CBs and PCDDs/Fs Levels in Fish Samples Following an Accidental Release from a Special Waste Treatment Center: 2000 Results

Alex MacKenzie[1], Weiping Chen[1], Michael G. Ikonomou[2], Stephan Gabos[1], Donald Schopflocher[1],

[1] Alberta Health, Canada, P.O. Box 1360, 10025 Jasper Ave. Edmonton, AB, Canada, T5J 2N3
[2] Institute of Ocean Sciences, P.O. Box 6000, 9860 West Saanich Road, Sidney, BC, Canada, V8L 4B2

Introduction

In early 1997, high levels of PCDDs/Fs and CBs were detected in fish tissues in Chrystina Lake in the Swan Hills area, Alberta, Canada, following an accidental release of these contaminants from a Special Waste Treatment Center in October 1996.[1] Chrystina Lake, near the facility, contains a stocked non-native population of eastern brook trout (*Salvelinus fontinalis*) which feed largely on benthic and planktonic invertebrates. The lake has been stocked every year with brook trout reared at a hatchery. Follow-up fish sampling was conducted in 2000 to examine changes in PCDDs/Fs and CBs concentrations in tissues of brook trout.

Materials and Methods

Sampling

Field collection was carried out during August and September, 2000. A total of 12 brook trout were collected from Chrystina Lake, about 1.5 km northeast of the facility, with an average total length of 295 mm and average weight of 318 g. All samples were kept frozen at -20°C prior to contaminants analysis.

Contaminants Analysis

PCDDs/Fs and CBs determinations of all samples were performed by the Fisheries and Oceans Regional Dioxin Laboratory at the Institute of Ocean Sciences in Sidney, British Columbia, Canada. The methodologies used to process the samples, the criteria used for identification and quantification and the quality assurance quality control protocols were described in detail elsewhere.[2] From each sample four aliquots were collected by the carbon-fibre fractionation, the last part of the sample clean-up process. Fraction-I contained the *di-ortho* CBs, fraction-II the *mono-ortho* CBs, fraction-III the *non-ortho* CBs and fraction-IV the PCDDs and PCDFs. In fractions I to III all possible 209 CB congeners were measured with minimum isomeric interference. Analysis of all fractions was conducted by high-resolution gas chromatograph/high-resolution mass spectrometry (HRGC/HRMS). For all analysis the MS was operated at 10 000 resolution under positive EI conditions and data were acquired in the Single Ion Monitoring Mode (SIM). The concentrations of identified compounds and their minimum detection limits (MDLs) were calculated by the internal standard method using mean relative response factors determined from calibration standard runs, made before and after each batch of samples. Detection limits ranged from 0.01 to 0.12 pg/g for PCDDs/Fs, 0.04 to 0.08 pg/g for *non-ortho* CBs, 0.1 pg/g for *mono-ortho* CBs and 0.1 to 0.2 pg/g for *di-ortho* CBs.

Results and Discussion

The mean values of ∑PCDDs/Fs are summarized in Table 1. Five of PCDD/F congeners were detected in brook trout muscle tissue from Chrystina Lake and 14 in the liver. The mean concentration of ∑PCDDs/Fs in the muscle in 2000 was 1.07 pg/g (wet weight) and 288 pg/g (lipid basis), which significantly declined as compared to those in 1997 (22 pg/g, wet weight and 5500 pg/g, lipid basis).[1] The mean value of ∑PCDDs/Fs in the liver was 7.33 pg/g, wet weight and 121 pg/g, lipid basis, which was significantly lower as compared to those in brook trout from Chrystina Lake collected in 1997 (227 pg/g, wet weight. Lipid basis data are not available).[1] The levels of ∑PCDDs/Fs in 2000 were similar to those in northern pike from two reference lakes (0.68-0.93 pg/g, wet weight in muscle and 1.2-7.5 pg/g, wet weight in the livers).[1] The prevalent congeners were OCDD and 2,3,7,8 TCDF, accounting for 45% of OCDD and 36% of 2,3,7,8TCDF in the muscle and 31% and 27% in the liver.

The mean values of ∑CBs and their homologues are summarized in Table 2-3. The mean concentration of ∑CBs was significantly decreased in the muscle (7455 ng/g, lipid basis) and the livers (2134 ng/g, lipid basis) as compared to those in 1997 (16041 ng/g, lipid basis in the muscle, the liver data was not available).[3] The dominating CB congeners were CB153 and CB138, accounting for 13% to 16% of ∑CBs in the muscle and liver and 10% to 12% of ∑CBs in the muscle and liver, respectively. The prevalent homologue groups were penta-CBs, hexa-CBs and hepta-CBs in *di-ortho* CBs in all types of samples.

