

# LONG-TERM MONITORING RESULTS OF PCBS AND PCDD/FS IN FISH FOLLOWING AN ACCIDENTAL RELEASE FROM A SPECIAL WASTE TREATMENT CENTER

Zhang W<sup>1\*</sup>, Ikonomou MG<sup>2</sup>, Gabos S<sup>1</sup>, Kinniburgh DW<sup>3</sup>

<sup>1</sup>Alberta Health, Canada, 23<sup>rd</sup> Floor TPNT, 10025 Jasper Ave. Edmonton, AB, Canada, <sup>2</sup>Institute of Ocean Sciences, P.O. Box 6000, 9860 West Saanich Road, Sidney, BC, Canada, <sup>3</sup>Alberta Centre for Toxicology, HM-B19 3330 Hospital Drive NW, University of Calgary, Calgary, AB, Canada

## Introduction

In early 1997, high levels of PCDD/Fs and PCBs were detected in fish in Chrystina Lake following an accidental release of contaminants from a nearby special waste treatment center (WTC) near Swann Hills, Alberta, Canada in October 1996.<sup>1</sup> Chrystina Lake near the facility contains 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 between 1997 and 2009 to examine changes in PCB and PCDD/F concentrations over time and to assess potential health risks.

## Materials and Methods

### Sampling

Field collection was carried out in 1997, 2000, 2003, 2007 and 2009. Brook trout were collected from Chrystina Lake, about 1.5 km northeast of the facility, with an average total length of 295 - 325 mm and average weight of 295 - 325 g. All samples were kept frozen at -20°C prior to contaminants analysis.

### Contaminants Analysis

PCDD/Fs and PCBs were analyzed by the Fisheries and Oceans Canada, Pacific Region Dioxin Laboratory in Sidney, British Columbia. 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.<sup>2</sup> From each sample four aliquots were collected using carbon-fibre fractionation, the last part of the sample clean-up process. Fraction-I contained the *di-ortho* PCBs, fraction-II the *mono-ortho* PCBs, fraction-III the *non-ortho* PCBs and fraction-IV the PCDDs and PCDFs. In fractions I to III all possible 209 PCB 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* PCBs, 0.1 pg/g for *mono-ortho* PCBs and 0.1 to 0.2 pg/g for *di-ortho* PCBs.

## Results and Discussion

The statistical summaries of  $\Sigma$ TEQ,  $\Sigma$ CB and  $\Sigma$ PCDD/F levels between 1997 and 2009 are presented in Table 1 and 2. The TEQ levels in the livers and muscles between 2000 and 2009 were significantly lower than the levels in 1997 ( $p < 0.01$ ) (Figure 1). The  $\Sigma$ TEQ levels in the livers between 2000 and 2009 were similar to those in northern pike collected from the reference lakes in 1997. The TEQ levels in the muscle collected between 2000 and 2009 were significantly higher than the levels in northern pike collected from the reference

lake in 1997. The  $\Sigma$ TEQ levels in muscle were significantly higher in 2007 than those in 2000, 2003 and 2009. The  $\Sigma$ TEQ levels in muscle in 2009 were similar to those in 2000 and 2003. The majority of  $\Sigma$ TEQ in all the samples was due to PCBs (64%–95% in muscle and 81%–93% in liver. The most important contributor was PCB-126, accounting for 70%–84% of  $\Sigma$ TEQ in muscle and liver. 2,3,7,8 TCDF was not a major contributor of  $\Sigma$ TEQ (4%–6% of  $\Sigma$ TEQ in muscle, and 4%–10% in liver.

The  $\Sigma$ PCB levels in liver and muscle between 2000 and 2009 were not statistically changed as compared to the levels in 1997, but the levels were still significantly higher than those in northern pike collected from the reference lakes in 1997 (Figure 2). The  $\Sigma$ PCB levels in muscle in 2007 and 2009 were significantly higher than those in 2000 and 2003. After controlling for weight in a multiple regression model,  $\Sigma$ PCB levels in muscle still remained higher. Thus, the size of fish was not found an important factor that influences the  $\Sigma$ PCB levels in 2007. The dominant PCB congeners were PCB-153 and PCB-138, accounting for 9% to 16% of  $\Sigma$ PCBs in muscle and liver and 10% to 12% of  $\Sigma$ PCBs in muscle and liver, respectively.

