

EMISSION OF DIOXINS FROM BUSH FIRES IN AUSTRALIA.

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Abstract

Samples from the smoke plumes of 18 field fires across Australia were collected and analysed to assess PCDD/F/PCB emission rates. Emission rates were variable across all fire classes (prescribed, wildfire, and savanna).. The measured emission factors for our forest fires (prescribed and wildfires) and savanna fires averaged 1 ± 0.5 pg TEQ (g C) which translates to approximately 0.5 ug TEQ t⁻¹. PCDDs contributed on average 70% of the emissions (expressed as TEQ), with PCDFs and PCBs contributing a further 20 and 10% respectively. Our results consistently show a congener pattern in which PCDD predominates over PCDF, and in which the higher chlorinated groups are more common than the less chlorinated groups. A major consequence of this congener pattern is relatively low toxicity when compared to emissions from other combustion sources. This data were consistent across 18 measurements at different sites across Australia. In 90% of these samples, the emission factor was less than 3.0 pg TEQ/ (g C) this is much lower than expected emissions based on literature values. The results suggest that the emission factors provided in the UNEP toolkit appear to overestimate emissions from bush fires in Australia.

Introduction

In Australia, a desktop study on dioxin emissions carried out in 1998 estimated that more than 80% of dioxin-like chemicals expressed as TEQ¹ found in Australia are emitted from biomass burning such as bushfires^[1]. This inventory, however, relied on emission factors (EFs) such as those provided by the UNEP^[2] toolkit. Prange et al.^[3] suggested that the role of forest fires as a primary source for dioxin-like chemicals is likely to be overestimated. In experiments that measured PCDD/F levels in fuel, soil and smoke of open chamber forest fire simulations they found no increase in the mass of Σ PCDD/F or OCDD pre and post combustion. Furthermore the study suggested that forest fires may be a key process for the redistribution of dioxin-like chemicals in Australia and elsewhere.

In experiments that compared emission factors from sugarcane in laboratory chamber burns and field burns Meyer et al. ^[4], found that emission factors from laboratory burns were substantially higher than those determined from field burns. They also noted that in laboratory burns, PCDFs contributed about 52% of the TEQ, whereas in the field burns PCDFs contributed only 8% to the overall TEQ. In studies reporting EFs for agricultural and field fires Gullett and Touati^[5, 6] found EFs for wheat and rice stubble (0.5 (μ g TEQ)/(t fuel)) similar to those from Australian cane fires (0.8 (μ g TEQ)/(t fuel)), however, the low dioxin to furan ratios are unlike our measurements.

For dioxin-like chemicals, the emission factors that are usually applied for biomass and agricultural fires have been derived from laboratory combustion experiments, and an uncertainty exists as to the applicability of emission factors derived from laboratory combustion experiments to field fires, (ie. emission factors may be over estimated).

¹ WHO TEQ

This study reports the results of field experiments on the emissions of dioxin-like chemicals from bush fires across Australia to determine emission factors from fires under natural conditions, covering a range of fuels and climatic and geo-botanic regions.

Materials and Methods



Figure 1. Locations of the 18 field burns sampled for PCDD/PCDF.

Field sampling Methodology

High-volume smoke sampling units were designed and constructed by CSIRO. These units could be mounted on the tray of a utility vehicle and located within the under canopy smoke plume as close to the fire front as was safe (usually 30 to 40 m). The time window available in which to collect the sample is dictated by the rate of spread of controlled (prescribed burns), the duration of crop residue fires or safety in the case of wildfires. Typical feasible sampling duration is 1-2h.

Air was drawn through a 1 - 4 m long snorkel at 0.5 to 1 m³/min. The PCDD/PCDF sampling head comprised an open face filter for particulate phase followed by a 130 mm diameter gas trap with polyurethane foam plugs (PUF) surrounding an XAD-2 layer containing 40 g resin. Flow rate and CO₂ concentration of the sampled smoke passing through the trap were measured and logged continuously and integrated throughout each sampling period, to determine when sufficient sample had been trapped prior to analysis. Analysis of the 29 PCDD/PCDF and dioxin-like PCB congeners (WHO 1998), and the PCDD/PCDF homologue groups collected on the filter and adsorbent (combined) was carried out at NMI Laboratories using isotope dilution technique and high resolution mass spectrometry based on US- EPA methods 1613B, 1668A and T09A.

Results and Discussion

Dioxin like chemicals were detected in smoke from all field burns and the calculated emission factors (EF) expressed on a carbon basis ranged from 0.39 pg TEQ/g C to about 5.8 pg TEQ/g C (Table 1). Non detects were

set to ½ MDL. The mean EF was 1 ± 0.5 pg TEQ/g C which translates to approximately $0.5 \mu\text{g TEQ t}^{-1}$ and for 90 % of all measured burns the EF was < 3 pg TEQ/g C. PCDDs contributed on average 70% of the emissions (expressed as TEQ), with PCDFs and PCBs contributing a further 20 and 10% respectively. The measured emission factors for our forest fires (prescribed and wildfires) and savanna fires fall at the lower end of the range suggested by the review^[1]. These data were consistent across 18 measurements at different sites across Australia and emissions are much lower than expected based on literature values.

