CHARACTERISTIC LEVELS OF CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS IN FISH FROM ONTARIO GREAT LAKES

E.J. Reiner, K.A. MacPherson, T.M. Kolic, A. Hayton and R.E. Clement
Ontario Ministry of Environment and Energy
Laboratory Services Branch
Etobicoke, Ontario, Canada, M9P 3V6

1. INTRODUCTION

The levels of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the Great Lakes became a major concern in the early 1970's with reports of herring gull chick edema disease[1]. PCDDs and PCDFs are widely distributed throughout the Great Lakes ecosystem in sediments[2] and fish[3-8]. Fish data show a specific congener preference: typically the 2,3,7,8- substituted PCDDs and PCDFs are the dominant congeners. Sources of PCDDs and PCDFs in the Great Lakes fish have been ascribed to general atmospheric deposition[1] as well as more specific sources such as pulp and paper mills, polychlorinated biphenyls (PCBs)[4] or chemical contamination[9]. Bioaccumulation rates for PCDDs are generally less than for PCBs with exception of 2,3,7,8-TCDD which has a relatively high bioaccumulation rate[10,11]. For most species, the levels of 2,3,7,8- substituted PCDD/Fs are the highest for the tetra dioxins and furans and typically decrease with increasing chlorination. Hepta and octa congeners are usually not detected unless there are specific sources such as pentachlorophenol[12,13]. Previous studies have focused mainly on lake trout and walleye samples from the American side of the Great Lakes[4,5]. This study reports data from a wider variety of species taken on the Canadian side.

2. EXPERIMENTAL

Typical samples were taken as skinless, boneless dorsal fillets. Some samples from the Credit River were processed with skin on. Data in Table 1 are averages from 4 to 10 (typically 5) samples. There was some variation in fish size (weight) for each location, therefore average sizes are listed. Fish were sampled for the Ontario Sports Fish Program. This program monitors sport fish in the Ontario fresh water lakes and issues consumption advisories through its biannual guide[14]. In light of this program, the fish sampled in this study are typically larger fish from suspect areas in order to obtain positive results and therefore be able to set consumption advisories.

The sample preparation procedure has been described in detail elsewhere[15]. Briefly,

samples were acid digested. Samples were extracted with hexane and the extract was cleaned using open column silica chromatography and a semi-automated high performance liquid chromatography (HPLC) cleanup with alumina and carbon columns.

Samples were analyzed by gas chromatography-tandem mass spectrometry on a Finnigan MAT TSQ 70 triple quadrupole mass spectrometer linked to a Varian 3400 GC equipped with splitless injection[16] or by gas chromatography high resolution mass spectrometry on a Fisons/VG AUTOSPEC mass spectrometer operated at 10,000 (10% valley) resolution. The GC was a Hewlett-Packard 5890 II equipped with a splitless injection system. Both Instruments used a 60 metre fused silica, 0.25 mm i.d., 0.25 micron film thickness DB-5 stationary phase, capillary column.

The precision of the method is <10% (% relative standard deviation) and the accuracy is ±10% for all 2,3,7,8- substituted congeners as determined from 8 replicate chinook salmon samples.

3. RESULTS AND DISCUSSION

The results for 2,3,7,8-TCDD, 2,3,7,8-TCDF, total TEQ (2,3,7,8-TCDD equivalents) and the TCDF/TCDD ratio are average values of the number shown in brackets next to the species type. The TCDF/TCDD ratios for Lake Ontario are significantly lower than those of the other Great Lakes. This pattern is similar to that observed by DeVault et al[4] and Dunn et al[5] for fish taken on the American side of Lake Ontario. Dunn et al[5] reported that levels in Lake Ontario were very homogeneous. Cook et al[7] reported an average value of 78 PPT (pg/g) for lake trout collected in Lake Ontario in 1978. DeVault (1984) reported that data from 13 species of fish from Lake Ontario with 2,3,7,8-TCDD levels typically below 20 ppt[8]. Also, 2,3,7,8-TCDD levels of up to 162 ppt in brown trout (1978) and up to 72 ppt in lake trout (1980) were detected[8]. Coho salmon taken at the Credit River contained 19 to 20 ppt of 2,3,7,8-TCDD[8]. The data in this report are from fish collected between 1989 and 1994. Results are in excellent agreement with those listed above. Except for lake trout, 2,3,7,8-TCDD levels reported in Table: 1 are typically below 20 ppt. Coho salmon sampled at the Credit River had a 2,3,7,8-TCDD result of 13 ppt. Average values for 2,3,7,8-TCDD were 19 ppt in lake trout and 9.4 ppt in brown trout. Although there is an insufficient amount data and a lack of compatibility in size of fish sampled in order to carry out a statistical comparisons with previous data, results suggest that PCDD/F levels are still decreasing in Lake Ontario, however, at a slower rate than during the previous decade. 2,3,7,8-TEQ and particulary 2,3,7,8-TCDD values are considerably higher in Lake Ontario than in the other Great Lakes. Also, for some species there is a net increase in the TCDF/TCDD ratio when moving from West to East in Lake Ontario (data has been listed from West to East in Table: 1, Part A). These data are consistent with a source (or previous source) of 2,3,7,8-TCDD in the western end of Lake Ontario. 2,4,5-trichlorophenol and other precursors of PCDDs and PCDFs are present at considerable levels in waste disposal sites on the Niagara River[9] and may be one of the specific sources of 2,3,7,8-TCDD for Lake Ontario.

