

The Levels of PCDDs and PCDFs in Soil Samples Collected From Conservation Areas Following Bush Fires

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Introduction

Following large scale bush fires, soil samples were collected from burnt and unburnt areas of the Brisbane Waters National Park and the Muogamarra Nature Reserve. These parks are conservation areas located 40 kilometres north of the central business district of Sydney, Australia (Figure 1). They comprise an area of over 12,000 hectares of rolling sandstone predominated by open woodland vegetation. The bush fires, aided by consistently hot, dry and windy weather, continued in the conservation areas for over two weeks in late January 1994, burning a major proportion of the vegetation.

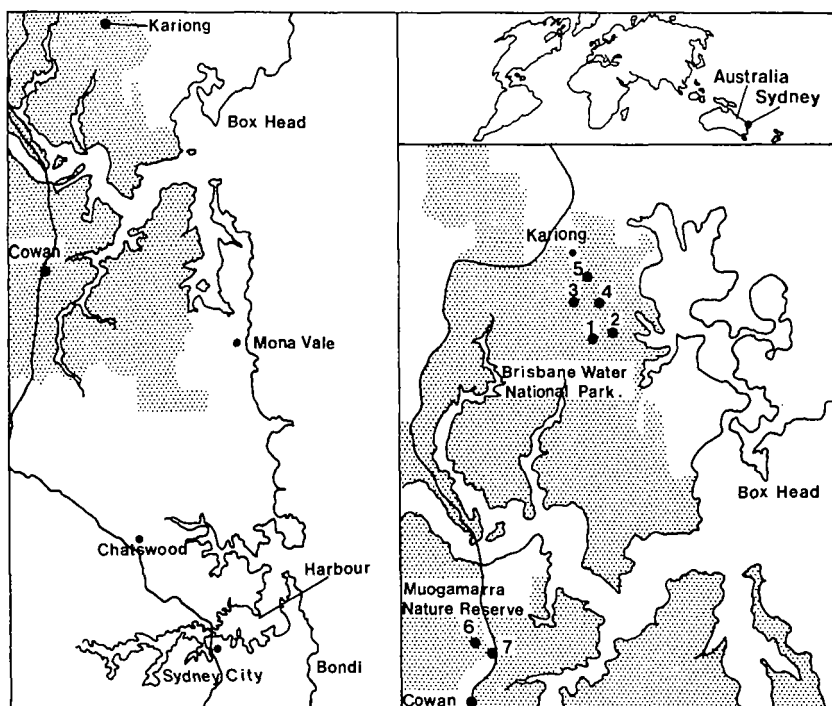


Figure 1. Sampling Locations

A single sample was also collected from a high traffic volume roadside intersection in the Sydney metropolitan area (population four million). All of the samples were analysed for PCDDs and PCDFs, chloride and lead.

Sampling

The samples were collected six weeks after the bush fires were extinguished. The approximate locations of the conservation area sampling sites are indicated on Figure 1. The Sydney metropolitan area sampling site was located approximately 10 kilometres south of the central business district. Further details of the sampling site locations are given in Table 1.

Table 1. Sampling Locations

Site Identification	Sampling Location and Description
Site 1 300 m	Burnt area, 300 m from Woy Woy Road, near Staples look-out.
Site 2 100 m	Un-burnt area, over 100 m from Woy Woy road, near Staples look-out.
Site 3 > 300 m	Burnt area, over 300 m from Woy Woy road, near the Bulgandry Aboriginal engraving site.
Site 5 Roadside	Un-burnt area, 5 m from Woy Woy road, before the residential area of Kariong.
Site 6 1 km off road	Burnt area, 1 km from Pacific highway, near the entrance to the Muogammarra Nature Reserve.
Site 7 Roadside	Un-burnt area, 5 m from Pacific highway, near the entrance to the Muogamarra Nature Reserve.
Site 8 Cnr ANZAC and Maroubra	Un-burnt high traffic volume area in metropolitan Sydney. Corner of ANZAC Pde and Maroubra Rd.

The samples were collected by taking 2 cm deep cores of the surface soil. Four cores were collected from each sampling site at points from the corners of areas about 30 m long and 10 m wide. Any stones larger than 2 cm were discarded. The four cores from each sampling site were then composited to provide a single sample.

Analysis

The samples were dried to constant mass at 65 °C. Prior to analysis for PCDDs and PCDFs the samples were spiked with a range of ¹³C₁₂-labelled internal standards. The samples were then Soxhlet extracted for 16 hours with toluene. The sample extracts were transferred to hexane and cleaned-up by partitioning with concentrated sulphuric acid. This was followed by a series of solid phase chromatographic separations on

modified silicas, alumina and Carbopak on Celite. The final extract was analysed using a VG70-250s mass spectrometer coupled to an OPUS data system. The mass spectrometer was operated in the electron impact mode, at a static resolution of 10,000.

