A COMPARISON OF TEQ CONTRIBUTIONS FROM CHLORINATED DIOXINS, FURANS AND DIOXIN-LIKE PCBS IN GREAT LAKES FISH

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Introduction

From the late 1970's to the present, a great deal of emphasis has been placed on the analysis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)[1] This particular group of very toxic compounds are persistent in the environment and are unwanted by-products from chemical and combustion processes[2]. There are 210 PCDD/Fs, but only 17 (2,3,7,8-substituted) have been deemed toxic. The toxicity of the sample is typically reported in equivalents of 2,3,7,8-TCDD (TEQ), the most toxic congener [3]. Another group of compounds with dioxin-like toxicity are polychlorinated biphenyls (PCBs) [3,4]. Recently, WHO (World Health Organization) has identified 12 of the 209 possible PCBs as being similar in toxicity to the PCDD/Fs. The list of 12 DLPCBs includes 4 coplanar (BZ#: 77, 81, 126, 169) and 8 mono-ortho congeners (BZ#:105, 114, 118, 123, 156, 157, 167 and 189) [5]. These 12 PCBs congeners are similar in structure and orientation to the 2,3,7,8-TCDD and therefore are referred to as Dioxin-like PCBs (DLPCBs). Both groups have a planar or somewhat planar orientation similar to that of 2,3,7,8-TCDD, which allows them to bind readily to the Ah-receptor and bioaccumulate in adipose tissue [3,6]. The following is an investigation into patterns and relative abundances based on TEQs (Toxic Equivalent Quantity) between PCDD/Fs and DLPCBs in fish found in the Ontario Great Lakes region. TEQ values are the sum of the TEF (Toxic Equivalent Factor), the relative toxicity of the specific congener normalized to 2,3,7,8-TCDD, multiplied by the concentration [3,6]. Zero was used for non detected values in the TEQ calculation. The WHO convention for TEFs was used in calculating TEQ values [5].

Experimental

Standards

Both DLPCBs and PCDD/Fs are quantified by isotope dilution. Standards used in the fish analysis were purchased from the following manufactures; DLPCB standards were purchased from Wellington Laboratories Inc. (Guelph, Ont) and PCDD/F standards were purchased from Wellington Laboratories Inc. (Guelph, Ont) and Cambridge Isotope Laboratories (Cambridge, Massachusetts).

Sample Preparation

Approximately 5 g of sample were used for analyzing biota samples. The samples were spiked with 15 $^{13}C_{12}$ - Labelled PCDD/Fs and 12 $^{13}C_{12}$ Labelled -DLPCB surrogates prior to extraction. Tissue samples were acid digested overnight in concentrated HCl and extracted the next day with hexane via liquid-liquid extraction.

Cleanup

The 4 coplanar DLPCBs were isolated along with the dioxins and furans using a 3 stage column cleanup (silica/alumina/carbon). This cleanup procedure was designed to force the polychlorinated diphenyl ethers into the mono-ortho PCB fraction, away from the PCDD/F fraction where they are known to cause interference problems. Details of methodology are listed in MOE method E3418[7].

Instrumentation

All analyses were performed on a VG Autospec GC-HRMS. An HP6890 *Plus* gas chromatograph was interfaced to the mass spectrometer. Chromatographic separations were carried out on a DB-5 column ; 60m 0.25mm X 0.25μm (J&W Scientific, USA). The GC-HRMS system was tuned to 10,000+ RP (10% valley definition). The coplanar DLPCBs were analyzed with the PCDD/PCDF fraction. The mono-ortho DLPCBs were analyzed as a separate fraction, with a 4 function MS experiment.

Results and Discussion

Table I, reports the average TEQ values in parts-per-trillion (ppt -pg/gram of fish sample). The number of fish analyzed (#) is in brackets following the species. Results for samples that had no congeners detected are reported as zero. Fish sample weights are based on the average weight (samples for which the weight was not available are noted as N.A). All fish samples were taken between 1996-1998.

Dioxin-like biphenyls (DLPCBs) were found to be present in all samples analyzed. This was not observed for PCDD/Fs. Samples in which PCDD/Fs were not detected, the average TEQ values for the corresponding DLPCB portion was typically low. In the northern most Great Lakes, Superior and Huron, the TEQ values for DLPCBs and PCDD/F are relatively low in comparison to the Lake Ontario fish samples. Also, there are isolated areas of elevated levels (e.g. TEQ = 83 ppt for DLPCBs and 23 ppt for PCDD/Fs) around the Algoma District and in Grand Bend and Bruce Districts, which have relatively higher TEQs for DLPCBs in comparison to the PCDD/Fs. The higher DLPCBs to PCDD/Fs ratio in Lake Trout and Carp from those areas indicate a potential point source of contamination for PCBs.

In certain heavily industrialized areas such as the case in the Niagara River and Hamilton Harbour locations , the TEQ ratio of DLPCB to PCDD/F is about 4 in the Niagara River and 9 in the Hamilton area. Moving eastward along Lake Ontario, the TEQ ratios of DLPCB to PCDD/Fs are on average around 4. The average ratio for all lakes is 6.5 (when the large value of 86 from the Welland River is omitted). Most of the lakes have similar average values (Superior -4.4, Niagara River – 2.9, Lake Ontario – 5.3 (Welland data removed)), except for Lake Huron with an average ratio of 11.4 and the Northern areas (Mattagami and Cochrane).