In the other three lakes (Table 1, Part B), the TCDF/TCDD ratios are significantly higher than in Lake Ontario. There is a limited number of samples for Lake Erie. The Western side which receives influx from the Detroit River, an industrialized area, has detectable levels of PCDD/F, while the Eastern side has low or non detectable levels. In Lake Huron, the highest

levels were detected at Grand Bend, just north of Sarnia/Port Huron where a number of chemical manufacturers are located. The remaining sites sampled in Lake Huron are away from industrial areas and have results with similar PCDD/F levels and except for the Fishing Islands catfish sample, similar TDCF/TCDD ratios. PCDDs and PCDFs detected in fish North of Grand Bend may arise from atmospheric deposition, however, PCBs as a source of PCDD and PCDFs can not be ruled out[4].

Data from Lake Superior gives rise to the largest variation and largest TCDF/TCDD ratios. There are several pulp and paper mills located on the North shore of Lake Superior. 2,3,7,8-TCDF as well as corresponding lower levels of 2,3,7,8-TCDD have historically been detected in pulp and paper wastes[8] and may be a source of the elevated 2,3,7,8-TCDF levels and TCDF/TCDD ratios in Lake Superior.

From the limited data, there appears to be a decrease in PCDD/F levels in the Ontario Great Lakes. As for Lake Ontario, data from Grand Bend and Cape Rich in Lake Huron and from Peninsula Harbour in Lake Superior indicate PCDD/PCDF levels remained the same or declined over the past 2 to 5 years. The differing values for TCDF/TCDD ratios among the different species indicate that there are significantly different rates of bioaccumulation of the different congeners between species. Patterns seen in most areas were strongly indicative of industrial influence. Atmospheric deposition typically results in congener patterns in soils and sediments favouring the more highly chlorinated congeners which are usually not detected in fish samples. The absence or low levels of hepta and octa congeners present in fish data indicate that they are not adsorbed or bioaccumulated readily and that PCDD/Fs from atmospheric deposition may only be a minor component of PCDD/F levels in fish, especially for carnivorous species such as trout, salmon and pike.

4. REFERENCES

1)Norstrom,R.J.; Clark,T.P. and Weseloh,D.W. (1985): Great Lakes Monitoring using Herring Gulls; In Hazardous Contaminants in Ontario: Human Environmental Effects. 86-98

2)Czuczwa,J.M. and Hites,R.A. (1986): Airbourne Dioxins and Dibenzofurans: Sources and Fates. Environ. Sci. Technol. 20, 195-200

3)Stalling,D.L.; Smith.L.M.;Petty,J.D.; Hogan,J.W.; Johnson,J.L.; Rappe,C. and Buser,H.R.: Residues of Polychlorinated Dibenzo-p-dioxins and Dibenzofuran in Laurentian Great Lakes (1983): Tucker,R.E., Young,A.L. and Grey,A.P. eds: Human and Environmental Risks of Chlorinated Dioxins and Related Compounds. 221-240

4)DeVault,D; Dunn,W.; Bergqvist,P.; Wiberg, K. and Rappe,C (1989): Polychlorinated Dibenzofurans and Polychlorinated Dibenzo-p-dioxins in Great Lakes Fish: A Baseline Comparison:: Environmental Toxicology and Chemistry, 8, 1013-1022

5)Dunn,W.J.; Stalling,D.L.; Schwartz,T.R.; DeVault,D.; Wold,S.; Bergqvist,K.; Wiberg,K. and Rappe,C. (1991): A Chemometric Study of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in Great Lakes Fish: In Environmental Carcinogens, Methods of Analysis and Exposure Measurement, Volume 11 Polychlorinated Dioxins and Dibenzofurans, IRAC Scientific Publications No. 108.

