Measurement of Dioxin Emissions in Australia.

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Introduction

Emissions from biomass burning are a major component of the global carbon cycle. Estimates of the global area of forest burned range from 170 Mha to 320 Mha from which between 1400 Tg and 1800 Tg of carbon are emitted (Kasischke and Penner, 2004). Australia contributes approximately 10% of this emission. The proportion of the carbon emitted in the form of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF), collectively known as dioxins, remains a topic of concern and investigation.

That fires are a major source of dioxins is not in dispute. In Australia, a desktop study on dioxin emissions carried out in 1998 estimated that more than 80% of dioxin-like chemicals expressed as TEQ found in Australia are emitted from biomass burning such as bushfires (EA, 2002). This inventory, however, relied on emission factors (EFs) such as those provided by the UNEP toolkit (UNEP, 2001), in which the recommended emission factors were sourced from measurements from experiments using combustion chambers and combustion rooms. These EFs varied by a factor of more than 20, and consequently the total dioxin emissions were highly uncertain. Taking the upper and lower end of the range EA (2002) reported that bushfires emit between 70g TEQ and 1700 g TEQ.

There are some indications that emission factors for Australian forests could fall at the lower end of the range. In experiments that measured PCDD/F levels in fuel, soil and smoke of open chamber forest fire simulations Prange et al. (2003) found no increase in the mass of dioxin following combustion. This group also measured the dioxin content of bushfire smoke sampled in the field and found the concentrations to be low, and dominated by the higher chlorinated congeners,

particularly OCDD (Prange et al, 2002). The comprehensive studies of (Gullett and Touati, 2003a, 2003b) also report low emission factors for wheat and rice stubble combustion of 0.5 µg TEQ (t fuel)$^{-1}$ however EFs for pine litter ranged from 1 to 56 µg TEQ (t fuel)$^{-1}$. The congener patterns of the latter were also different from the patterns, observed by Prange et al. (2003) with the less chlorinated furans forming a significant fraction of the emissions.

These issues led to a more comprehensive measurement campaign in Australia. The measurement programme concentrated on sampling in the field at a range of low intensity prescribed fires conducted for fuel reduction in forests, and some high intensity forest wildfires, and savanna grassland fires. The focus on field measurements was based on the difficulty in defining and implementing in a laboratory environment the combustion patterns observed in the field, and the possibility that factors such as soil heating may also influence the nature of the emissions. Nevertheless some laboratory studies were undertaken focusing on crop residues which are generally difficult to sample in the field.

Fires in Australia

Biomass burning in Australia has been classified for National inventory purposes by activity and by State. The four fire classes are wildfire, prescribed fires (generally for fuel reduction, but also slash removal following logging, and some other minor cases), savanna fires, which include fires of all classes in the savanna woodlands of tropical Australia, the arid zone woodlands and grasslands, and the temperate zone grasslands, and agricultural residue burning, principally cereal stubble and sugar cane). On average approximately 10% of the land area of Australia is exposed to fire each year. The distribution of the fires greater than 400 ha in area is shown in Figure 1.
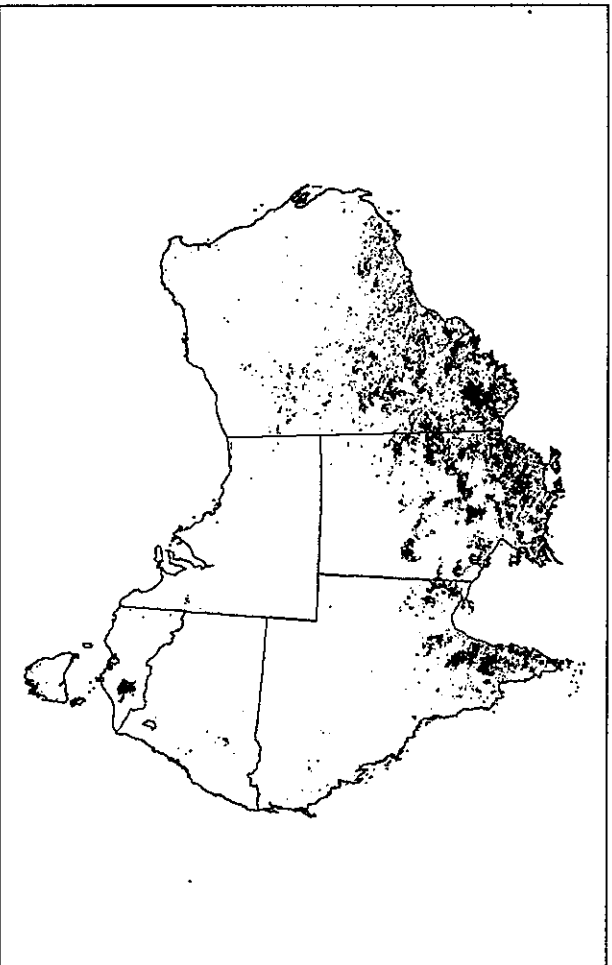
Figure 1 Distribution of fires in Australia for the inventory year 2007

