

LEVELS IN BIOTIC COMPARTMENTS

ANALYSIS OF DIOXIN-LIKE PCBs IN VEGETATION SAMPLES SURROUNDING A METAL RECLAMATION INCINERATOR

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Introduction

Polychlorinated biphenyls (PCBs) have been used in numerous applications since 1929¹. The extensive accumulation of PCBs in the environment was not discovered until 1966 when they were identified as interfering compounds in the analysis of DDT². This group of chemicals consists of 209 congeners ranging from mono to deca chloro substitution. Initial analytical techniques used technical PCB mixtures such as Aroclors to identify and quantify PCBs in environmental samples. As more toxicological data became available, it was determined that some congeners were considerably more toxic than others. Congener specific methods were developed in order to identify the more toxic congeners and to more accurately quantify aged (weathered) samples. The co-planar congeners with 4 or more non-ortho substituted chlorines exhibit strong dioxin-like characteristics and are considered the most toxic PCB congeners. Initially, it was thought that these dioxin-like PCBs (DLPCBs) were not present in Aroclor mixtures or at concentrations that were too low to be of any toxicological significance.

In 1998 the WHO identified 12 PCBs to be dioxin-like (DLPCBs - non-ortho: 77, 81, 126, 169 and mono-ortho: 105, 114, 118, 123, 156, 157, 167 and 189)³. Determination of DLPCBs allows results to be converted into TEQ (toxic equivalent quantity of 2,3,7,8-TCDD) values at very low (sub ppt (pg/g)) levels. This method uses GC/HRMS with isotope dilution and produces results that are more accurate than Aroclor matching or congener methods and can be used as an indicator of source contamination⁴. PCB results reported as TEQ of 2,3,7,8-TCDD are a more accurate representation of toxicity because the result determined is relative to one specific toxicological process, the binding of these compounds to the aryl hydrocarbon receptor (AhR)⁵.

A survey of vegetation samples surrounding a metal recovery incinerator was conducted to assess spatial and temporal trends for DLPCBs from the long term operation of the incinerator. The incinerator initially processed both mercaptan tanks and light ballasts with components containing less than 50 ppm PCBs. Light ballasts containing up to 30,000 ppm PCB were burned beginning in February 2000. The plant had high level PCB containment facilities to eliminate fugitive emissions of PCBs. Vegetation samples were harvested in September (1999 – 2 sets, 2000 and 2001) from Maple and Ash trees surrounding the incinerator at varying distances (see Figure 1). Tree leaves are exposed to atmospheric deposition of PCBs for about 5 months (May to September) and the levels determined in vegetation samples are representative of DLPCBs in the atmosphere surrounding each tree.

The metal reclamation furnace uses a natural gas fired primary burner with heat input of 1.58×10^6 kJ/hr and a natural gas fired afterburner with heat input of 3.17×10^6 kJ/hr. Exit gasses are treated by an Anderson 2000 design packed column scrubber with a polypropylene Intalox saddle packing to a height of 1.69 m. The pressure drop across the scrubber is 1.5 KPa with a caustic recirculation rate of 283 L/min. The maximum gas flow rate of 2.16 m³/s was exhausted through a stack with an exit diameter of 0.3 m and height of 15.5 m above grade. Combustible materials within electric equipment, mainly light ballasts, were burned in the primary chamber. Products of combustion passed to the secondary/mixing

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chamber and high temperature afterburner. Up to 1000 kg of electrical equipment that contained up to 30% combustible materials were placed in steel baskets and loaded by forklift into the preheated furnace. The afterburner maintained gas temperature at 1200°C with at least 3% excess air for minimum of 2 s. The processing time for 1000 kg loads was about 3.5 hr.

