Levels of PCBs, PCDDs and PCDFs in Deer and Moose in Alberta, Canada Following Accidental Release from a Special Waste Treatment Center

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Introduction

Wildlife monitoring program was initiated in early 1997 to examine magnitude of these contaminants in deer and moose. Whitetail deer (*Odocoileus virginianus*), mule deer (*Odocoileus hemionus*) and moose *(Alces americana*) are primary terrestrial herbivores observed throughout the study area and harvested by local residents as supplemental and primary food sources. Deer and moose are exposed to contaminants via terrestrial food web. They can be used as an indicator to assess environmental contamination in local ecosystem and exposure potential for local residents.

Materials and Methods

Sampling

Two types of samples were collected for this study: fresh and frozen samples. Fresh deer samples are taken directly from the area designated for this study. Frozen deer and moose samples are taken from animals preserved in home freezers and donated by local licensed hunters and First Nations people. Three whitetail deer were collected at distances of 10 km, 20 km, 30 km to the east of the facility. Eleven road-kill adult deer carcasses were collected from other locations of Alberta as a control group. Approximately 40 people donated sixty frozen deer and moose meat samples collected between October 1996 and February 1997 from within a 30 km kilometer radius of the facility. All specimens consisting of muscle, liver and kidney were kept frozen at - 20 °C prior to laboratory analysis.

Chemical Analysis

Analytical methods and QA/QC assurance were described in Environmental Canada EPS 1/RM/23 (1992), Environmental Canada AMD 96-05 (1996) and USEPA Method 1613 (1994). Each sample was homogenized and subsampled for analysis. Prior to the initial

extraction, samples were fortified with fifteen $^{13}C_{12}$-labeled PCDD/F with the exception of OCDF and eight $^{13}C_{12}$-labeled PCBs. Samples were digested overnight in concentrated hydrochloric acid and then extracted with 50/50 dichloromethane/hexane for one hour. This extraction was repeated several times. Lipid content was determined gravimetrically from the remaining extract. The extracts were subjected to an acid/base silica cleanup, reconcentrated and split into two equal portions by weight. One portion, for PCDD/F analysis, was cleaned up on alumina following the standard operating procedure for PCDDs/PCDFs. The PCB portion was cleaned up on a modified alumina column. Extracts were analyzed separately for PCBs and PCDD/Fs on an Autospec Ultima High Resolution Mass Spectrometer, interfaced with a Hewlett Packard Gas Chromatograph. PCBs were separated at EI 8,000 mode and PCDD/Fs at EI 10,000 mode. Fused silica capillary columns (60 meter, 0.25 mm ID, 0.25 μm film thickness) were used for determining PCDD/Fs and PCB congeners, respectively. Injector temperature was 265 °C. The total time of the GC run was 50 min. Congeners were detected in the selected ion monitoring (SIM) mode.

Results and Discussion

Means for $\sum PCB_{homologs}$ and $\sum PCCD/F_{homologs}$, whole weight, were significantly elevated for all liver ($p<0.05$) and fat samples ($p<0.05$, with the exception of PCDD/Fs) in the study area relative to the Alberta control areas. ∑dioxin-like TEQ levels were significantly elevated in all types of samples ($p<0.05$) in the study area. ∑PCCD/F TEQ levels increased with a decrease of distance from the facility of 10, 20 and 30 km ($r= -0.849$, $p<0.005$). No apparent correlation was observed between contaminant levels and age and sex of deer.

The results of $\sum PCB_{congener}$ and $\sum PCDD/F_{congener}$ levels in fresh samples are presented in Table 1. A wide range of individual PCB congeners were detected. Hexa- (36%) and hepta- chlorobiphenyls (25%-30%) were the major PCB homologue groups in the samples from the study area while tri-, tetra-, octa- and deca- chlorobiphenyls were minor constituents. PCB 8, 138, 153, and 180 constituted 55% to 64% of $\sum PCB_{congener}$ in liver and muscle samples from the study area. With the exception of muscle samples from the study area, the majority of ∑dioxin-like TEQ was due to PCDD/Fs, ranging from 65% to 78%. 2,3,4,7,8-penta CDF was prevalent in the liver samples from the study area, accounting for 30% of ∑dioxin-like TEQ. In contrast, 1,2,3,6,7,8-hexa CDD was the major congener in the liver (37%) and muscle (44%) from the control areas. 2,3,7,8-TCDD was not detected in the samples from the study area at a detection limit of 0.5 ng/kg whole weight. ∑dioxin-like TEQ in muscle from the study area was largely due to PCBs. *Non-ortho* CB 126 was prevalent, accounting for 97% of ∑dioxin-like TEQ. CB126 was not detected in the control samples. The findings are consistent with the results in the company's monitoring programs and other two relevant studies in which PCB 126, 138, 153 and 180 were found as major contributors in vegetation, soil, spruce needle and snow pack near the facility.[1-4]

PCBs and PCDD/Fs were detected in 21 out of 50 frozen muscle samples and in 8 out of 10 liver and kidney samples. Means for $\sum PCB_{homologs}$ and $\sum PCCD/F_{homologs}$ were significantly elevated for all muscle samples from within the 20 km radius relative to outside the 20 km radius of the facility. Hexa-chlorobiphenyls was the dominating PCB homologue group (76%) in all muscle samples. The majority of ∑dioxin-like TEQ was due to PCBs, with CB 126 accounting for 86% of ∑dioxin-like TEQ.

