CBs and PCDDs/Fs Levels in Deer Tissue Samples Following an Accidental Release from a Special Waste Treatment Center: 1999 Results

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Introduction

In early 1997, high levels of PCDDs/Fs and CBs were detected in deer and moose tissues from the Swan Hills area, Alberta, Canada, following accidental release of these contaminants from a Special Waste Treatment Center in October 1996.[1] Follow-up wild game sampling was conducted in 1998/99 to examine changes in PCDDs/Fs and CBs concentrations in the tissues of whitetail deer (*Odocoileus virginianus*) and mule deer (*Odocoileus hemionus*) collected in the same geographic location as in 1997.

Materials and Methods

Sampling

Field collection was carried out in December 1998 and January 1999. Nine whitetail deer and mule deer were collected at distances of 1 - 25 km to the east and west of the Special Waste Treatment Center. Ten deer were collected at a distance of 100 km to the west of the facility as a control group. Representative muscle and liver samples were taken from each deer. All samples were kept frozen at - 20 ^{o}C prior to contaminants analysis.

Contaminants Analysis

PCDDs/Fs and CBs determinations for 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 followed are described in detail elsewhere.[2,3] From each sample four aliquots were collected from 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 the possible 209 CB congeners are measured with minimum isomeric interference.[3] Analyses of all fractions were conducted by high-resolution gas chromatograph/high-resolution mass spectrometry (HRGC/HRMS).[2,3] For all analyses the MS was operated at 10000 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 was run. Detection limits range 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, ∑CBs and their homologues and ∑TEQ are

summarized in Table 1-3. The concentrations of the contaminants (with the exception of PCDD/Fs in the muscle samples from the impacted area) were significantly higher in the samples from the impacted area than the control area. The highest PCDDs/Fs levels were detected in the tissues of the two deer collected at a distance of 1 km and 4 km to the west of the facility. In comparison with the 1997 results[1], the CBs and the PCDDs/Fs levels have decreased and similarly as in 1997 the concentrations decreased with distance from the facility. The inverse relationship between contaminant concentration and distance to the facility suggests that the occurrence of contamination was limited to the immediate vicinity of the facility.All the 2,3,7,8- substituted PCDD/F congeners (17 in total) were detected in the liver samples from the study area. The 2,3,4,7,8-pentaCDF congener was the most prevalent in all samples accounting for 60% of ∑PCDDs/Fs concentration. This is a marker congener present in the emissions of the waste treatment facility as has been found to be the major component in soil, vegetation, sediment, fish and voles collected near the facility.[4-6] Eight PCDDs/Fs congeners were detected in the muscle samples from the study area. OCDD contributed to 70% of the total PCDD/F in the muscle samples from the study area and 64% in the control area. All liver and muscle tissue samples were analyzed for full congener CBs as well. *Di-ortho* CBs constituted 79% to 84% of ∑CBs for samples from the study area and 55% to 58% in control. The abundant congeners in ∑CBs were CB-138 (9%), CB-153 (19%), CB-170 (6%) and CB-180 (9%) for samples from the study area. For samples from the control area, CB-8, CB-28, CB-138, CB-153 and CB-180 accounted for 11%, 6%, 4%, 6% and 2% of ∑CBs, respectively.

Major contributors in deer from the control site were lower-chlorinated congeners. Lower chlorinated congeners are likely to persist in vegetation. Thus, they are more frequently detected in herbivores. High proportion of some higher chlorinated congeners observed in deer from the study area suggests different exposure sources for deer of this area. *Non-ortho* CBs constituted very small proportion of ∑CBs. Major contributors in the *non-ortho* CBs group were CB-11, CB15 and CB-37 for all samples from both areas. CB-126 concentrations were significantly higher in the liver from the study area (30 pg/g, wet weight) than those in the control (0.35pg/g, wet weight). High proportion of CB-126 were often observed in various environmental samples collected near the facility. CB-126 may also be a marker congener in the emissions from the facility.The major component of the ∑TEQ in all samples from the study area was due to 2,3,4,7,8-pentaCDF which accounted for 84% of ∑TEQ in the liver and 43% in the muscle samples. Another major congener was CB-126, contributing 25% to the ∑TEQ in the muscle and 8% in the liver samples. In the control area, 1,2,3,6,7,8-hexaCDD and CB-126 were the major contributors in the muscle samples, accounting for 58% and 12% of ∑TEQ. Major congeners contributing to ∑TEQ in the liver were 2,3,4,7,8-pentaCDF (36%), 1,2,3,6,7,8-hexaCDD (13%) and 1,2,3,7,8-pentaCDD (13%).

In summary, overall levels of ∑PCDDs/Fs, ∑CBs and ∑TEQ in deer collected near the facility in 1999 have declined since 1997 when a similar study was conducted. The overall concentrations of all contaminants examined were substantially higher in the study area samples in comparison to the controls. Distribution patterns of ∑PCDDs/Fs, ∑CBs and ∑TEQ were consistent with those observed in the 1997 study and the annual monitoring programs conducted by the company. The inverse relationship between concentrations and distance to the facility suggests that the contamination is limited to the immediate vicinity of the facility.