Methods and Materials

Analyses of vegetation samples for WHO DLPCBs was carried out using Ontario Ministry of the Environment method E3418⁶. Briefly, 6 grams of wet sample were cut into approximately 1 cm squares. Samples were spiked with ¹³C-labelled surrogate dioxin and PCB standards and extracted in a Soxhlet extractor using 20% acetone/hexane as solvent. Extracts were subjected to a sequential cleanup using, sulphuric acid wash followed by a modified silica column, an alumina column, and a 5% Amoco PX21/ activated silica column. Analysis by HRGC/HRMS was carried out using SIM with an Micromass Autospec HRMS equipped with a Hewlett-Packard 6890 GC and a 0.25 mm i.d. 60 m DB-5 column (0.25 mm stationary phase).

Plant process samples were analysed for PCBs using the above method (E3418 with toluene as extraction solvent) and an Aroclor matching procedure, MOE method E3153⁷. In method 3153, samples were extracted with acetone/hexane in a Soxhlet apparatus. One/ten ml of a 100 ml extract of unburned/ burned ballasts were cleaned using silica and florisil (1% benzene/hexane as elution solvent) and analysed on a HP 5890 GC with a DB-5, 30 m, 0.53 mm i.d. 1.0 mm stationary phase column with ECD detection.

Results and Discussion

Analytical results for the in-plant samples are summarized in Table 1. In-plant samples were taken over a 3 day period: Feb 1 – 3, 2000. High levels of PCBs were present in the feed stock materials to the incinerator (up to 30,000 ppm). The Aroclor detected in the feed stock materials resembled Aroclor 1242. Ash, waste water and stack train samples analyzed for DLPCBs show that 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 stack⁸ were determined as 22 mg/s and are most like a source of PCBs in surrounding vegetation.

Analytical results for the vegetation samples surrounding the incinerator are listed in Table 2. 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 is the highest value. This site is about 100 m from the stack and the closest sampling station to the expected point of impingement. This result is significantly different from the mean (99% confidence interval) of the 16 results reported and more than 10 times the levels detected for the average of the 3 control sites (14 and 15a & b). The Aroclor pattern for Site 4 resembles Aroclor 1242 and is similar to those detected in patterns observed in the in-plant samples.

There is a general trend in decreasing levels of concentration 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. There are subtle differences in congener patterns between these samples, but the differences are too small to form any conclusions identifying an alternate source. Temporal trends could also not be established during the current sampling period.

Conclusions

DLPCBs can be used to identify and monitor sources of PCBs contamination in vegetation samples at sub pg/g TEQ levels. Patterns can be matched with those characteristic of Aroclor mixtures or other PCB mixtures and patterns specific to weathered or mixed PCB sources.

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Table 1. Analytical Results for In-plant Samples

Sample Matrix	Results (TEQ from DLPCBs only)	Number of samples (N)
Unburned Ballasts	Total PCB: 18.2 % by weight	15
Tar (Inside Ballasts)	Total PCB - Range: 465 – 8700 ug/g	15
Process Waste Water	Total PCB - Range: 50 – 200 ng/L DLPCBs – 0.15 pg/L TEQ	3 1
Burned Ballasts	Total PCB: < 0.4 ng/g	15
Ash	Total PCB: < 20 ng/g DLPCBs – Range: 0.14 – 0.98 pg/g TEQ	15 3
Stack samples	Active trains: Range: 2.7 – 4.9 pg/m ³ TEQ (DLPCB) Blank train: 1.9 pg/m ³ TEQ (DLPCB)	3 1

Table 2. Analytical Results for Vegetation Samples (Data in pg/g TEQ – DLPCBs only)

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	0.20	0.25	0.14	0.15	0.061	0.20
2001	0.19	1.87	0.13	N/A	0.072	0.072	0.083	0.072
Average	0.163	1.52	0.230	0.131	0.124	0.197	0.0878	0.198

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			
1999 ^a	0.31	0.70	0.20	0.70	0.16	0.17	0.31	N/A
1999b	N/A	0.63	N/A	N/A	0.19	0.070	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
Average	0.193	0.430	0.137	0.483	0.224	0.0960	0.190	0.0940

N/A – not analyzed, not sampled.

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

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

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