TEQ variations within locations such as the Niagara River area were also noted and can be attributed due to species, age, size, feeding habits, sex and lipid content. In the case of Chinook, Channel Catfish, Rainbow Trout, Lake Trout and Brown Trout, they are more likely to have higher levels simply based on the fact that they have a higher lipid levels and their diet consists of smaller fish (top feeding). Other species such as Perch, Whitefish, and Carp diets consist of plankton and insects [8]. Piscivorus fish showed elevated levels of both DLPCBs and PCDD/Fs due to bioaccumulation.

There were a number of general trends among the different fish species based on the patterns of the planar biphenyls and mono-ortho PCB 189 concentrations. Amongst most of the fish species, the relative concentrations among the co-planar biphenyls were PCB 77 > PCB 126 > PCB169. The mono-ortho PCB 189 was found to be higher in concentration relative to PCB 77 in Lake Trout found in the Lake Superior area, however, it was the reverse in Lake Huron and Lake Ontario. Also, in locations where there were higher PCDD/F concentrations (e.g. Eastern Lake Ontario), PCB 77 was found to be greater relative to PCB 189 in Chinook, Carp and Brown Trout. The Chinook samples from Lake Huron were reversed, with PCB 189 greater than PCB77.

When comparing the PCDD/F TEQ values at locations with the same fish species against those previously analysed [9], there is a general decrease in PCDD/F levels in the Ontario region lakes. With respect to DLPCBs, there is no previous record to compare or determine relative trends. Very little data for DLPCBs have been published to date. Determination of DLPCBs in other matrices such as soil/sediment, vegetation, and water will greatly aid in identification of point and long range transboundary sources contributing to the different congener pattern distributions that are observed in the different fish species.

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Table I **DLPCB and PCDD/F Average TEQs**

Main Body of Water	Location	Species	Avg. PCB TEQ	Avg. PCDD/ F TEQ	PCB (TEQ) / PCDD/F (TEQ)	Average Weight (g)
Lake Superior	Black Bay	Lake Trout(5)	9.4	0.68	14	1984
	Jackfish Bay	Lake Trout (5)	13	5.3	2.5	2045
	Peninsula Harbour	Lake Trout (5)	9.5	2.8	3.3	1370
	Algoma Area	Lake Trout (5)	83	23	3.7	2481
	Algoma-Agawa Bay	L. Whitefish (5)	4.5	5.4	0.83	1676
	Goulais Bay	L. Whitefish (5)	4.1	1.8	2.3	1318
Lake Huron	Manitoulin Island	L. Whitefish(5)	1.4	0	>1.4	791
	Nottawasaga River	Chinook (5)	14	0.94	15	5194
	Nottawasaga River	Rainbow Trout (5)	6.9	0	>6.9	3006
	Tobermory	L. Trout (5)	21	3.5	5.9	2367
	Oliphant/Fishing Is.	L. Trout (5)	12	0.75	17	1481
	Oliphant/Fishing Is.	L.Whitefish (5)	4.4	2.7	1.7	1015
	Bruce Cty	Carp (5)	31	2.1	14	4073
	Grand Bend	L. Trout (5)	22	0.76	29	2360
Lake Erie	Western Basin	Ch. Catfish (5)	55	8.1	6.8	1441
Niagara River	Niagara River Bar	Lake Trout (5)	79	22	3.5	2950
	Niagara River Bar	Chinook (5)	52	12	4.4	6860
	Niagara River Bar	Brown Trout (5)	21	4.6	4.5	3050
	Niagara River Bar	White Perch (5)	6.2	3.2	1.9	241
	Niagara River	Rainbow Trout (5)	22	4.8	4.6	3464
	Niagara River	White Bass (4)	1.6	0	>1.6	208
Lake Ontario	Welland River	Carp (5)	11	0.13	86	5339
	Hamilton Harbour	Carp (5)	25	1.9	13	4088
	Hamilton Harbour	Ch. Catfish (5)	58	6.7	8.7	1064
	Bronte Creek	Brown Trout (5)	56	8.3	6.7	2225
	Port Credit	Lake Trout (4)	72	19	3.8	3047
	Credit River	Brown Trout (5)	41	10	4.1	2650
	Credit River	Chinook (5)	39	8.7	4.5	8590
	Don River	White Sucker (5)	16	4.4	3.6	940
	Whitby Harbour	Carp (5)	27	40	0.66	7526
	Whitby /Pickering	Chinook (5)	29	6.8	4.3	2900
	Cobourg	L. Trout (5)	67	26	2.6	3242
	Trent River	Chinook (5)	182	59	3.1	1519
	Trent River-4	L. Whitefish (5)	52	5.8	9.0	6640
	Upper Bay of Quinte	Whitefish(5)	8.7	7.0	1.2	708
	L. Bay of Quinte	L.Trout (5)	110	29	3.8	3695
	Cataraqui River	Carp (5)	57	4.7	12	N.A.
Northern Areas	Mattagami River	White Sucker (5)	21	0	>21	1560
	Cochrane	White Sucker (5)	21	0	>21	1560