To establish an independent control to ensure method calibration is adequate. A second source external standard is included in each and every sequence run. This external standard is provided by the standards chemist to the instrument analyst, who then includes one in each sample sequence. The recovery of the standard is measured against the calibration curve and must be within 20% variation of the reference value. If the variation is ≥20%, then the instrument analyst and standards chemist are notified to take corrective action.

Measurement:

Set up the instrument sequence for automated runs of standards, spiked method blanks, the method blank and the sample extracts. Set up the data acquisition system to capture and quantitate the target compounds for CBs, PCBs, OCs and PAHs, using peak area calculations, an external standard and multi-point calibration. Load the autos-ampler tray with the vialed samples and standards as set up in the sequence and start the run.

Identification of Polynuclear Aromatic Hydrocarbons:

The chromatograms, spectra and reports are checked for symmetrical peak shape and for well-resolved and properly-integrated peaks. The sensitivity throughout the run, as indicated by the standard responses of the quantitation ions of the target compounds in the calibration standards, should not vary by more than 30%. If greater variation occurs, the instrumental analysis should be repeated, either from the beginning or from the point where the inconsistency occurred, after the problem has been corrected. Document the non-conformance and the corrective action taken on the analysis non-conformance sheet.

A compound is reported as positively identified if the retention time of the quantitation ion is within 0.05 min of that of the calibration standard. The ratio of the abundances of the confirmation ions also must compare within 30% of the calibration standard.

Initially, and throughout the run, the instrument analyst performs a visual check of the standard chromatograms for peak separation, resolution and repeatability on the lowest standard and the continuous calibration standard. If any abnormalities are viewed, corrective action is taken, such as removal of outliers, instrument maintenance and possible the re-running of the total sample sequence.

To establish linearity of the 6 point, the six standard chromatograms are processed or quantities by the assigned analyst in the TARGET analysis software to establish a relative response factor (RRF).

Each compound is then checked for its initial calibration R square value. If the

value of 0.985 or higher is achieved, then the calibration curve is linear. If the R square value of less than 0.985 is assigned then the instrument analyst and standards chemist are notified to take corrective action (as above).

Table 03-3751-5: Analytical Tray Pattern for PAH Analysis

POSITION #	SAMPLE ID/ SAMPLE TYPE
1	Calibration Blank† (CB1)
2	Performance Check (PC1)
3	Calibration Standard (S1)
4	Calibration Standard (S2)
5	Calibration Standard (S3)
6	Calibration Standard (S4)
7	Calibration Standard (S5)
8	Calibration Standard (S6)
9	External Standard
10	Method Blank (MB1)
11	Spiked method blank (RF1)
12	Unknown
13	Unknown
14	Unknown
15	Continuing Calibration (CC1)
16	Spiked method blank (RD1)
17	Unknown
18	Unknown
19	Unknown

20	Unknown
21	Continuing Calibration (CC2)
22	Unknown
23	Unknown
24	Unknown
25	Unknown
26	Unknown
27	Continuing Calibration (CC3)
28	Performance Check (PC2)

† Instrument blank