The  $\Sigma$ PCDD/F levels in the liver and muscle between 2000 and 2009 were significantly lower than the levels in 1997 (Figure 3). The  $\Sigma$ PCDD/F levels in the liver and muscle between 2000 and 2009 were similar to those in fish collected from the reference lakes in 1997. The prevalent congeners were OCDD and 2,3,7,8 TCDF, with OCDD accounting for 20% - 45% of  $\Sigma$ PCDD/Fs in muscle and 21% -31% in liver and with 2,3,7,8 TCDF accounting for 36% - 95% of  $\Sigma$ PCDD/Fs in muscle and 27% - 85% in liver in various years.

Distribution patterns of  $\Sigma$ PCDD/Fs,  $\Sigma$ PCBs and  $\Sigma$ dioxin-like TEQs in brook trout in the 2000, 2003, 2007 and 2009 studies were consistent with those observed in the 1997 study and the annual monitoring programs conducted by the company.<sup>3</sup> Similarity of distribution patterns of the contaminants in various media indicates that the sources of contamination could come from the facility.

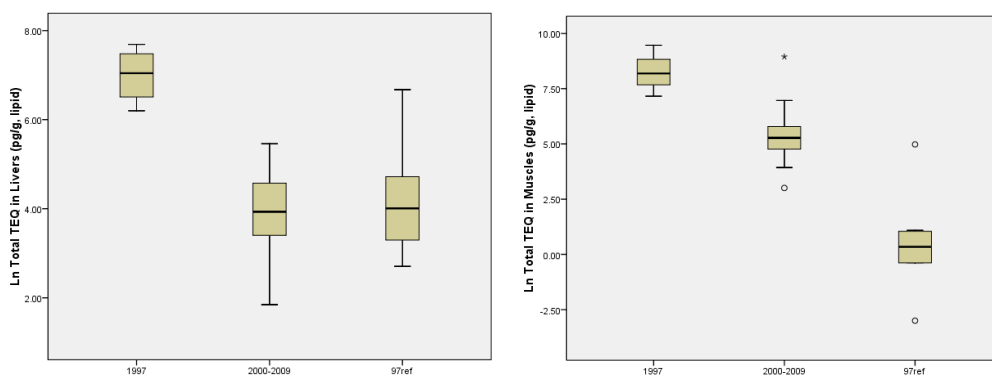
**Table 1 Summary of Mean of  $\Sigma$ TEQ and  $\Sigma$ PCB Levels in Brook Trout, 1997-2009**

Year	N	$\Sigma$ TEQ (pg/g, lipid basis)					$\Sigma$ PCBs (ng/g, lipid basis)				
		Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max
<i>Liver</i>											
1997	16	1,257	1,173	730	492	2,188	-	-	-	-	-
2000	12	55	37	39	22	137	2,134	1,765	1,152	765	4,402
2003	11	123	125	60	49	235	3,381	2,711	2,051	1,103	7,285
2007	15	76	63	48	22	193	3,122	3,085	2,281	770	10,458
2009	15	44	29	45	6.3	166	4,323	2,181	4,459	1,170	17,629
Ref_97	9	172	55	261	15	792	218	93	301	44	1,006
<i>Muscle</i>											
1997	16	5,340	3,601	5,135	1,288	2,832	7,584	4,869	7,129	2,505	18,093
2000	12	161	145	77	68	338	7,457	6,655	3,980	2,122	16,067
2003	11	210	152	204	63	720	7,654	5,336	8,301	1,799	29,765
2007	15	835	249	1,906	132	7,674	21,554	12,524	23,217	6,880	88,811
2009	15	257	144	241	20	838	15,813	12,181	11,707	4,205	48,324
Ref_97	9	17	1.0	48	nd	145	144	123	136	33	423

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

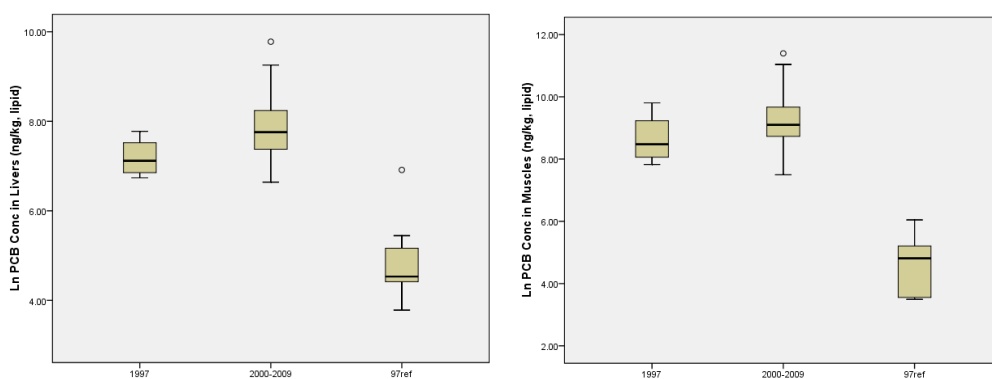
**Table 2 Summary of Mean of PCDD/F Levels in Brook Trout, 1997-2009**