The mean values of ∑TEQ are summarized in Table 1. The mean concentration of ∑TEQ was decreased in the muscle (0.93 pg/g, wet weight and 259 pg/g, lipid basis) and liver (5.7 pg/g, wet weight and 81.6 pg/g, lipid basis) as compared to those in 1997 (12.4 pg/g, wet weight and 3 100 pg/g, lipid basis in the muscle and 61 pg/g, wet weight in the liver). The majority of ∑TEQ in all the samples was due to CBs (94% in the muscle and 87% in the liver). The most important contributor was CB-126, accounting for 51% and 54% of ∑CB-TEQ in the muscle and liver, respectively. CB-126 also accounted for 48% and 47% of ∑TEQ in the muscle and liver, respectively. 2,3,7,8 TCDF and 2,3,4,7,8 PeCDF were prevalent in brook trout, accounting for 63% and 22% of ∑PCDD/F-TEQ in the muscle and 32% and 37% in the liver. However, they were not major contributors of ∑TEQ (4% and 1.5% of ∑TEQ in the muscle, and 4% and 5% in the liver). The findings are comparable to the results of the annual environmental monitoring program for the Special Waste Treatment Facility in which elevated levels of CB-126 TEQ, 2,3,7,8TCDF TEQ and 2,3,4,7,8 PeCDF TEQ were found in Labrador tea leaves, live moss and soils.

Combustion processes could be the source of the elevated environmental levels of the coplanar congeners characterized by 3,3',4,4' substitution such as CB77, CB126, CB169, CB105, CB156, CB157, CB170 and CB189. The comparable CBs and PCDs/Fs profiles suggested that the air emissions from the facility may contribute to the elevated levels of CBs and PCDDs/Fs in brook trout from Chrystina Lake.

Table 1 Summary of Mean of PCDDs/Fs and ∑TEQ Levels in Fish (pg/g, lipid basis)

Parameter	Muscle		Liver	
	Conc.	%	Conc.	%
Lipid content		0.42		5.98
2,3,7,8-TCDD	0.00	0.00	1.02	0.85
1,2,3,7,8-PeCDD	0.00	0.00	1.43	1.18
1,2,3,4,7,8-HxCDD	0.00	0.00	1.67	1.38
1,2,3,6,7,8-HxCDD	32.03	11.12	12.75	10.53
1,2,3,7,8,9-HxCDD	0.00	0.00	1.63	1.34
1,2,3,4,6,7,8-HpCDD	16.68	5.79	9.53	7.87
OCDD	129.09	44.80	38.62	31.88
2,3,7,8-TCDF	104.64	36.31	34.96	28.86
1,2,3,7,8-PeCDF	0.00	0.00	1.22	1.01
2,3,4,7,8-PxCDF	5.73	1.99	7.67	6.33
1,2,3,4,7,8-HxCDF	0.00	0.00	0.00	0.00
1,2,3,6,7,8-HxCDF	0.00	0.00	0.00	0.00
1,2,3,7,8,9-HxCDF	0.00	0.00	1.31	1.08
2,3,4,6,7,8-HxCDF	0.00	0.00	0.00	0.00
1,2,3,4,6,7,8-HpCDF	0.00	0.00	3.04	2.51
1,2,3,4,7,8,9-HxCDF	0.00	0.00	1.79	1.48
OCDF	0.00	0.00	4.50	3.71
∑PCDDs/Fs	**288**	**100**	**121**	**100**
∑PCDDs/Fs-TEQ [a]	16.8		11.0	
∑CBs-TEQ [b]	242.2		70.6	
∑TEQ	**259**		**81.6**	
% of ∑PCDDs/Fs-TEQ in ∑TEQ		6.5		13.5
% of ∑CBs-TEQ in ∑TEQ		93.5		86.5

a. NATO-CCMS I-TEFs. b. WHO-IPCS I-TEFs.

