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

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Introduction

Following an accidental release of contaminants from a special waste treatment center (WTC) in October 1996 near Swan Hills, Alberta, Canada high levels of PCBs and TCDD/Fs were detected in deer.[1] As a follow-up, wild game monitoring was conducted between 1997 and 2010 to determine the concentration of PCBs and PCDD/Fs over time in tissues of whitetail deer (*Odocoileus virginianus*) and mule deer (*Odocoileus hemionus*) and to assess potential human health risks.[1,2,3,4]

Materials and Methods

Sampling

Field collection was carried out in 1997, 1999, 2001, 2003, 2007, 2009 and 2010. All whitetail and mule deer samples were collected within a 30 km radius to the east and west of the Waste Treatment Center. Representative muscle, liver, and fat samples were taken from each deer. All samples were kept frozen at -20 ^{o}C prior to the laboratory analysis.

Contaminants Analysis

PCBs and PCDD/Fs were determined from all samples and the analysis was performed by Fisheries and Oceans Canada, Pacific Region Dioxin Laboratory and AXYS Analytical Services in Sidney, British Columbia, Canada. The methodology used to process the samples, and the criteria used for the identification and quantification and the quality assurance quality control protocols were described in detail elsewhere.[5] 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 PCDD/Fs. 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, before and after each batch of samples. Detection limits ranged from 0.01 to 0.12 pg/g for PCDD/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 ΣTEQ, ΣPCB and ΣPCDD/F levels between 1997 and 2010 are presented in Table 1 and 2. ΣTEQ levels in liver samples and muscle samples in 1999-2010 were significantly lower as compared to levels in 1997 ($p < 0.01$). The contaminant levels were not significantly different from those in the muscle samples from the reference area ($p = 0.3$), but the levels in the liver samples were still significantly higher than those in the reference area ($p < 0.001$). The majority of ∑TEQ in all the samples was due to

2,3,4,7,8_PeCDF (10%–55% in muscles and 18%–79% in livers) between 1999 and 2007. The majority of ∑TEQ in all the samples was due to PCB-126 (89%–90% in muscles and 83%–95% in livers) between 2009 and 2010.

ΣPCB levels between 1999 and 2010 were decreased as compared to the levels in liver samples ($p < 0.001$) and muscle samples ($p < 0.01$) in 1997, but the levels were still significantly higher than those in deer collected from the reference area in 1999 ($p < 0.001$ for muscles and $p < 0.05$ for livers). The dominant PCB congeners were PCB-153 (9% - 28%), PCB-138 (6% - 17%) and PCB-180 (3% - 17%). Non-ortho PCBs constituted a very small proportion of ∑PCBs. Major contributors in the non-ortho PCB group were PCB-11, PCB-15 and PCB-37 for all samples from the study and reference areas.

ΣPCDD/F levels in liver and muscle samples in 1999 - 2010 were statistically lower as compared to levels in 1997 ($p < 0.05$). The ΣPCDD/F levels in liver and muscle samples in 1999 - 2010 were not significantly different from the levels in the reference areas. OCDD was a major congener in muscle in the 1999, 2003, 2009 and 2010 studies. 2,3,4,7,8-PeCDF was a major congener in liver samples in 1999, 2001, 2003 , 2007, 2009 and 2010 studies. 2,3,4,7,8-PeCDF may be a marker congener present in the emissions of the special waste treatment facility as it has been observed to be the major congener in soil, vegetation, sediment, fish, and voles collected near the facility since 1996.[6]

ΣTEQ, ΣPCB and ΣPCDD/F concentrations as a function of distance from the facility fence in deer tissues collected between 1999 and 2010 are presented in Figure 1-3. A hierarchical multiple regression analysis was conducted to determine the joint effects of distance from the WTC, the year in which the deer was taken, and the interactions on the chemical concentrations in muscle and liver. Due to a skewed distribution, ΣTEQ has been transformed to its natural logarithm prior to analysis. The distance from the facility is the most important factor in estimating contaminant concentrations. Contaminant concentrations in all the samples decreased with increased distance from the facility fence. This finding suggests that contamination from the facility has occurred in the ecosystem in the immediate vicinity of the facility.

Table 1 Summary of Mean of ∑TEQ and ∑PCB Levels in Deer, 1997-20010

Year	N	∑TEQ (pg/g, lipid basis)					∑PCBs (ng/g, lipid basis)				
		Mean	**Median**	**SD**	**Min**	**Max**	**Mean**	**Median**	**SD**	**Min**	**Max**
		Liver					*Liver*				
1997	4	12,467	8,880	13,692	72	32,037	2,408	2,464	2,214	215	4,490
1999	9	733	52	1,477	14	4,274	47	13	44	4.9	130
2001	6	9,455	39	21,653	3.0	53,586	317	30	677	5.3	1,694
2003	7	216	218	150	21	423	92	79	103	15	308
2007	14	1,882	438	3,067	9.0	7,994	85	10	145	0.83	356
2009	3	234	17	385	6	679	99	2.04	168	1.27	293
2010	16	245	33	402	10	1,229	44	2.5	77	0.8	245
Ref_99	10	8.0	1.3	18	0.9	58	5.0	3.7	1.7	2.3	7.7
		Muscle					*Muscle*				
1997	4	788	76	1,476	nd	3,000	987	191	1,728	nd	3,565
1999	6	4.8	2.4	6.0	0.6	17	21	8.1	28	3.2	84
2001	9	30	1.3	54	0.01	135	291	238	605	4.3	84
2003	7	2.7	2.5	1.2	0.9	3.9	39	44	14	11	52
2007	14	19	16	19	0.9	71	67	11	113	2.0	370
2009	3	25	0.01	43	0.01	75	71	1.17	122	1.0	212
2010	16	3.9	0.03	6.8	0.0	18	39	2.17	69	0.49	222
Ref_99	10	1.0	1.0	0.5	0.3	2.0	5.3	4.5	3.1	1.5	10