Year	N	$\Sigma$ PCDD/F (pg/g, lipid basis)					$\Sigma$ PCDD/F (pg/g, lipid basis)				
		Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max
		<i>Liver</i>					<i>Muscle</i>				
1997	16	9,122	6,606	7,755	2,879	20,400	3,466	3,826	2,235	835	5,375
2000	12	288	254	233	107	976	121	74	114	46	436
2003	11	99	74	95	39	377	67	63	33	34	151
2007	15	559	408	367	124	1,247	294	171	377	55	1,495
2009	15	77	59	44	28	185	203	164	128	88	536
Ref_97	9	332	167	429	nd	1,333	188	139	207	nd	583



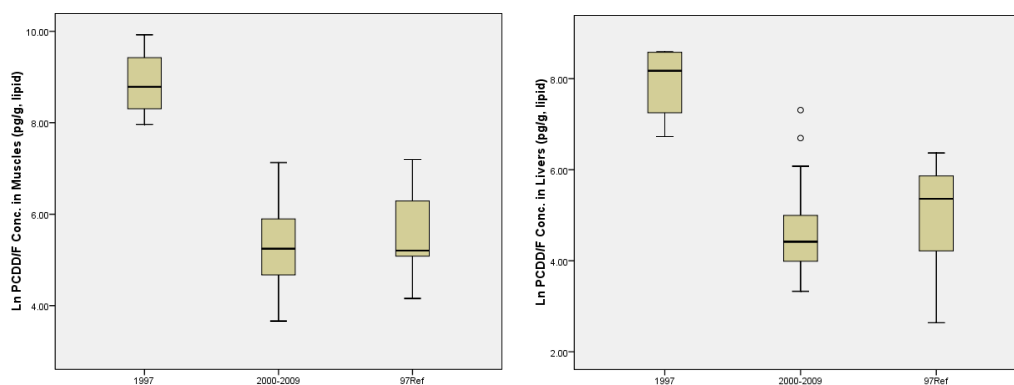
**Figure 1  $\Sigma$ Dioxin-like TEQ Levels in Brook Trout in Chrystina Lake, 1997\_2009**

t – test for concentrations in 1997 vs. 2000-2009 in liver and muscles ( $p < 0.01$ ). The concentrations in northern pike in the reference lake in 1997 vs. 2000 – 2009 in livers ( $p = 0.33$ ) and muscles ( $p < 0.001$ ).



**Figure 2  $\Sigma$ PCB Levels in Brook Trout in Chrystina Lake, 1997\_2009**

t – test for concentrations in 1997 vs. 2000 – 2009 in livers ( $p = 0.05$ ) and muscles ( $p = 0.30$ ). The levels in northern pike in the reference lake in 1997 vs. 2000 – 2009 in livers and muscles ( $p < 0.001$ ).



**Figure 3  $\Sigma$ PCDD/F Levels in Brook Trout in Chrystina Lake, 1997\_2009**

t – test for concentrations 1997 vs. brook trout in 2000 – 2009 in livers and muscles ( $p < 0.01$ ). The levels in northern pike in the reference lake in 1997 vs. in 2000 – 2009 in livers ( $p = 0.61$ ) and in muscles ( $p = 0.77$ ).

#### **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 DD, Schindler D, Guidotti TG, Schechter A, Lastoria C, Ramamoorthy S, Watert J, Grimsrud K, Shaw S, Chen W. (1998) *Organohalogen Compounds* 39: 173-176.
- (2) Ikonomou MG, Fraser TL, Crewe NF, Fischer MB, Rogers IH, He T, Sather PJ, and Lamb R. (2001) Fisheries and Oceans, Canada, Sidney, BC, ISSN 0706-6457.
- (3) Swan Hills Treatment Centre (2011) Annual Report No. 1744-02-02, Alberta, Canada.