All 2,3,7,8-substituted PCDDs and PCDFs were determined isomer specifically. The total toxic equivalents of each sample was calculated using the I-TEF values. For isomers present at less than the limit of detection, half the limit of detection value was used in the calculation of the toxic equivalents contributed by that isomer.

The samples were also analysed for leachable lead and leachable chloride. A portion of the sample was shaken for one hour with dilute hydrochloric acid. The dilute acid was filtered and the lead levels determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). A further portion of the sample was shaken for one hour with water. The water was filtered and the chloride levels determined by ion chromatography.

Results

The analytical results are summarised in Table 2. All results are reported on a dry weight basis.

Table 2. Summary of the Analytical Results

Site Description, Designation	PCDDs and PCDFs, Sum †, (TE ‡) (pg g ⁻¹)	Leachable Lead (µg g ⁻¹)	Leachable Chloride (µg g ⁻¹)
Site 1 300 m, (B)	1,310, (2.2)	31	14
Site 2 100 m, (U)	1,050, (3.0)	12	19
Site 3 > 300 m, (B)	27,300, (35.1) 28,200, (38.5)	13	14
Site 5 Roadside, (U)	7,160, (8.7)	18	12
Site 6 1 km off road, (B)	2,030, (3.1)	72	32
Site 7 Roadside, (U)	7,700, (10.0)	94	6.7
Site 8 Cnr ANZAC and Maroubra, (M)	22,300, (42.6)	158	29

(B) = Burnt area (U) = Unburnt area (M) = Metropolitan area

† = Sum of the tetra- to octachlorinated PCDDs and PCDFs.

‡ = Toxic equivalents calculated using I-TEF values.

The site 3 sample was analysed for PCDDs and PCDFs in duplicate. The laboratory blank contained less than 6 pg g⁻¹ of any PCDD or PCDF isomer and had a TE of 1.8 pg g⁻¹, calculated from the limit of detection values and the average weight of the samples. The

laboratory blank contained less than $0.8 \mu\text{g g}^{-1}$ of leachable lead and less than $3 \mu\text{g g}^{-1}$ of leachable chloride.

Discussion

The levels of lead in the conservation area samples varied from 12 to $94 \mu\text{g g}^{-1}$. The single metropolitan area sample contained $158 \mu\text{g g}^{-1}$. A potential source of the elevated level of lead in this high traffic volume area is the emission from motor vehicles using leaded gasoline. The levels of leachable chloride in all of the samples varied over a narrower range, 12 to $32 \mu\text{g g}^{-1}$.

The sums of the levels of PCDDs and PCDFs measured in the unburnt conservation area samples were 1,050, 7,160 and $7,700 \text{ pg g}^{-1}$ (3.0, 8.7 and 10.0 pg g^{-1} I-TEF). The sums of the levels of PCDDs and PCDFs measured in the burnt conservation area samples were 1,310, 2,030 and $27,800 \text{ pg g}^{-1}$ (2.2, 3.1 and 36.8 pg g^{-1} I-TEF). The sum of the PCDDs and PCDFs in the single metropolitan area sample was $22,300 \text{ pg g}^{-1}$ (42.6 pg g^{-1} I-TEF).

A grid survey of 5 cm deep core soil samples collected in Britain gave average results for the sum of the PCDDs and PCDFs of 732 pg g^{-1} in rural and semi-urban samples¹⁾ and $12,010 \text{ pg g}^{-1}$ in urban samples²⁾. All of the conservation area samples had higher levels than the average for the British rural and semi-urban samples. The level for one of the conservation area samples (Site 3, Burnt) was higher than both the Sydney metropolitan area sample and the average for the British urban samples.

The levels of PCDDs and PCDFs in the conservation and Sydney metropolitan area samples were dominated by OCDD. This single isomer contributed 94 - 97 % of the sum of the PCDDs and PCDFs in the conservation area samples and 80 % of the sum of the PCDDs and PCDFs in the Sydney metropolitan area sample. The tetra- and pentachlorinated PCDFs contributed less than 1 % to the sum of the PCDDs and PCDFs in any of the samples. In these samples, the proportion of OCDD is higher, and the proportion of tetra- and pentachlorinated PCDFs lower, than that measured in the emissions to air from a range of combustion sources, including various incinerators³⁾, motor vehicles running on leaded gasoline⁴⁾ and prescribed forest fires⁵⁾.

The levels of PCDDs and PCDFs in ambient air samples collected from the Sydney metropolitan area have been previously reported⁶⁾. The sum of PCDDs and PCDFs varied from 3.7 to 15 pg m^{-3} , with OCDD contributing an average of 72 % of this total. This high proportion of OCDD in the Sydney air samples indicates atmospheric deposition is a potential source of the PCDDs and PCDFs present in the conservation and Sydney metropolitan area soil samples.

The results of this limited survey indicate that bush fires have not had a major impact on the levels of PCDDs and PCDFs measured in conservation area soil samples.

References

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