Dioxins, Furans and PCBs Determinations in Sediment and Fish Tissue Following Forest Fires

Michael G. Ikonomou[1], Stephan Gabos[2], Donald Schopflocher[2], Jay White[3], Ellie Prepas[3], Dennis Prince[4], Weiping Chen[2]
[1]Institute of Ocean Sciences, P.O. Box 6000, 9860 West Saanich Road, Sidney, BC, Canada, V8L 4B2; [2]Alberta Health, Edmonton, AB, Canada, T5J 2N; [3]Sustainable Forest Management Network, Edmonton, Canada, T6G 2E9; [4] Water West Consulting, Edmonton, Canada.

Introduction

The warm and dry winter conditions in the Boreal Plain ecozone of western Canada following El Niño in 1997-1998, and the high occurrence of older, more fire-susceptible forest stands in this region, were important factors behind the above-average fire activity in north-central Alberta during the summer of 1998. These fast moving fires were among the most extensive ever recorded in North America. In Alberta alone, over 350 000 hectares of coniferous forest were burnt in over 50 separate fire. The largest and most extensively burned one was in the Virginia Hill area, Northern Alberta. In the fall of 1998, a pilot study was conducted to examine persistent organic pollutants following forest fires. The purpose of this study was to assess the impact of the forest fires in terms of PCDDs/Fs and CBs loadings in the greater area of Virginia Hill. The environmental samples examined were sediments and fish collected in streams within the impacted area.

Materials and Methods

Sampling

Field collection was carried out at three selected sites in September 1998. Site A (54^{o} 26.989 N, 116^{o} 07.590 W) was located on a reach of the Sakwatamau River which ran through the forest fire area. This site was in a partially burned area on the edge of the forest fire zone. Site B (54^{o} 35.659 N, 115^{o} 39.694 W) was a completely burned area near the middle of the forest fire zone on the Freeman River. Site C (54^{o} 15.536 N, 117^{o} 06.458 W) was on the Little Smoke River in an area that had not experienced forest fires during the year. Five representative sampling locations with a sediment deposition zone in only 1-2 feet of water were selected from each river site. The top 1 cm of sediment was collected and placed in a clean glass jar. At Site B, some sediment samples contained abundant burned pine needles. Two arctic graying (weight of 40 grams) and two mountain whitefish (weight of 60 to 65 grams) were collected at Site A and Site C, respectively. All samples were kept frozen at -20 ^{o}C prior to laboratory 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. Samples were analyzed in batches of twelve, each containing a procedural blank, a certified reference material and nine samples out of which one was analyzed in duplicate. 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.[1-2] 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 chromatography/high-resolution mass spectrometry (HRGC/HRMS).[1-3] 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

Typical total PCDDs/Fs concentrations detected in the sediments from Sites A, B and C were 1.82, 4.98 and 4.88 pg/g, dry weight, respectively. Total organic carbon (TOC) was 0.55% at Site A and 2.2% at Site B and C. After adjusting TOC, mean values were 330, 226 and 221 pg/g TOC. The five most prominent PCDDs/Fs congeners detected in all samples were: 1,2,3,6,7,8-hexa-CDD, 1,2,3,4,6,7,8-hepta-CDD, OCDD, 1,2,3,4,6,7,8-hepta-CDF and OCDF. The relative abundance of these congeners were similar in all sites examined (Figure 1) with OCDD being the most prevalent component. The PCDDs/F levels reported here are very low and can only be considered as typical background contamination. The total PCDDs/Fs concentrations detected in these sediments are substantially lower than what is considered as typical atmospheric deposition (i.e. 1 ng/g) by a number of investigators.[4-6] Our data do not show levels high enough and/or distinct patterns that would suggest that the sediments in the streams examined have been impacted by PCDDs/Fs produced from the forest fires.

The sediment samples were examined for all 209 CB congener also. The average levels of homologue totals for each of the CB groups are listed in Table 1. The overall total CBs concentrations in the three sites examined were similar, 258, 283 and 247pg/g, dry weight, respectively for sites A, B and C. Out of these grant totals the *non-ortho* CBs account for 5% to 7%, the *mono-ortho* for 28% to 32% and the *di-ortho*-CBs for 62% to 65%. The CBs data were also analyzed in terms of homologue series totals for each of the three groups, *non-, mono-, and di-ortho*, see Figure 2. The patterns observed were very similar in all three sites. The DiCBs were the most prevalent in the *non-ortho* group, the TrCBs in the *mono-ortho* group and the TeCBs, PeCBs and HxCBs in the *di-ortho* group as they represent approximately 63% to 74% of the total *di-ortho* CBs. Similarly as per PCDDs/Fs measurements the CBs concentrations detected are considered as background levels and do not reflect contamination due to forest fires. Average total CBs concentrations measured in this study are similar to those measured in surficial sediments collected in the Arctic (260 pg/g).[7]

Fish muscle tissue from the species collected in Sites A and C was also analyzed for PCDDs/Fs and CBs. Average total levels of PCDDs/Fs measured were 0.78 pg/g wet weight in Site A and 0.48 pg/g in Site C. The total CB concentrations measured were 514 pg/g wet weight in Site A and 502 in Site C. Very low levels of PCDDs/Fs and CBs in these fish may be attributed to small size fish and low background levels of these contaminants in water system.

