Isomers of Dechlorane Plus® in Lake Winnipeg and Lake Ontario food webs

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Introduction

For over 40 years, Dechlorane Plus® (DP, $C_{18}H_{12}Cl_{12}$) has been used as an additive flame retardant in electrical wires and cables, computer connectors, and plastic roofing materials. Commercial grade DP is synthesized by the Diels-Alder addition of 2 moles fully chlorinated cyclopentadiene to 1 mole of cyclooctadiene. The main products of the reaction are two stereoisomers, *syn* and *anti*-, and small amounts of byproducts arising from impurities within the cyclooctadiene starting material.

Despite its commercial longevity, DP has only recently been detected in the environment. Hoh *et al*. (2006) were the first to report on the isomers in air, fish, and sediment samples from the Great Lakes region. The chemical structure of the DP-isomers would suggest that their physical chemical properties should be similar to that of the higher brominated flame retardants (BFRs) like decabromodiphenylether (BDE-209); based on what is known about the environmental behaviour of BDE-209, the detection of the DP-isomers in the environment comes as no surprise. What is surprising is that the compound has remained unreported for so long.

The recent detection of the DP-isomers in Great Lakes biota spurred our efforts to examine the bioaccumulation potential and trophic transfer of the isomers in food webs from Lake Winnipeg and Lake Ontario (Canada). The current study builds on our earlier work reporting on select BFRs in both food webs (Tomy *et al*. 2004, Law *et al.* 2006). The *syn*- and *anti*-isomers of DP that are predominant in the technical mixture are now commercially available and were used in this study to produce more accurate environmental occurrence data and to assess whether there were differences in the accumulation potential between them.

Materials and Methods

Sample Information. Detailed sample information can be found in Law *et al*. (2006) and Tomy *et al*. (2004). Samples for both studies were collected between 2000 and 2003.

Gas chromatography/mass spectrometric analysis. Lake Winnipeg and Ontario extracts were analyzed at FWI and EC, respectively. Both laboratories employed identical methodologies: analyses were performed on Agilent 5973 GC-mass selective detectors (Mississauga, ON, Canada) fitted with a 10 m DB-5 capillary column (0.25 µm film thickness x 0.25 mm i.d; J&W Scientific, Folsom, CA, USA). Splitless injections of 2 µL were made onto an injector set isothermally at 280ºC. The initial oven temperature was set at 90ºC with no hold time, ramped at 20ºC/min to 310ºC, and held for 5 min. The MS analysis was performed in the electron capture negative ion mode using methane as the buffer gas. Source and quadrupole temperatures were both set to 150ºC. The dominant peak in the molecular ion cluster of the two 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. Extraction efficiencies of the BDE congeners 71, 126, 197 and 207 were measured using the $[Br]^-$ ions (*m/z* 79 and 81) while that of the CDE-99 congener was done using the $[Cl]^-$ ions (*m/z* 35 and 37).

Method detection limits (MDLs) were estimated from the procedural blanks which consisted of Ottawa sand. Trace amounts of both isomers (*syn*: 0.6 pg, *anti*: 2.6 pg) were present in the blanks. Using an average sample mass of 15 g, MDLs of 0.3 pg/g and 1.5 pg/g for *syn*- and *anti*-isomers were determined. The linear dynamic range of the instruments 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.

Results and Discussion.

Lake Winnipeg. Concentrations of DP isomers in the Lake Winnipeg food web are given in Table 1. The *syn*-isomer was consistently detected in all samples while the *anti*-isomer was less frequently detected (~ 45% of samples). In biota, concentrations of the *syn*-isomer was greatest in burbot (range: 67 – 773 pg/g, lw, median: 415 pg/g), zooplankton (range: 469 – 647 pg/g lw, median: 542 pg/g) and mussels (range: 76 – 823 pg/g lw, median: 504 pg/g) while the *anti*-isomer was greatest in walleye (range: 608 – 883 pg/g lw, median: 714 pg/g) and goldeye (range: 594 – 932 pg/g lw, median: 763 pg/g). Concentrations of both isomers were similar in whitefish but varied considerably in walleye and goldeye; respective concentrations of the *anti*-isomer were 25 and 14 times greater than that of the *syn*-isomer in these species. Sediments contained small pg/g (dry weight) concentrations (*syn*: 11.7 pg/g, *anti*: 18.3 pg/g dry wt) of both isomers.