A result of significantly higher levels of PCBs and PCDD/Fs in deer from the study

area and similar PCB congener patterns observed in various media near the facility indicate that contamination has occurred in the ecosystems near the facility. Specifically, an air-plant-herbivore pathway of contamination is implicated. Many studies have shown that an increased atmospheric deposition of PCBs contributes to an increased PCB burden in plants and herbivores.[5-7] Lichens, moss and browse as primary food items of herbivores for the winter are abundant in the vicinity of the facility and used to monitor airborne pollutants. The mobility of deer and moose is restricted in a relatively small area in harsh winters. Deer and moose in the study area are likely to consume plants nearby. The inverse relationship between measured contaminant levels in deer and distance from the facility suggested the occurrence of the air-plant-herbivore pathway.

Accumulation of PCB congeners varies within different types of environmental samples and locations. The higher-chlorinated congeners have been more frequently observed in marine food chain and predators while the lower-chlorinated congeners are abundant in herbivores because lower chlorinated congeners are more likely to persist in vegetation.[7-8] Some studies reported an increased level of lower-chlorinated congeners in various animals in recent years.[5,9] The similar distribution of lower and higher chlorinated congeners in Alberta control samples implies that the potential exposure for deer in most of Alberta come from remote air transport and diverse sources.

Non-ortho PCBs (77, 126 and 169) are widely distributed in the environment but at very low levels.[5] Low levels of *non-ortho* PCBs were found in deer from Alberta controls. But a very high level for CB126 was observed in deer from the study area. *Non-ortho* PCBs were also detected in the samples of tea leaves, live moss, soil and voles near the facility in company's monitoring program.[3-4] Combustion processes could be the source of the increased environmental levels of the coplanar congeners characterized by 3,3',4,4' substitution such as 169, 126, 77, 105, 156, 157, 170 and 189.[10-11] CB 77 has been found to be more biodegradable than CB126 and CB169.[12-13] The increased level of CB126 in environmental media and highly biodegrable nature of CB77 may cause a high level of CB126 in deer collected near the facility.

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Table 1 Summary of PCB and PCDD/F Levels in Fresh Deer Samples

Parameter	Study Area		Alberta Control	
	Liver	Muscle	Liver	Muscle
Sample size	3	3	11	11
Detects of PCBs	3	1	7	5
Detects of PCDD/Fs	3	2	10	4
Lipid content (%)	3.20	1.87	3.42	1.64
Mean of $\Sigma PCB_{congener}$* (μg/kg, lipid basis)	1178	509	194	158
(range)	(103-2799)	(ND-1527)	(ND-1177)	(ND-821)
% of $\Sigma PCB_{congener}/\Sigma PCB_{homologs}$	43	43	39	26
% of measured congeners from each homologue group** / $\Sigma PCB_{congener}$				
di-CB	10.43	26.20	17.11	12.60
tri-CB	2.28	2.08	15.65	21.56
tetra-CB	3.32	4.56	13.38	15.51
penta-CB	8.60	9.14	12.17	11.50
hexa-CB	36.84	30.25	27.33	27.67
hepta-CB	36.17	24.64	9.05	10.52
octa-CB	2.38	2.88	0.45	0
deca-CB	0.19	0.26	0	0
TEQ (ng/kg, lipid basis)				
Σ *non-ortho* PCB***	1259	986	1	3
Σ *mono-ortho* PCB***	20	9	35	2
Σ *di-ortho* PCB ***	12	4	0.06	0.09
Σ PCDD/F	4698	32	100	9
Σ Dioxin-like compounds**** (range)	5989	1031	136	13
	(74-9198)	(14-3038)	(15-819)	(0.98-92)
% of ΣPCB/ΣDioxin-like compounds	22	97	26	35
% of ΣPCDD-F/ΣDioxin-like compounds	78	3	74	65
% of Σ*non-ortho*-PCB/ΣDioxin-like compounds	21	96	0.77	21

* Sum of 44 individual congener levels ** congener #8 in di-CB, #18, #28, #33, #37 in tri-CB, #44, #49, #52, #70, #74, #77, #81 in tetra-CB, #87, #99, #101, #114, #118, #119, #123, #126 in penta-CB, #128, #137, #138, #151, #153, #156, #157, #158, #167, #168, #169 in hexa-CB, #170, #177, #180, #183, #187, #189, #191 in octa-CB, NA in nona-, and #209 in deca-CB. *** *non-ortho-* = PCB (nos.) 77, 126, 169, *mono-ortho-* = PCB (nos.) 105, 114, 118, 123, 156, 157, 167, 189, *di-ortho-* = PCB (nos.) 170, 180 **** ΣPCB-TEQ plus ΣPCDD/F-TEQ