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

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Introduction

Fish monitoring program was initiated in early 1997 to examine magnitude of these contaminants in fish. 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. Northern pike (*Esox lucius*) is a predatory fish commonly found in lakes in the study area and consumed by local people. These two species were selected for chemical analysis and used to assess environmental contamination in local ecosystems and exposure potential for local residents.

Materials and Methods

Sampling

Field collection was carried out during June and July, 1997. A total of 16 brook trout were collected from Chrystina Lake, about 1.5 km northeast of the facility, with an average age of 2.0 years (a range of 1 to 3) and average weight of 112 g (a range of 60 to 229). Seventeen northern pike were collected from Roche Lake, about 20 km east of the facility, with an average age of 4.4 years (a range of 3 to 6) and average weight of 1.2 kg (a range of 0.8 to 2.3). A total of 32 northern pike were collected from Chip Lake (a reference lake) with an average age of 5.4 years (a range of 4 to 7) and average weight of 1.1 kg (a range of 0.6 to 1.5). Both muscle and liver were analyzed. For Chrystina and Roche Lake samples, each composite sample was formed from 4 (or 5) fish from a single species from the same lake with approximately the same length and weight. For Chip Lake samples, each composite sample was formed from 6 or 7 fish. A total of 26 composite samples were formed. All specimens 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

Summary of PCB and PCDD/F levels in all species and locations are presented in Table 1. $\sum PCB_{congener}$ and $\sum PCCD/F_{congener}$ concentrations in brook trout from Chrystina Lake were significantly higher ($p<0.01$) than those in northern pike from Roche and Chip lakes which did not differ from each other. Under normal circumstance, northern pike, a predator, would be expected to have higher contaminant concentrations than brook trout which feed planktonic invertebrates.[1] Pike with lager size and greater age would also contribute to this effect. The lower contaminant values in pike from Roche and Chip lakes indicate very low contaminant background. In contrast, brook trout caught for chemical analysis were smaller and younger. Concentrations of these contaminants were generally one order of magnitude higher in brook trout compared to northern pike.

A wide range of individual PCB congeners were detected. Hexachlorobiphenyl (about 50%) was a prevalent homologue group while di-, tri-, tetra-, octa- and deca- chlorobiphenyls were minor constituents across all species and locations. PCB 101, 118, 138, 153, and 180 constituted 50% of $\sum PCB_{congener}$ for brook trout, 60% for pike liver and 70% for pike muscle. The findings also are consistent with the results in the company's monitoring programs and other two relevant studies in which PCB 138, 153 and 180 were found as major contributors in vegetation, soil, spruce needle and snow pack near the facility.[2-5]

The majority of $\sum$dioxin-like TEQ in all samples was due to PCBs. The most important contributors were *non-ortho* congeners which accounted for 78% of $\sum$dioxin-like TEQ in brook trout muscle, 73% in brook trout liver, over 90% in pike with the exception of pike muscle from Chip Lake. CB 169 alone contributed 58% to 70% of $\sum$dioxin-like TEQ in brook trout liver and muscle, respectively. CB 126 was not detected in northern pike. A major contributor in pike muscle from Chip Lake was CB 118, constituting 53% to $\sum$dioxin-like TEQ. This finding is comparable to the results of the company's monitoring program in which elevated levels of *non-ortho* PCBs were found in Labrador tea leaves, live moss and soils.[4-5] 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.[6-7] The air emission from the facility may contribute to higher levels of *non-ortho* PCBs in brook trout.

2,3,7,8-tetra CDF and 2,3,4,7,8-penta CDF were prevalent in brook trout, accounting for 22% (muscle) to 27% (liver) of ∑dioxin-like TEQ. OCDD and 1,2,3,7,8-penta CDF represented 44% of ∑dioxin-like TEQ in pike muscle from Chip Lake. PCDD/Fs were minor constituents in pike liver and muscle from Roche Lake and pike liver from Chip Lake. 2,3,7,8-TCDD was not detected among species and locations at detection limits of 0.5 ng/kg whole weight. The patterns of PCDD/Fs for most incineration sources are likely to be almost every congener.[8] 2,3,7,8-TCDF was observed in northern pike in Northern Alberta and Northwest Terittory.[9-11] The results from the company's environmental monitoring program showed that the high levels of 2,3,7,8-tetra CDF and 2,3,4,7,8-penta CDF were measured in Labrador tea leaves, live moss, wild game and voles near the facility, with TCDF predominating in tea leaves and live moss and 2,3,4,7,8-penta CDF in wild game and voles.[2-3] The results are consistent with those from the current study in which the most prominent congeners in brook trout were 2,3,7,8-TCDF and 2,3,4,7,8-penta CDF. The comparable PCB and PCDD/F profiles suggested that air emission from the facility could attribute to the elevated levels of PCBs and PCDD/Fs in brook trout from Chrystina Lake.

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

Tissue	Muscle			Liver		
Lake	Chrystina	Roche	Chip	Chrystina	Roche	Chip
Fish species	*brook trout*	*northern pike*	*northern pike*	*brook trout*	*northern pike*	*northern pike*
Sample size (composite)	4	4	5	4	4	5
Detects of PCBs	4	4	3	4	4	5
Detects of PCDD/Fs	4	4	3	4	3	4
Lipid content (%)	0.4	0.6	0.3	N/A	4.3	3.6
Mean of $\Sigma PCB_{congener}$ (µg/kg, ww) (range)	18[a] (9.7-27)	1.0 (0.3-2.8)	0.25 (0.04-0.7)	70[a] (41-117)	7.8 (1.2-14)	6.4 (3-18)
% of $\Sigma PCB_{congener}/\Sigma PCB_{homologs}$	34	38	19	32	31	34
% of measured congeners from each homologue group* / $\Sigma PCB_{congener}$						
di-CB	0.3	0	2	0.2	1	0.9
tri-CB	1.4	2	7	2	1.6	4
tetra-CB	10	5	0	10	8	7
penta-CB	20	25	19	20	23	25
hexa-CB	48	48	52	47	47	50
hepta-CB	19	18	4	19	18	12
octa-CB	0.9	0.8	0	1	1	0.9
deca-CB	0.2	1	16	0.2	0.3	0.2
Mean of $\Sigma PCDD/F_{congener}$ (ng/kg, ww) (range)	22[a] (12-30)	0.93 (0.7-1.1)	0.68 (ND-1.2)	227[a] (55-351)	1.2 (ND-2)	7.5 (ND-19)
Mean of TEQ (ng/kg, ww)						
Σ *non-ortho* PCB**	9.4	0.22	0	44	2.9	2.2
Σ *mono-ortho* PCB**	0.2	0.01	0.002	0.7	0.1	0.1
Σ *di-ortho* PCB **	0.1	0.006	0.0001	0.3	0.03	0.02
Σ PCDD/F	2.7[a]	0.003	0.002	16[a]	0.2	0.1
Σ Dioxin-like compounds*** (range)	12.4[a] (6-19)	0.24 (0.01-1)	0.004 (ND-0.007)	61[a] (24-107)	3.2 (0.7-5.5)	2.4 (1-7)
% of ΣPCB/ΣDioxin-like	78	98	56	73	93	95
% of ΣPCDD-F/ΣDioxin-like	22	2	44	27	7	5

a: Difference statistically significant at $p < 0.01$

* 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

*** Sum of ΣPCB-TEQ and ΣPCDD/F-TEQ