Lake Ontario. Concentrations of the isomers in the Lake Ontario food web are given in Table 2. Both isomers were detected in all samples with *anti*-DP consistently greater than that of the *syn* isomer. Similar concentrations of both isomers were observed in trout (median: *syn*=44.3, *anti*=47.2 pg/g lw), smelt (median: *syn*=5.5, *anti*=6.5 pg/g lw), alewife (median: *syn*=48.3, *anti*=54.2 pg/g lw) and sculpin (median: *syn*=626, *anti*=777 pg/g lw). Concentrations of the *anti* isomer were approximately 2.5 times greater than the *syn*-isomer in *Diporeia*, 3 times greater in *Mysis* and 2 times greater in plankton. In sediments, the *anti*-isomer comprised ~85% of the total DP concentrations (mean ΣDP = 206 ng/g dry wt), which were orders of magnitude greater than those from Lake Winnipeg.

Biomagnification. Trophic magnification factors (TMFs) was used as a descriptor for biomagnification and is derived from the slope of the regression between an organism's lipid-normalized contaminant concentrations and trophic position, as determined by stable isotopes of nitrogen. Regressions of the TL against concentrations was statistically significant for both isomers only in the Lake Winnipeg food web. For Lake Ontario, plots were constructed using wet weight (not presented) and lipid weight concentrations but neither plot yielded significant relationships for either isomer. Regression analysis for the Lake Winnipeg food web suggested that with a lipid weight TMF value of 2.5 (r^2=0.12, p=0.04), the *anti*-isomer was biomagnifying throughout the entire food web while the *syn*-isomer with a lipid weight TMF value of 0.45 (r^2=0.17, p=0.01) was being diluted with increasing TL.

Table 1. Concentrations [arithmetic mean ± 1 x standard error (SE)] of *syn*- and *anti*-DP isomers in fish (pg/g, lipid adjusted and blank corrected) and sediment (pg/g, dry wt) from the south basin of Lake Winnipeg.

Sample	$\delta^{15}N$ (mean ± 1SE)	TL (mean ± 1SE)	Mean % lipid	DP isomers		
				syn-	*Anti*-	f_{anti}[1]
Walleye	17.8 ± 0.3	2.39 ± 0.07	1.15	29 ± 21	730 ± 120	0.961
Burbot	16.6 ± 1.6	2.09 ± 0.37	0.33	450 ± 120	<mdl	0.003
Emerald shiner	16.0 ± 0.1	1.92 ± 0.03	3.18	35 ± 16	<mdl	0.041
Whitefish	12.0 ± 0.2	0.87 ± 0.05	8.78	30 ± 11	24 ± 16	0.445
White sucker	15.2 ± 0.6	1.72 ± 0.16	2.27	37 ± 1	<mdl	0.039
Goldeye	16.1 ± 0.2	1.95 ± 0.06	2.34	56 ± 3	760 ± 170	0.932
Zooplankton	9.7 ± 1.1	1	13.67	550 ± 40	<mdl	0.003
Mussels	9.5 ± 0.6	0.21 ± 0.15	0.32	430 ± 140	<mdl	0.004
Sediment				11.7 ± 1.1	18.3 ± 2.1	0.610

Table 2. Concentrations [arithmetic mean ± 1 x standard error (SE)] of *syn* and *anti*-DP isomers in fish (pg/g, lipid adjusted and blank corrected) and sediment (ng/g, dry wt) from Lake Ontario. For comparison, concentrations (pg/g, lw) of other contaminants are also given.

Sample	$\Delta^{15}N$[1] (mean ± 1SE)	TL (mean ± 1SE)	Mean % lipid	DP isomers		
				syn	*anti*	f_{anti}
Trout	17.6 ± 0.4	3.80 ± 0.11	13.4	100 ± 60	105 ± 64	0.512
Smelt	15.3 ± 0.4	3.21 ± 0.10	1.32	7 ± 2	8 ± 2	0.533
Alewife	11.7 ± 0.3	2.18 ± 0.07	3.51	57 ± 13	64 ± 16	0.529
Sculpin	15.8 ± 0.2	3.32 ± 0.04	2.20	653 ± 192	901 ± 308	0.580
Diporeia	10.3 ± 0.1	1.86 ± 0.02	1.32	1307 ± 554	3108 ± 898	0.704
Mysis	11.3 ± 1.1	2.46	3.83	117	383	0.766
Plankton	7.0 ± 2.1	1	0.2	719	1332	0.650
Sediment				29.6 ± 11.8	176.4 ± 50.5	0.860