Table 2 Mean of CBs Homologues in Fish Muscle (ng/g, lipid basis)

Group	Conc.	%	Group	Conc.	%
*Non-ortho**			*Di-ortho****		
di-CBs	1.94	0.03	*di-CBs*	0.41	0.01
tri-CBs	46.42	0.62	*tri-CBs*	8.79	0.12
tetra-CBs	15.70	0.21	*tetra-CBs*	315.10	4.23
penta-CBs	1.64	0.02	*penta-CBs*	1215.13	16.30
hexa-CBs	0.07	0.00	*hexa-CBs*	2923.18	39.21
Total *non-ortho*	**65.77**	**0.88**	*hepta-CBs*	1460.16	19.59
			octa-CBs	251.26	3.37
*Mono-ortho***			*nona-CBs*	9.19	0.12
di-CBs	2.20	0.03	*deca-CBs*	0.88	0.01
tri-CBs	65.47	0.88	**Total *di-ortho***	**6184**	**83**
tetra-CBs	475.65	6.38			
penta-CBs	575.74	7.72	**Total CBs**	**7455**	**100**
hexa-CBs	81.94	1.10			
hepta-CBs	4.19	0.06			
Total *mono-ortho*	**1205**	**16.17**			

Table 3 Mean of CBs Homologues in Fish Liver (ng/g, lipid basis)

Group	Conc.	%	Group	Conc.	%
<u>*Non-ortho*</u>*			<u>*Di-ortho*</u>***		
di-CBs	0.65	0.03	*di-CBs*	0.23	0.01
tri-CBs	1.52	0.07	*tri-CBs*	2.93	0.14
tetra-CBs	1.84	0.09	*tetra-CBs*	49.62	2.32
penta-CBs	0.46	0.02	*penta-CBs*	306.22	14.35
hexa-CBs	0.03	0.00	*hexa-CBs*	1002.02	46.95
Total *Non-ortho*	**4.50**	**0.21**	*hepta-CBs*	431.74	20.23
			octa-CBs	77.11	3.61
<u>*Mono-ortho*</u>**			*nona-CBs*	2.10	0.10
di-CBs	1.50	0.07	*deca-CBs*	0.14	0.01
tri-CBs	17.20	0.81	**Total *di-ortho***	**1872**	**87.7**
tetra-CBs	46.42	2.17			
penta-CBs	167.12	7.83	**Total CBs**	**2134**	**100.00**
hexa-CBs	24.31	1.14			
hepta-CBs	1.05	0.05			
Total *mono-ortho*	**257.6**	**12.07**			

* Non-ortho CBs: di- (no.11-14), tri- (no. 35-39), tetra- (no. 77-81), penta- (no. 126, 127) and hexa- (no. 169). ** *Mono-ortho* CBs: di- (no.5-9), tri- (no. 20-23, 25-26, 28-29, 31, 33-34), tetra- (no. 55-58, 60-61, 63, 66-67, 68, 70, 72, 74, 76), penta- (no. 105, 107, 108, 111,114, 118, 120, 122-124), hexa- (no. 156, 157, 159, 162, 167) and hepta- (no.189). *** *Di-ortho* CBs: di- (no.4, 10), tri- (no. 16-19, 24, 27, 30, 32), tetra- (no. 40-54, 59, 62, 64, 69, 71, 73, 75), penta- (no. 82-104, 109-110, 112-113, 115-117, 119, 121, 125), hexa- (no. 128-155, 158, 160, 161, 163-166, 168), hepta- (no. 170-188, 190-193), octa- (no. 194-205), nona- (no.206-208) and deca- (no. 209).

Acknowledgements

The contribution of those who assisted with the analytical work at the Fisheries and Oceans regional dioxin laboratory is gratefully acknowledged.

References

(1) Gabos S., Schopflocher, D., Muir, D.D., Schindler, D., Guidotti, T.G., Schecter, A., Lastoria, C., Ramamoorthy, S., Watert, J., Grimsrud, K., Shaw, S., Chen, W. (1998). Organohalogen Compounds, Vol. 39, 173.

(2) Ikonomou, M.G., Fraser, T.L., Crewe, N.F., Fischer, M.B., Rogers, I.H., He, T., Sather, P.J., and Lamb, R. (2001). A Comprehensive Multiresidue Ultra-Trace Analytical Method, Based on HRGC/HRMS, for the Determination of PCDDs, PCDDFs, PCBs, PBDEs, PCDEs, and Organochlorine Pesticides in Six Different Environmental Matrices. Fisheries and Oceans, Canada, Sidney, B.C., ISSN 0706-6457.

(3) Unpublished data (1997), Alberta Health and Wellness, Edmonton, Alberta, Canada.