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

Table 2 Summary of Mean of PCDD/F Levels in Deer, 1997-2009

Year	N	∑PCDD/F (pg/g, lipid basis)					∑PCDD/F (pg/g, lipid basis)				
		Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max
		Liver					*Muscle*				
1997	4	74,271	44,062	94,249	555	208,404	165	128	181	nd	405
1999	9	3,125	347	6,020	151	17,618	118	65	174	17	573
2001	6	29,980	244	68,107	73	168,749	110	15	189	nd	478
2003	7	1,313	1,585	699	102	2,006	72	28	86	nd	236
2007	14	7,921	2,471	12,037	238	32,744	72	52	61	10	222
2009	3	124	75	110	47	250	16	5.6	19	3.9	38
2010	16	225	158	172	39	668	8.3	6.2	6.2	2.1	26
Ref_99	10	138	37	277	23	921	61	44	45	13	128

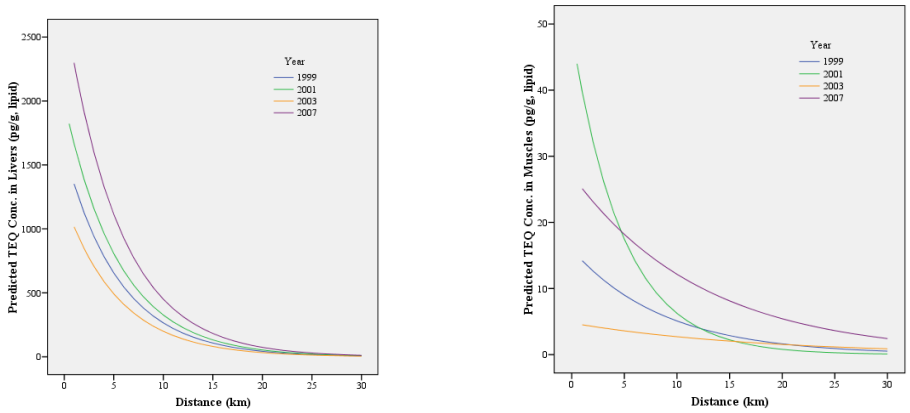

Figure 1 ΣDioxin-like TEQ Levels in Deer vs. the Distance of the Facility

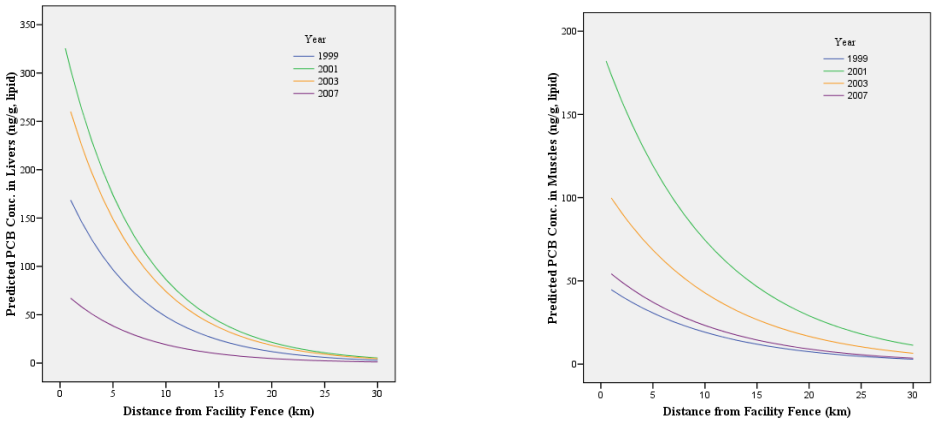

Figure 2 ΣPCB Levels in Deer vs. the Distance of the Facility

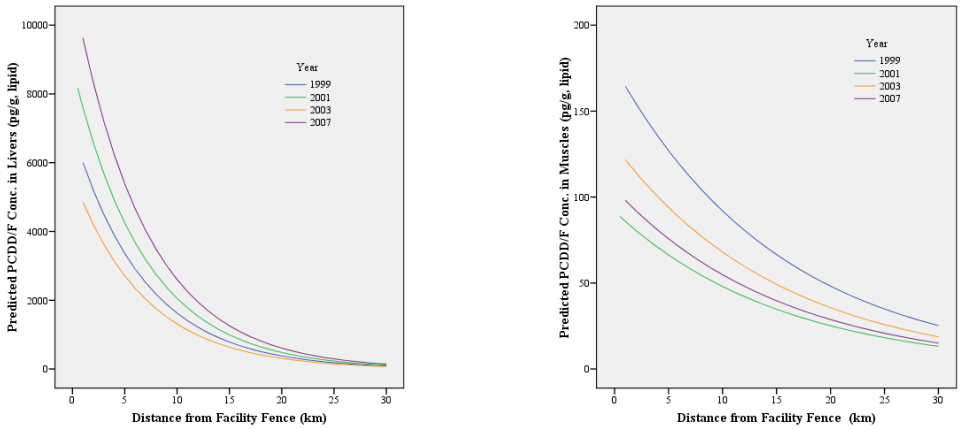

Figure 3 ΣPCDD/F Levels in Deer vs. the Distance of the Facility

Acknowledgements

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