6)Rappe,C.; Bergqvist,P.A.; Hanson,M.; Kjeller,L.O.; Lindstrom,G.; Marklund,S. and Nygren,M. (1984): Chemistry and Analysis of Polychlorinated Dioxins and Dibenzofurans in Biological Samples. Biological Mechanisms of Dioxin Action. Banbury Report 18: 17-25

7)Cook,P.M.; Erickson,R.J.; Spehar,R.L.; Bradbury,S.P. and Ankley,G.T. (1993): U.S. EPA, Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Risks to Aquatic Life and Associated Wildlife.
8)Canadian Council of Ministers of the Environment (CCME) (1995): Canadian Environmental Quality Guidelines for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. Draft Copy, January
9)Silverman, G.B. (1989): Environmental Reporter: Love Canal: A Retrospective: 20,no.20, 835-850
10)Mehrle,P.M.; Buckler,D.R.; Little,E.E.; Smith,L.M.; Petty,J.D.; Peterman,P.H.; Stalling,D.L.; Graeve,G.M.; Coyle,J.J. and Adams,W.J. (1988): Toxicity and Bioconcentration of 2,3,7,8-tetrachlorodibenzofuran in Rainbow Trout, Environ. Toxicol. Chem. 7, 47-62
11)Branson,D.R.; Takahashi,I.T.; Parker,W.M. and Blau,G.E. (1985): Bioconcentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8,-tetrachlorodibenzofuran in Rainbow Trout: Environ. Toxicol. Chem. 4, 779-788
12)Kuehl,D.W.; Cook,P.M. and Batterman,A.R. (1987): Uptake and Depuration Studies of PCDD's and PCDF's in Freshwater Fish: Chemosphere 15, 2023-2026
13)Kuehl,D.W.; Cook,P.M.; Batterman,A.R. and Butterworth,B.C. (1987): Isomer Dependent Bioavailability of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans From Municipal Incinerator Flyash to Carp: Chemosphere 16, 657-666
14)Guide to Eating Ontario Sport Fish (1995): Ontario Ministry of Environment and Energy
15)Thompson,T.S.; Kolic,T.M. and MacPherson,K.A. (1991): Dual Column HPLC Cleanup Procedure for the Determination of PCDD's and PCDF's in Fish Tissue: Journal of Chromatography, 49-58
16)Reiner,E.J.; Schellenberg,D.H. and Taguchi,V.Y. (1991): Environmental Applications for the Analysis of Chlorinated Dibenzo-p-dioxins and Dibenzofurans Using Mass Spectrometry/Mass Spectrometry: Environmental Science and Technology: 25, 110-117

Table 1: 2,3,7,8-TCDF/2,3,7,8-TCDD Concentrations in Ontario Great Lakes

LAKE	AREA	SAMPLE DATE	SPECIES	TEQ	2378-TCDD	2378-TCDF	TCDF/TCDD	WEIGHT (AVE)
ONTARIO	Niagara River	02/91	Rainbow Tr(4)	19	10	11	0.92	3900
	Niagara Bar	08/94	Carp(5)	5.0	3.9	1.7	0.44	2700
	Niagara Bar	08/94	Brown Tr(5)	6.2	5.0	5.6	1.1	2100
	Jordan Harbour	02/90	Lake Tr(5)	57	34	23	0.69	3900
	Port Dalhousie	09/93	Rainbow Tr(5)	7.2	5.4	3.7	0.69	3100
	Grimsby	09/94	Lake Tr(5)	10	6.4	6.5	1.0	1300
	Hamilton Harbr	10/94	Brown Tr(5)	6.8	6.4	5.9	0.92	2400
	Hamilton Harbr	09/94	Rainbow Tr(5)	13	9.0	8.0	0.89	2500
	Hamilton Harbr	09/94	Chinook Sal(5)	7.2	4.8	4.3	0.89	5000
	Bronte Creek	11/91	Chinook Sal(5)	25	18	6.0	0.33	11000
	Bronte Creek	11/91	Rainbow Tr.(5)	11	8.0	4.0	0.50	2600
	Credit River	10/91	Chinook Sal(10)	21	16	5.8	0.36	10300
	Credit River	10/91	Coho Sal(10)	18	13	11	0.90	5300
	Credit River	10/91	Brown Tr(7)	15	11	12	1.1	3300
	Credit River	10/91	Rainbow Tr(8)	12	9.1	6.6	0.73	3500
	Humber Bay (TO)	10/92	Brown Tr(5)	18	12	12	1.0	3900
	Humber Bay (TO)	10/93	Brown Tr(5)	8.6	5.8	6.7	1.1	3500
	Toronto Area	09/94	Chinook Sal(5)	7.2	5.8	3.1	0.53	3800
	Toronto Area	10/94	Lake Tr(5)	33	21	18	0.89	2800
	Ashbridges Bay(TO)	10/93	Brown Tr(5)	10	6.9	6.3	0.91	2800
	Bluffers Pk (TO)	10/90	Brown Tr(5)	20	15	12	0.80	2700
	Bluffers Pk (TO)	10/90	Lake Tr(5)	63	37	56	1.5	4100
	Scarboro Bluffs(TO)	10/93	Brown Tr(5)	10	7.4	8.8	1.2	2900
	Pickering	12/94	Brown Tr(5)	10	6.8	10	1.5	3000
	Pickering	09/94	Rainbow Tr(4)	7.0	5.6	5.7*	<0.89	3400
	Whitby	09/93	Chinook Sal(5)	10	6.3	2.6	0.41	4700
	Ganaraska River	10/89	Lake Tr(5)	48	24	45	1.9	4400
	Ganaraska River	04/92	Rainbow Tr(5)	10	6.5	4.1	0.63	2900
	Ganaraska River	07/94	Rainbow Tr(5)	8.7	6.5	6.3	0.97	2600
	Brighton	08/93	Lake Tr(5)	23	14	20	1.5	2300
	Brighton	08/93	Chinook Sal(5)	8.0	6.0	3.3	0.53	6100
	Bay of Quinte	01/94	Whitefish(5)	18	10	28	2.8	1400
	Scotch Bonnet	01/90	Lake Tr(5)	23	16	28	1.7	2500
	Eastern Lake Ont	09/94	Whitefish(5)	42	22	53	2.4	1700
	Eastern Lake Ont	09/94	Lake Tr(5)	11	7.5	10	1.4	2300
	Eastern Lake Ont	01/94	American Eel(5)	13	7.0	<1	<0.15	1200
	Main Duck Isl.	08/91	Lake Tr(5)	21	12	17	1.5	2500