Isomeric profiles. Tables 1 and 2 clearly show that there are differences in the relative concentrations of the isomers in environmental samples from both lakes. This can be expressed numerically as the mean fractional abundance (f_{anti}) of the *anti*-isomer which is the mean concentration of the *anti*-isomer divided by the sum of the mean concentrations of *syn*- and *anti*-isomers. There are three industrial formulations of the technical mixture which differ only in the particle size of the final product. This suggests that the isomeric compositions of the technical mixtures are likely to be similar, although the variation between batches is unknown. The mean f_{anti} of the technical mixture obtained in this study was calculated to be 0.650.

The mean f_{anti} values in sediments from both lakes are remarkably dissimilar. While the isomeric profile in Lake Winnipeg sediments (mean f_{anti} = 0.610) closely resembles that of the technical mixture,

sediments from the central basin of Lake Ontario were clearly depleted in the *syn*-isomer (mean f_{anti} = 0.860). These observations are in contrast to those of Hoh et al. (2006) where air and sediment samples furthest from a known production source area exhibited smaller f_{anti} than sites closer to the Niagara source region which had values approaching that of the technical mixture (*1*). Although the isomeric composition of the different formulations of technical DP should be the same, it cannot be assumed that both lakes are receiving DP inputs with the same isomeric composition. The input of environmental 'weathered' or 'aged' DP would confound any interpretation of interlake variability in f_{anti} values in sediments. Another consideration is that if heat is required to infuse the technical DP-mixture into the end-product, changes in the isomeric ratios of the technical mixture may occur. A similar chemical change occurs during the thermal infusion of technical HBCD into its intended product. As well, DP sources may not be limited to manufacturing location(s) of the raw product, but may also extend to areas where DP is applied as a flame retardant as part of a commercial formulation (*i.e.*, cable coatings industry).

There are also clear interlake differences in the accumulation pattern of the isomers in lower TL organisms. In plankton, for example, mean f_{anti} values in Lake Ontario (0.65) is very similar to that of the technical mixture, while the syn-isomer is dominant in plankton from Lake Winnipeg, although the *syn*-isomer is enriched in plankton relative to sediments in both Lakes. It is not clear why the same species would show such a different accumulation pattern. If accumulation of DP-isomers by zooplankton is solely by diffusion from water, then differences in concentration profiles of the isomers in water between the lakes might explain these differences. Clearly, a better understanding of limnology of the two lakes might be needed to tease out these differences.

Another noteworthy difference in mean f_{anti} values are for *Diporeia* and sediment from Lake Ontario. *Diporeia* are benthic organisms and accumulation of contaminants from sediments is thought to be their primary exposure route. The mean f_{anti} value of 0.704 for *Diporeia* from Lake Ontario compared to the 0.860 for sediment indicates that stereoselective accumulation may be taking place. Biotransformation is less likely as *Diporeia* are thought to have low metabolic capabilities.

In biota, there were no clear trends between mean f_{anti} values and TL. However, the range of f_{anti} values in biota with increasing trophic level from the lakes (Lake Winnipeg: 0.962 to 0.003; and Lake Ontario: 0.766 to 0.512) strongly suggests that the overall extent of depletion and resulting enrichment of the *syn*- and *anti*-isomers, respectively, is much greater in the Lake Winnipeg ecosystem. These observations lend further support to the argument that interspecies differences in bioaccumulation and biotransformation are likely driving factors in the distribution of the isomers in the environment.

References

Hoh E, Zhu L, Hites RA. 2006 Environ Sci Technol 40, 1184-1189.

Law K, Halldorson T, Danell RW, Stern GA, Gerwutz S, Alaee M, Marvin C, Whittle DM, Tomy GT. 2006. Environ Toxicol Chem 25, 2177-2186.

Tomy GT, Budakowski WR, Halldorson T, Whittle DM, Keir MJ, MacInnis G, Alaee M. 2004. Environ Sci Technol 38, 2298-2303