Most of the area (approximately 95%) and most of the carbon emissions (77%) are due to savanna burning. While wildfires are more intense and destructive, their contribution to emissions is relatively minor (14%). Low intensity prescribed fires contribute 3% and crop residue burning accounts for the remaining 6%. This distribution poses a major challenge for comprehensive sampling. Most of the burning occurs in extremely remote regions where access is difficult and expensive. Wildfires pose a major safety risk, and access to the fire front is generally restricted by the incident controllers. Crop residue fires, like grassfires, are rapid and intense and in many cases the plume rises beyond the reach of ground-based sampling. Prescribed fires, however, are tractable because they are closely managed by fire crews. Nevertheless, the objective was to measure emissions from all these classes of fires, and to the extent practicable and possible a sampling strategy was designed to measure emissions from all these classes.

Measurement methodologies

Emission factors of trace gases are usually measured using a dual tracer method. This is described in detail in Andreae and Merlet (2001). In brief, the ratio of emissions of the chemical species of interest (Ei) to the emission of a quantifiable trace (in our case fuel carbon, Ec) is equal to the ratio of the increase in their concentrations above background in the smoke plume, i.e.

$$E_i/E_c = ([i] - [i]_{amb}) / ([c] - [c]_{amb})$$

The atmospheric concentration of pyrolised fuel carbon is the total of $\Sigma C = CO_2 + CO + CH_4 + $ volatile organic compounds + particulate C. In most cases more than 90% of the emission is CO_2 and therefore CO_2 is a good surrogate for ΣC. The emission ratio is equivalent to the EF expressed relative to fuel carbon. The carbon content of biomass fuels ranges from 0.4 to 0.55, averaging approximately 0.5, therefore the EF on a fuel carbon basis is approximately two times the EF relative to fuel mass.

High-volume smoke sampling units were designed and constructed by CSIRO to sample a sufficient volume of the smoke plume to collect an analyzable mass of dioxins. These units could be mounted on the tray of a utility vehicle and located within the smoke plume as close to the fire front as was safe. 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 CO_2 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 homologue groups collected on the filter and adsorbent (combined) was carried out at National Measurement Institute congeners (WHO 1998), and the PCDD/PCDF and dioxin-like PCB

Laboratories in Sydney using isotope dilution technique and high resolution mass spectrometry based on US- EPA methods 1613B, 1668A and T09A.