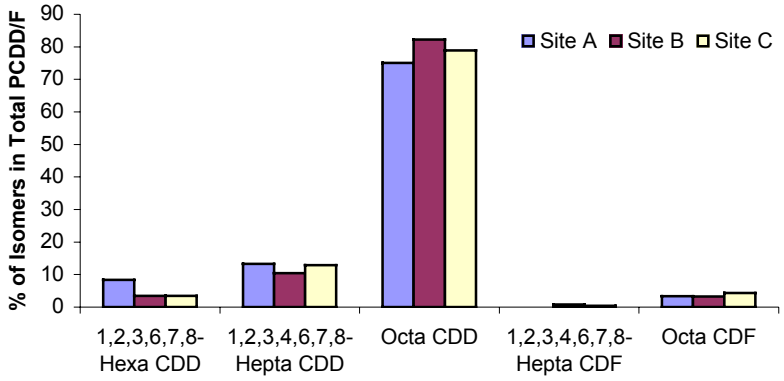

Figure 1. Distribution Patterns of PCDDs/Fs in Sediment Samples

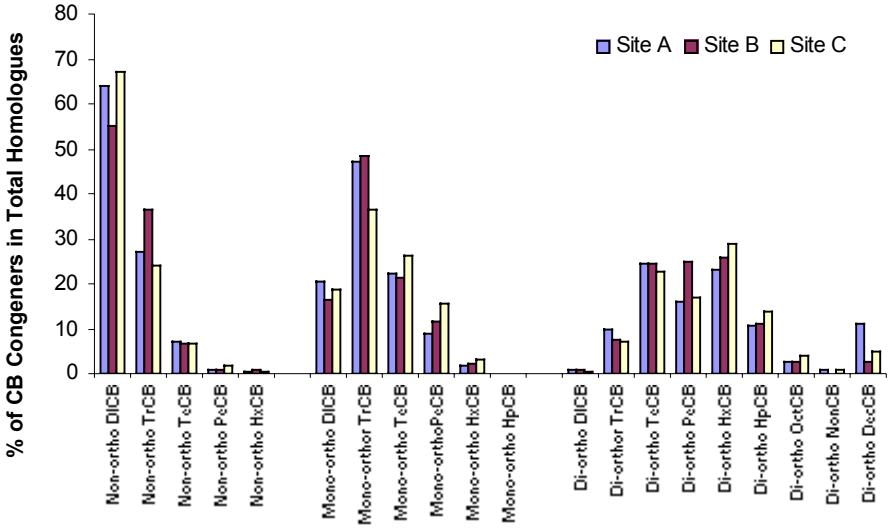

Figure 2. Patterns of homologue series total CBs detected in sediment samples. (The data are summarized in three different groups reflecting the three distinct CBs structures, non-, mono- and di-ortho. The data are normalized within each group but they are not inter group normalized.)

Table 1 Mean of CB Homologue Totals in Sediment Samples (pg/g)

Group	Site A	Site B	Site C	Group	Site A	Site B	Site C
Non-ortho*				Di-ortho***			
di-CB	8.7	8.7	13.2	*di-CB*	1.6	1.4	0.9
tri-CB	3.7	5.8	4.7	*tri-CB*	16.2	13.1	11.2
tetra-CB	0.98	1.1	1.3	*tetra-CB*	40.0	42.9	36.6
penta-CB	0.15	0.1	0.3	*penta-CB*	26.7	44.0	27.5
hexa-CB	0.08	0.1	0.1	*hexa-CB*	38.3	45.3	46.8
Total *Non-ortho*	**13.6**	**15.8**	**19.3**	*hepta-CB*	17.2	19.8	22.4
				octa-CB	4.5	4.7	6.2
Mono-ortho**				*nona-CB*	1.3	0.4	1.4
di-CB	16.2	14.9	12.5	*deca-CB*	18.6	4.7	8.0
tri-CB	37.7	44.2	24.1	**Total *di-ortho***	164	176	161
tetra-CB	17.6	19.5	17.5				
penta-CB	7.0	10.5	10.2	**Total CBs**	**258**	**283**	**246**
hexa-CB	1.4	1.8	2.0	% of *non-ortho*	5	6	7
hepta-CB	0.04	Nd	0.07	% of *mono-ortho*	31	32	28
Total *mono-ortho*	**80**	**91**	**66**	% of *di-ortho*	64	62	65
				TOC-adjusted (ng/g)	**47**	**13**	**11**

• *Non-ortho* CB: di- (no.11-14), tri- (no. 35-39), tetra- (no. 77-81), penta- (no. 126, 127) and hexa- (no. 169). ** *Mono-ortho* CB: 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* CB: 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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References

(1) MacDonald, D.D., Ikonomou, M.G., Rantalainen, A-L, Rogers, H.I., Sutherland, D., van-Oostdam, *J. Environm. Tox. Chem*. **1997**, 19, 479-490.

(2) Macdonald, R.W.; Ikonomou, M.G.; Paton, D.W. *Environ. Sci. Technol.,* **1998**, 32, 331-337.

(3) Ikonomou, M.G.; Sather, P.; He, T.; Crewe, N.; Fraser, T. Organohalogen Compounds, 1998, 35, 33-38, ISBN 91-89192-04-4

(4) Bonn, B. A. *Environ. Sci. Technol*. **1998**, 32, 729-735.

(5) Rose, C. L., McKay, W. A., Ambidge, P. E., *Chemosphere* **1994**, 29, 1279-1292.

(6) Eitzer, B. D. *Environ. Sci. Technol*. **1993**, 27, 1632-1637.

(7) Indian and Northern Affairs Canada. Canadian Arctic Contaminants Assessment Report, **1997**, ISBN 0-662-25704.