TABLE 1: CONTINUED (PART B)

LAKE	AREA	SAMPLE DATE	SPECIES	TEQ	2378-TCDD	2378-TCDF	TCDF/TCDD	WEIGHT (AVE)
ERIE	Western Basin	10/93	Carp(5)	2.9	<1	4.5	>4	4900
	Western Basin	05/90	Catfish(5)	9.0	2.8	2.0	0.70	1100
	Eastern Basin	10/93	Coho Sal(5)	<1	<1	3.1	>3	2200
	Eastern Basin	09/93	Walleye(5)	<1	<1	<1		2400
HURON	Grand Bend	10/90	Lake Tr(5)	13	4.3	26	6.1	3500
	Grand Bend	02/94	Lake Tr(10)	10	3.0	18	6.0	2900
	Burnt Island	09/92	Lake Tr(5)	6.2	2.1	9.2	4.1	2300
	Bayfield	10/92	Lake Tr(4)	9.1	2.8	20	7.0	2700
	Bayfield	10/92	Whitefish(5)	7.1	1.9	12	6.3	1600
	Cape Rich	08/92	Lake Tr(5)	7.2	2.1	7.2	4.3	3100
	Cape Rich	08/92	Whitefish(5)	<3*	<1	5.4	>5	1400
	Cape Rich	02/94	Lake Tr(5)	5.4	<1	4.6	>4.6	2100
	Grey County	08/93	Lake Tr(5)	<1	<1	4.6	>4.6	1900
	Fishing Islands	09/93	Lake Tr(5)	5.6	1.5*	7.4	>4.9	3300
	Fishing Islands	09/93	Catfish(5)	5.3	2.1	1.7*	<0.89	2100
	Oliphant	08/91	Chinook Sal(5)	4.8	1.8	4.8	2.7	7200
SUPERIOR	Thunder Bay	08/92	Lake Tr(4)	15	2.9	38	13	4600
	Welcome Islands	10/91	Lake Tr(5)	3.0	1.2	9.9	8.3	2400
	Jackfish Bay	07/89	Lake Tr(5)	13	5.7	30	5.3	2500
	Peninsula Harbr	07/89	Lake Tr(5)	15	7.1	34	4.8	1800
	Peninsula Harbr	06/92	Lake Tr(5)	8.2	4.3	24	5.5	3100
	Jarvis Bay	08/92	Whitefish(5)	<2	<1	4.8	>4.8	1900
	Goulais Point	12/92	Lake Tr(5)	<1	<1	3.3	>3	860
	Caribou Island	03/93	Lake Tr(5)	<1	<1	9.2	>9.2	1400

- Concentrations of TCDD, TCDF, and TEQs are in parts-per-trillion (ppt); picograms (10^{-12}grams) per gram of sample
- Weight (average) of fish in grams
- Number of samples for each site is listed in brackets next to species type
* - non-detect values used in average
(TO) - Toronto (Ontario) Area
- Detection limits typically 1 ppt for tetra to hepta congeners and 2 ppt for octa congeners