COMPARISION OF DIOXIN-LIKE PCBs IN PASSIVE AIR AND VEGETATION SAMPLES SURROUNDING A METAL RECLAMATION INCINERATOR

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Introduction

In 1998 the WHO identified 12 PCBs to be dioxin-like (DLPCB). This list includes 4 coplanar: 77, 81, 126, 169 and 8 mono-ortho: 105, 114, 118, 123, 156, 157, 167 and 189 congeners[1]. Determination of DLPCBs allows results to be converted into TEQ (toxic equivalent quantity of 2,3,7,8-TCDD) values and enables data comparison at very low (sub ppt (pg/g)) levels.

Vegetation and air samples were collected from an area surrounding a metal recovery incinerator[3] in order to assess spatial and temporal trends for DLPCBs stemming from the long term operation of the incinerator. Foliage samples were harvested in September (1999 – 2 sets, 2000 to 2003) from maple and ash trees surrounding the incinerator at varying distances (see Figure 1). Mature tree leaves are exposed to atmospheric deposition of PCBs for about 4 months (June to September) and the levels determined in foliage are representative of DLPCBs in the atmosphere surrounding each tree.

Additionally, a passive air sampling technique based on the sorption of gaseous pollutants on XAD-2 (a styrene-divinylbenzene co-polymer) resin was used for measuring long-term average gas-phase concentrations in the area surrounding the incinerator[2]. Ten passive samplers were placed adjacent to trees previously sampled for DLPCBs[3] at locations presented in Figure 1. The deployment period, lasting approximately 4 month (June to September 2003), corresponds to the time that mature leaves were present on the adjacent trees. Four other air samplers were placed close to a main highway in Toronto in order to compare the concentration of DLPCB in the urban area with the concentration in the rural area surrounding the incineration facility.

Passive air samplers allow the characterization of the gaseous distribution of DLPCBs in the atmosphere. The advantages of using this technique are that it is independent of the atmospheric conditions (winds, precipitation, UV exposure) and can be used for sampling year round. Atmospheric deposition is expected to control the concentration of DLPCB in plant foliage.

Methods and Materials

The passive air sampler consists of a long thin cylinder made of a fine stainless steel mesh filled with XAD-2 resin placed in a protective sampling shelter with an opening at the bottom. Analyses of vegetation samples and passive air samples for WHO DLPCBs was carried out using Ontario Ministry of the Environment method E3418[4]. Briefly, 6 grams of wet vegetation sample was extracted in a Soxhlet extractor using 20% Acetone/Hexane as solvent. Extracts were subjected to a sequential cleanup using a sulphuric acid wash followed by modified silica column, alumina, and 5% Amoco PX21/ activated silica columns. XAD-2 from the air sampling container was transferred to a Soxhlet thimble and extracted with Toluene followed by a 3-stage chromatographic cleanup procedure similar to the vegetation extract. HRGC/HRMS analysis was done by SIM with a Micromass Autospec HRMS equipped with a Hewlett-Packard 6890 GC and a 0.18 mm i.d. 40 m DB-5 column (0.18 μm stationary phase)[4].

Results and Discussion

In-plant samples were taken over a 3 day period: Feb 1 – 3, 2000. PCBs were present at high levels in the feed stock materials used in incinerator (up to 30,000 ppm). PCBs detected in the feed stock materials resembled Aroclor 1242. DLPCBs levels in the ash samples were under 1pg/g TEQ, in the waste water under 0.15pg/L TEQ and in the stack train samples approximately 3pg/g TEQ. Total PCBs in the burned ballasts was less than 0.4ng/g. These values indicate that the PCB levels are reduced significantly during the incineration process and TEQ values are well below respective guidelines for these matrices. Particle emission levels from the stack were determined to be 22 mg/s[6] and are most likely the source of PCBs in surrounding vegetation.

DLPCB concentrations in passive air and vegetation samples surrounding the incinerator are listed in Table 1. Results are reported in 4 groupings by varying distance from the incinerator stack. Averages for all sites are also reported. Site 4 is closest to the incinerator and clearly shows the highest value. This site is about 100 m from the stack and the sampling station closest to the expected point of impingement. Its concentration is significantly different from the mean (99% confidence interval) of the 16 stations and more than 10 times higher than the average of the 3 control sites (14 and 15a & b). The congener pattern in vegetation for Site 4 resembles Aroclor 1242 and is similar to the patterns observed in the in-plant samples. TEQ- DLPCBs concentrations in the vegetation samples collected at Site 4 in 2002 were lower in 1999. A rain event occurring a few days before the collection date in 2002 most likely washed particulate matter from vegetation reducing contributions from particulates bound DLPCBs. In 2003, an increase in the TEQ-DLPCB concentrations occurred for all locations around the incinerator site compared to previous years. This may be due to drier weather in 2003.