The sampler was deployed in the field campaign covering 3 savanna fires, 2 wildfires, 13 prescribed fires and 2 cane fires in the locations shown in Figure 2.
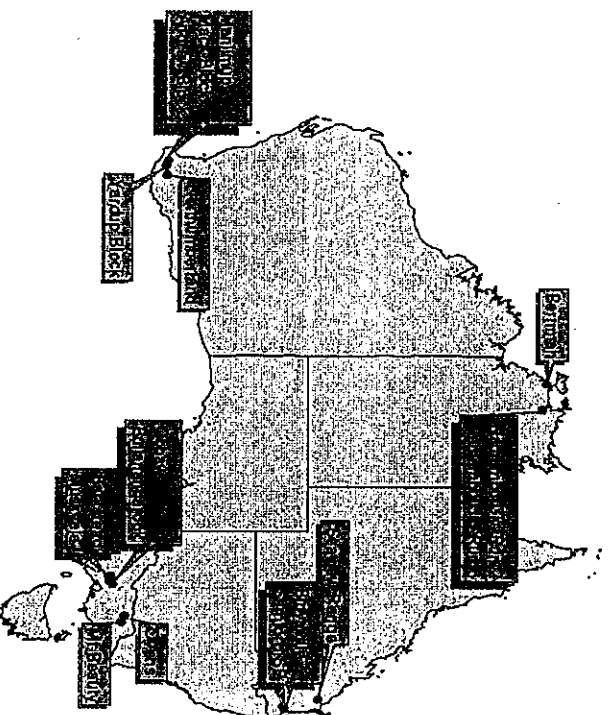

Figure 2   Location of the field measurement sites.

The sampler was also deployed in laboratory tests. These were conducted in a test facility designed for measuring fire behaviour in buildings, but which was easily adapted for burning biomass fuels in a manner approximating the field situation in which a fire front propagates across a bed of fuel. The combustion chamber was an open ended corridor, 10m long, 1m wide and 2m high lined with fibro-cement sheeting. The smoke vented into an exhaust hood where the dioxin sample was collected. Nineteen laboratory tests were conducted using cereal straw, a native grass fuel from the savanna woodlands near Darwin, NT, sugar cane residue and

fine fuel collected from the floor of a forest near Barkstead, 100km west of Melbourne.

Results

Field measurements

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. The data are summarized in Table 1. The mean EF was 1 ± 0.5 pg TEQ/g C which translates to approximately 0.5ug 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 (EA, 2002). These data were consistent across 20 measurements at different sites across Australia and emissions are much lower than expected based on literature values.

Table 1. Emission factors for dioxins (PCDD), Furans (PCDF) and coplanar PCB expressed relative to emitted fuel carbon

	Emission Factor, (pg TEQ)/(g C)				
	Cane	PF	WF	SF	
PCDD	1.8	1.2	0.65	2.0	
PCDF	0.14	0.36	0.13	0.16	
PCB	0.07	0.18	0.13	0.07	
Total	2.0	1.8	0.9	2.3	
Stdev	1.3	1.3	1.0	3.1	

† PF: Prescribed fires; WF: wildfire; SF: Savanna woodland fire.

Total emission factors ranged from 0.05 to 2.9 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 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 (EA, 2002). There is additional evidence supporting

these wildfire data. In a companion study, ambient measurements were made in the dense smoke plume 100 km downwind of 2003 wildfires in NE Victoria (Gras and Mueller, 2004). In these, the two integrated weekly samples of particulate matter peaked at 700 μg m^{-3}, confirming the protracted impact of a concentrated smoke plume with a corresponding peak in non-salt potassium concentration confirming that the particulate matter was predominantly from biomass combustion. However the ambient dioxin concentration measured during this period of 0.3 fg TEQ m^{-3} was less than the background air concentration observed in the preceding months. Therefore the wildfire smoke plume was extremely low in dioxin content.

The emission profiles of all classes for fires were dominated by PCDD which contributed between 75% and 92% of total mass emissions. The fully substituted dioxin, OCDD, accounted for 32%, 43% and 80% of the total PCDD/PCDF mass emitted from prescribed fires, savanna fires and cane fires, respectively, but was a less significant component of wildfire emissions. The other dioxin groups TCDD, PeCDD, HxCDD and HpCDD comprised 11%, 4% 10% and 11%, respectively, of total emissions averaged across all fire classes. In contrast, the only significant furan group observed in the smoke was TCDF, which accounted for approximately 19% of PCDD/PCDF mass emissions.