Total emission factors² ranged from 0.05 to $2.9 \text{ pg TEQ (g fuel)}^{-1}$ as observed in the field burns for total PCDD/PCDF and (PCBs) with means of 0.9, 1.2, and $0.5 \text{ TEQ (g fuel)}^{-1}$ for total PCDD/PCDF for prescribed fires, savanna fires, wildfires, respectively. Emission factors observed for the two wild fires tested were very low, and at variance with previous speculation that high temperature fires might be large emitters of dioxins^[7]. The measurements were made in the dense smoke plume during fires in NE Victoria, (samples 8&9) the two integrated weekly samples peaked at 25 and 30 times the weekly average of $0.31 \text{ fg TEQ m}^{-3}$ preceding the fire.

Table 1. Toxic equivalent emission ratios, in picograms per gram carbon, for dioxins, furans and PCBs from field-burn samples.

Location	Sample #	Fire type	PCDDs	PCDFs	PCBs	Total TeQ
Manjimup	1	Forest	1.33	0.04	0.27	1.64
Northumberland	2	Forest	0.80	0.24	0.04	1.08
Yardup Block	3	Forest	0.25	0.04	0.10	0.39
Mack Block	4	Forest	0.36	0.07	0.22	0.65
Andrew Block	5	Forest	0.23	0.05	0.06	0.34
Ovens	6	Forest	0.12	0.02	0.06	0.20
Mt Beauty	7	Forest	1.19	0.24	0.20	1.62
Barkstead	8	Wildfire	1.07	0.16	0.10	1.34
Cobaw	9	Wildfire	1.12	0.57	0.29	1.98
Bullanangarook	10	Forest	1.37	0.37	0.16	1.90
Muskvale	11	Forest	0.45	0.46	0.20	1.11
Griffith Uni	12	Forest	2.56	0.24	0.36	3.16
Binya ville	13	Woodland	1.80	0.10	0.07	1.97
Seaview Range	14	Woodland	3.16	1.82	0.33	5.31
Samford State Forest & Mt Nebo	15	Woodland	1.51	0.58	0.08	2.18
Namambu Ck -Run 2	16	Savanna	0.32	0.11	0.03	0.45
Namambu Ck -Run 3	17	Savanna	0.42	0.05	0.06	0.53
Berrimah- sample	18	Savanna	5.35	0.31	0.12	5.78

² To obtain estimates in terms of fuel, we assume that the carbon content of the fuel is 50%. Results are not corrected for moisture content.

This data supports our field measurements and confirms that these extensive and highly intense wild fires did not produce substantial emissions of PCDD/F in the smoke plumes. Levels of PCDD/F in field samples were typically only 2 to 3 orders of magnitude greater than the concentration recorded at the ambient measurement site at comparable times. The PCB concentration in the smoke were also generally two orders of magnitude greater than the concentrations found in ambient air, although, on occasion some dioxin congeners and PCB species were close to ambient. Previously, wildfires in the forests of southern Australia were thought to be large sources of PCDD/PCDF, our study indicates that they are relatively low emitters. The previous estimate of emissions outside the savanna regions is between 2.3 and 23 times larger than the new estimate. We conclude, therefore, that emissions of PCDD/PCDF from bushfires in Australia were probably grossly overestimated in the past, particularly in southern Australia. The number of observations was too small to demonstrate significant differences between classes of field burns; however, one significant and unexpected outcome was that when individual wildfires and prescribed burns were compared, prescribed burns were the stronger PCDD emitters.

PCDDs formed 70% of the TEQ, with PCDFs and PCB contributing a further 20 and 10% respectively. The PCDD/F homologue profiles showed some trends, with an increase in the contribution of OCDD particularly in samples collected from Queensland and the Northern Territory. It is however still unclear whether the higher emission of OCDD is due to the presence of the OCDD in the first place or whether specifics related to the fuel or process result in a shift in the emission profile. Congener profiles in our field measurements particularly from SE QLD were consistent with published field measurements from prescribed fires and soil congener profiles. Our results consistently show a congener pattern in which PCDD predominates over PCDF, and in which the higher chlorinated groups are more common than the less chlorinated groups. This pattern appears in heated soils, in fuels, and in emissions to the atmosphere^[4]. The pattern is observed in studies with such totally independent experimental and sampling methodologies, that the possibility that it is an artifact seems very unlikely.

Acknowledgement

EnTox is a partnership between Queensland Health and The University of Queensland.
This project was funded by the Australian government Department of the Environment and Heritage.

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