Duplicate passive air samplers were deployed at 5 locations around the incinerator (sites 2,3,4,10,15) in 2003. The TEQ-DLPCB (total pg) obtained are included in Table 1. Contaminants are adsorbed by the XAD-2 resin from the atmosphere via diffusion in the vapor-phase[5]. The shelter design of the passive air sampler does not allow large aerosol particles to settle on the XAD medium. DLPCB concentrations in units of pg/g TEQ in air samples were slightly higher than the concentrations in vegetation samples collected at the same locations. Fugitive emissions from feed material storage might be responsible for higher levels in passive air samples. The PCB uptake in

the passive air samplers is independent of wind, precipitation and UV light exposure[7] and might also explain the difference between the results in passive air sampler and vegetation samples. The congener composition in passive air samples for Site 4 is very similar to the pattern found in vegetation. The DLPCBs concentration for air samplers in the urban area close to the highway are presented in Table 2. The concentrations of DLPCB in air samples collected in the rural area around the incinerator and in the urban area close to the highway are very similar.

There is a general trend of decreasing concentrations with increasing distance from the incinerator except for sites 10, 12 and 13. These 3 sites are situated to the south of the incinerator and may be elevated due to a secondary source. Site 12 shows an increase in the concentration of DLPCBs in 2003 which suggests that the secondary source may have increased its emissions. There are subtle differences in congener patterns between these samples, but the differences are too small to reach any conclusions or identify an alternate source. Temporal trends could also not be established during the current sampling period.

Table 1: Analytical Results for Vegetation and Air Samplers (Data in pg/g TEQ – DLPCBs for vegetation and total pg TEQ for air samples)

Site	**1** (Maple)	**4** (Ash)	**5** (Ash)	**6** (Maple)	**2** (Maple)	**3** (Maple)	**7** (Maple)	**9** (Ash)
Year	< 250 m from incinerator				> 250 m < 500 m from incinerator			
1999a	0.21	1.55	0.25	0.015	0.16	0.37	0.12	0.25
1999b	N/A	1.54	0.34	N/A	N/A	N/A	N/A	0.27
2000	0.088	1.11	0.2	0.25	0.14	0.15	0.061	0.2
2001	0.19	1.87	0.13	N/A	0.072	0.072	0.083	0.072
2002	0.183	0.893	0.124	N/A	0.068	0.149	0.222	0.172
2003	0.221	4.100	0.324	0.217	0.144	0.274	0.064	0.221
Average	0.178	1.844	0.228	0.161	0.117	0.203	0.110	0.197
Passive Air Samples	N/A	6.769	N/A	N/A	0.277	0.366	N/A	N/A
	N/A	7.580	N/A	N/A	0.204	0.252	N/A	N/A

Site	8 (Maple)	10 (Maple)	11 (Maple)	12 (Ash)	13 (Ash)	14 (Ash)	15a (Ash)	15b (Maple)
Year	> 500 m < 1 km from incinerator				> 1 km from incinerator			
1999a	0.31	0.7	0.2	0.7	0.16	0.17	0.31	N/A
1999b	N/A	0.63	N/A	N/A	0.19	0.07	0.16	N/A
2000	0.12	0.32	0.063	0.28	0.071	N/A	0.12	0.065
2001	0.14	0.067	0.15	0.47	0.47	0.048	0.17	0.13
2002	0.178	N/A	0.111	N/A	N/A	N/A	0.179	0.114
2003	0.234	0.066	N/A	1.081	0.402	0.366	0.265	0.351
Average	0.196	0.357	0.131	0.633	0.259	0.164	0.201	0.165
Passive Air Samples	N/A	0.134	N/A	N/A	N/A	N/A	0.242	
	N/A	0.144	N/A	N/A	N/A	N/A	0.205	

N/A – not analyzed, not sampled.

Table 2: Analytical results for DLPCBs in air samplers in urban area close to highway (total pg-TEQ). Passive air samplers were used in 2003 only.