While OCDD is the dominant toxic congener in terms of mass, its TEF is very low (0.0001) and, consequently, in terms of toxicity the PCDD/PCDF emissions are dominated by 1,2,3,7,8-PeCDD. This congener accounts for 50%, 38%, 40% and 38% of total emitted TEQ from cane fires, prescribed fires, wildfires and savanna fires, respectively. Of the other toxic PCDDs congeners, 2,3,7,8-TCDD contributed approximately 13%, 1,2,3,4,6,7,8-HpCDD contributed 11% and the HxCDD isomers each contributed approximately 5% of total toxic emissions. The only significant furan was 2,3,4,7,8-PeCDF, which contributed between 2% and 12% depending on fire class. Overall, PCDD accounted for 93%, 83%, 86% and 79% of toxic emissions from cane fires, prescribed fires, wildfires and savanna fires, respectively.

Laboratory measurements

In contrast to the field measurements, emissions measured in the laboratory tests were dominated by the lower chlorinated furans. While total mass emission were similar for most of the laboratory and field results, the higher fraction of toxic furans resulted in significantly higher emission factors for all the grass fuels. The forest litter emission factors measured in the laboratory, in contrast, were lower than in the field. The differences between the two sets of measurements appeared to be associated with a long residence time at temperatures above 200 °C (Figure 3). In the field, rapid entrainment of ambient air cools the pyrolysed gases below the temperature required for heterogeneous dioxin formation chemistry (Stanmore, 2004). In our laboratory tests, when the smoke plume was confined within the tunnel at temperatures above 200 °C significant furan formation occurred. Consequently the laboratory measurements are most likely strongly affected by sampling artifacts and therefore do not describe the real world. Only the field measurements were used in subsequent inventory accounting.
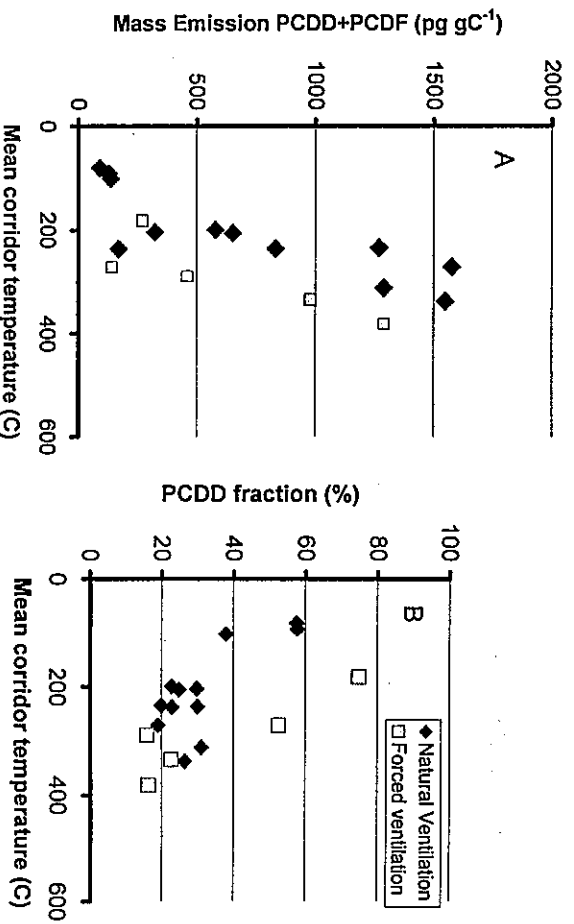

Figure 3   Relation between mean corridor temperature above the fuel bed and emission factor (A) and the fraction PCDD in emitted mass (B)

National Emissions

The field-measured emission factors were used to estimate the National emissions from bushfires in Australia. The methodology is modified from Australia's National Greenhouse Gas Inventory (NGGI) Methodology (AGO, 2003) with activity and parameter values replaced by appropriate probability density functions and the emissions calculated by a Monte Carlo simulation. This allows the uncertainties to be aggregated correctly though the inventory calculations and produces uncertainty ranges for the total emission estimates. All factors other than the PCDD/PCDF and PCB emission factors were sourced from the National Greenhouse Gas Inventory (NGGI, 1998).