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

Parameter	Study Area		Control Area	
	Liver	Muscle	Liver	Muscle
Lipid content (%)	3.0	2.3	3.7	3.5
2,3,7,8-TCDD	2.3	<0.08	<0.08	<0.08
1,2,3,7,8-PeCDD	29*	<0.08	2.2	<0.08
1,2,3,4,7,8-HxCDD	44.3	<0.10	4.5	<0.10
1,2,3,6,7,8-HxCDD	70.6	8.9	23.9	6.5
1,2,3,7,8,9-HxCDD	29.5*	<0.10	2.7	<0.10
1,2,3,4,6,7,8-HpCDD	258	6.0	58.7	8.0
OCDD	253	81.8	92.4	39
2,3,7,8-TCDF	17.7*	1.0	<0.05	<0.05
1,2,3,7,8-PeCDF	4.5	<0.06	<0.06	<0.06
2,3,4,7,8-PxCDF	1843**	6.3	12.3	<0.06
1,2,3,4,7,8-HxCDF	218**	1.0	3.3	<0.08
1,2,3,6,7,8-HxCDF	120**	<0.08	2.4	<0.08
1,2,3,7,8,9-HxCDF	96**	<0.08	1.8	0.5
2,3,4,6,7,8-HxCDF	0.6	<0.08	0.6	0.2
1,2,3,4,6,7,8-HpCDF	65.5*	4.63	4.9	3.9
1,2,3,4,7,8,9-HxCDF	6.6	<0.10	0.8	0.3
OCDF	17.9	8.56	3.3	4.0
∑PCDDs/Fs	**3077**	**118**	**214**	**62**
∑PCDDs/Fs-TEQ [a]	1 000	5.2	13	1.4
∑CBs-TEQ [b]	85	1.9	1.0	0.3
∑TEQ	1 085	7.1	14	1.7
% of ∑PCDDs/Fs-TEQ in ∑TEQ	92%	70%	88%	85%
% of ∑CBs-TEQ in ∑TEQ	8%	30%	12%	15%

a. NATO-CCMS I-TEFs. b. WHO-IPCS I-TEFs. * Statistically significant difference ($p<0.05$).
** Statistically significant difference ($p<0.01$)

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

Group	Study Area	Control Area	Group	Study Area	Control Area
*Non-ortho**			*Di-ortho****		
di-CBs	0.40	0.23	*di-CBs*	0.04	0.06
tri-CBs	0.24	0.08	*tri-CBs*	0.34	0.31
tetra-CBs	0.09	0.06	*tetra-CBs*	0.75	0.49
penta-CBs	0.07	0.01	*penta-CBs*	1.25	0.53
hexa-CBs	0.004	0.002	*hexa-CBs*	7.58	1.00
Total *non-ortho*	**0.80**	**0.38**	*hepta-CBs*	4.74	0.46
			octa-CBs	1.83	0.16
*Mono-ortho***			*nona-CBs*	0.24	0.04
di-CBs	0.32	0.72	*deca-CBs*	0.08	0.07
tri-CBs	0.92	0.68	**Total *di-ortho***	**16.86**	**3.11**
tetra-CBs	0.39	0.20			
penta-CBs	1.32	0.21	**Total CBs**	**21**	**5.3**
hexa-CBs	0.51	0.06	% of non-ortho	4%	7%
hepta-CBs	0.06	0.002	% of *mono-ortho*	17%	35%
Total *mono-ortho*	**3.52**	**1.87**	% of *di-ortho*	79%	58%

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

Group	Study Area	Control Area	Group	Study Area	Control Area

*Non-ortho**			*Di-ortho****		
di-CBs	0.84	0.53	*di-CBs*	0.18	0.04
tri-CBs	0.28	0.10	*tri-CBs*	1.01	0.21
tetra-CBs	0.18	0.04	*tetra-CBs*	2.19	0.41
penta-CBs	0.96	0.02	*penta-CBs*	3.26	0.37
hexa-CBs	0.03	0.002	*hexa-CBs*	8.43	0.40
Total *Non-ortho*	**2.28**	**0.70**	*hepta-CBs*	12.07	0.75
			octa-CBs	11.69	0.52
*Mono-ortho***			*nona-CBs*	0.41	0.03
di-CBs	0.35	0.34	*deca-CBs*	0.18	0.04
tri-CBs	1.16	0.89	**Total *di-ortho***	**39.42**	**2.77**
tetra-CBs	0.92	0.15			
penta-CBs	1.90	0.12	**Total CBs**	**47**	**5**
hexa-CBs	0.93	0.04	% of non-ortho	5%	14%
hepta-CBs	0.09	0.002	% of *mono-ortho*	11%	31%
Total *mono-ortho*	**5.35**	**1.54**	% of *di-ortho*	84%	55%

* 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).

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