	<10m from Hwy		>100m <300m from Hwy	
Site	**1**	**2**	**3**	**4**
DLPCB TEQ (Total pg/g)	0.203	0.183	0.150	0.160

TEQ values were determined using ½ detection limit for non-detected congeners.

Conclusions

Air and foliage samples can be used to identify and monitor sources of DLPCBs contamination at sub pg/g TEQ levels. Patterns can be matched with those characteristic of Aroclor mixtures and patterns specific to weathered or mixed PCB sources. On a g/g basis the PCBs levels in air samples proved to be slightly higher than those in vegetation. PCBs are adsorbed by the XAD-2 resin through diffusion from the atmosphere gas phase into the sampling medium. Uniform construction of the passive air samplers facilitates comparability between different locations and time periods. Passive air samplers proved to be a rugged method to monitor PCBs levels in the atmosphere (independent from the weather conditions). Plant foliage is a natural passive sampling medium with an uptake capacity dependant on the species, location, season and atmospheric conditions (precipitation, winds, UV light exposure). Atmospheric deposition of the particulate matter on the plant foliage contributes to the concentration of the DLPCB in the vegetation sample.

Determination of the DLPCB in the passive air samplers and vegetation samples proved to be two complimentary techniques for determination of DLPCB in the vapour phase and particulate matter present in the atmosphere.

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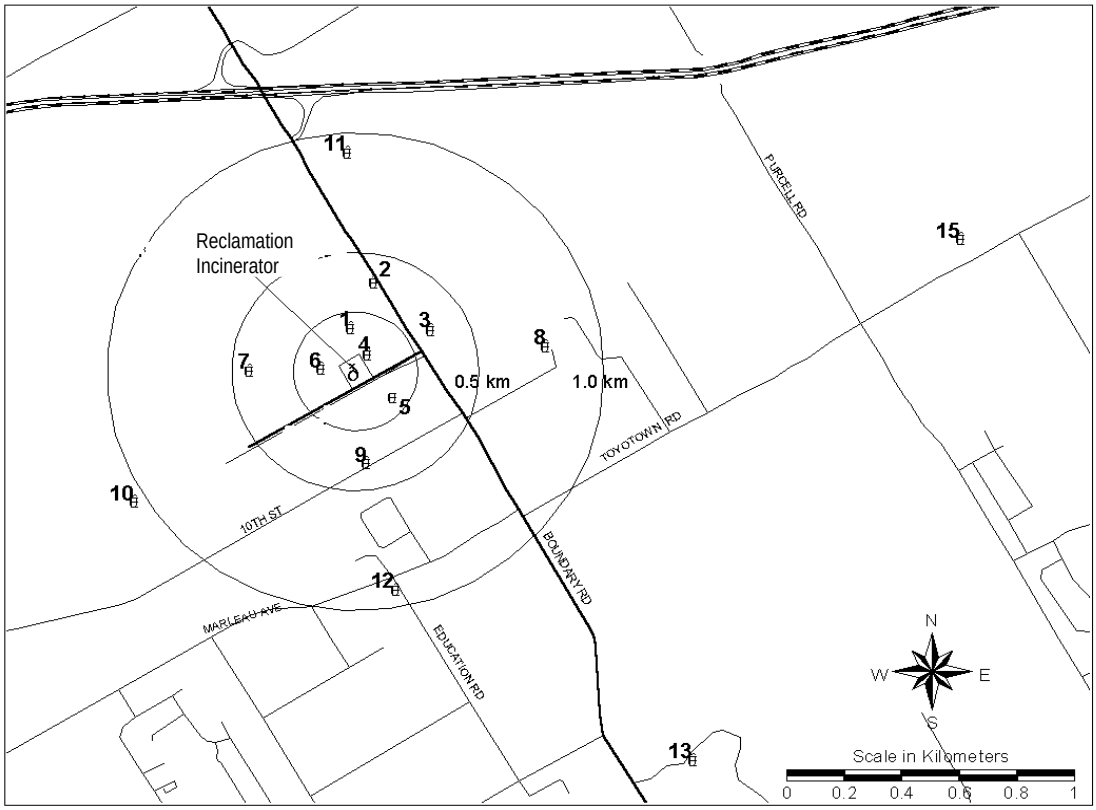

Figure 1: Vegetation Sampling Locations
***** Site 14 is located to the East (left) of Figure 1.