The 2002 dioxin and furan inventory (EA, 2002) was calculated using activity data for the 1994 inventory year. Using the measured field emission factors from Table 1 in our uncertainty analysis we estimate the total emission of dioxins, furans and dioxin-like PCBs in 1994 was 142 g TEQ with a 95% confidence range of 31 to 494 g TEQ (Table 2). This overlaps the previous inventory range of 72 to 1708 g TEQ however, because the latter is essentially a uniform distribution with no central estimate, comparison between the two inventories can only be made at the extremes of their ranges. On this basis the impact of the field measured emission factors is to reduce the emission estimates by 56% at the lower limit and by 72% at the upper limit. Almost 84% of the emission occurs in the savanna woodlands of tropical northern Australia and arid zone grasslands of central Australia; wildfires and prescribed fires in the southern temperate forests account for 9% and 4% respectively with the remainder produced from the burning of crop residues in the field. This distribution is similar to the lower bound of the 2002 estimate but is a major shift from the upper estimate in which savanna fire emissions comprise only 72% of the total. The difference in the distribution of emissions between fire classes resides in the relatively low emissions factors for the southern Australian forest, particularly wildfires in comparison to the savanna emission factors.

There was a substantial increase in emission between 1990 and 2001, primarily due to increased savanna burning. In 1990, total annual emissions of PCCD/F and PCBs were approximately 46.5 kg. By 2001, these emissions increased 67% to 76.1 kg. In terms of mass, emissions in the savanna woodlands are dominated by OCDD, however despite relatively low toxicity of OCDD, total TEQ emissions also increased by 67% between 1990 and 2001 from 140 g TEQ to 233 g TEQ. Emissions from forest fires and crop residues fires decreased slightly over this period therefore the increase in emissions were largely confined to the unpopulated regions of northern and central Australia.

Table 2. Total emissions (g TEQ) of PCDD/PCDF and coplanar PCB from bushfires in Australia in 1994.

Source	Emission (g TEQ)	
	This study	EA, 2002
Crop residue	3.2	(1.8 – 5.6)	3-260
Prescribed fires	3.6	(1.4-7.9)	
Wildfire	4.9	(1.2 – 15)	7-400
Savanna	130	(20 – 476)	62 – 1240
All	142	(31 – 494)	72 – 1700

Emerging areas

The study produced several unexpected findings; the emission factors from all classes of fires when measured in the field, were low. For wildfires, this was unexpected because it was assumed that their high temperatures would support greater rates of PCDD and PCDF production sources than would the cooler prescribed fires. However, the finding is consistent with the hypothesis raised by Prange et al (2003) and others, that PCDD, PCDF and PCB present in smoke may have been released by volatilization from the soil pool rather than produced *de novo* during combustion. Intense wildfires, particularly crown fires, spread quickly producing less heating of the surface soil than the lower intensity but slow moving prescribed fires which are confined to the fuel load on the forest floor.

Additional work, which will be presented, also indicates that the soil may be a source of dioxin emissions, however whether this is a physical process of revolatilization is not clear. Apart from its importance for emissions accounting, the involvement of precombustion sources in emissions from fires could have implications for the way fires are classified in inventories. Currently they are classified primarily by fire class. If the dioxin content of soil and fuel are significant determinants of emissions, then the classification should instead primarily be a regional one based on soil chemistry.

The laboratory tests are difficult to interpret as other than artifacts of the sampling system. While it is not the case that all laboratory tests will be similarly affected, it does suggest that particular attention should be given to minimising the length of time the combustion products remain at dioxin formation temperature.

Conclusions

The studies indicate that, in Australia at least, EFs from bushfires fall at the lower end of the published range. From this, it is estimated that Australia produced approximately 230 g TEQ dioxins annually from bushfires in 2001, a test year that has been comparable in fire activity to the subsequent years. This falls within the range of the EA (2002) estimate, however the 95% uncertainty range is now considerably smaller, 41 g to 840 g. Clearly there is considerable scope for future work to further refine these emissions estimates.

Acknowledgements

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