3 Results and discussion

3.1 Dioxin emissions from bushfires

In total, 40 fires were sampled comprising 19 laboratory burns, and 21 field burns (Tables 2.1 and 2.3). Of these, one dioxin sample (L_sorghum-2) was lost during extraction and only the lower PUF plug was analysed. This provided useful confirmation that most of the PCDD, PCDF and PCB content were trapped on the filter, and resin. The only congeners found in substantial concentration were OCDD and OCDF, both of which were found at less than 40% of the concentrations of the replicates L-sorghum_1 and L-sorghum_3. This indicates the there was little risk that material was lost by breaking through the filter and trap. Additionally, one test was not completed successfully. The last laboratory burn (L_litter_Qld) failed to propagate successfully and was terminated before completion. However, the sample was collected and analysed successfully and was included in the data set.

Field sample concentrations of all PCDD/PCDF species were typically 2 to 3 orders of magnitude greater than the concentrations recorded at the ambient measurement sites at comparable times. Similarly, the laboratory samples were 10 to 100 times greater than the ambient concentration of air in the laboratory. The PCB concentrations in the smoke were also generally up to two orders of magnitude greater than the concentrations in ambient air, although on occasions some PCB congeners and PCB species were close to ambient.

The complete data set comprising sample masses, sample air volume, and the mass of CO_2-C derived from combustion (the integral of the (sample CO_2 concentration - ambient CO_2 concentration) are presented in Tables A3.1 to A3.3.

The derivation of emission factors and emission ratios is presented in detail in Appendix 2.

Emission ratios of PCDD/PCDDF to emitted CO_2 are calculated as:

$$ER_{CO2} = ([X] - [X_{amb}])\_/([CO_2]-[CO_2]_{amb}) \quad \text{Eq. 3.1}$$

where [X] and $[X_{amb}]$, $[CO_2]$ and $[CO_2]_{amb}$ are the concentrations of species X, and CO_2 in the sample and in ambient air respectively. In most cases [X] was very much greater than $[X]_{amb}$ as indicated above. Most of the fuel carbon released during combustion, typically >90% (Table 2.3b), is converted to $[CO_2]$ and, therefore, the emission ratios relative to CO_2 are approximately equivalent to emission ratios for total volatilised fuel carbon which in turn are proportional to the emission factor (emission relative to fuel mass) by the fuel carbon content (see Appendix 2), i.e.

$$ER_C = \Sigma X_{emitted}/\Sigma \text{ fuel-}C_{emitted} \quad \text{Eq. 3.2}$$

where Σ fuel-$C_{emitted}$ represents the mass of total volatilised fuel carbon.

Emission ratios for the complete data set are presented in Tables A4.1.1a-f. Because the CO_2-based emission ratios and carbon-based emission factors are very close, throughout the remainder of this report they are used interchangeably.

Figures 3.1 to 3.4 present the results of the study in graphical form, with the results grouped into laboratory burns (grass and forest fuels) and field burns (prescribed burns, non-prescribed burns). Figures 3.1 and 3.2 give the mass emission rates and Figures 3.3 and 3.4 present the toxic equivalents separated by congener.

The laboratory tests divide into grass fuel samples (wheat straw, sorghum, and sugar cane), and forest litter. The grass fuel emission factors were large, both in total mass (Figure 3.1) and toxicity (Figure 3.3) compared with the forest litter.

The grass fuels produced a wide range of PCDD/PCDF congeners, with the lower chlorinated species (TCDD/TCDF) the most abundant, and the PCDF species substantially more abundant than the PCDDs (Figure 3.1). In the litter fuels, the TCDF homologue group dominated the furan emissions while in the dioxins, all groups were present in similar amounts. Similar differences between grass fuel and litter fuel emissions were seen in the 2,3,7,8 congener patterns. In the grass fuels 2,3,7,8- TCDD and 1,2,3,7,8-PeCDD were the main dioxins while in the furans, the dominant congener was 1,2,3,7,8-PeCDD, but the tetra and hexa congeners were present in reasonable abundance (Figure 3.3). In the litter fuels all the 2,3,7,8-PCDD congeners were present.

In the field samples, emission rates were variable across all fire classes (prescribed, wildfire, savanna, and sugar cane) with the two wildfire samples being at the lower end of the emissions. The variation in congener and homologue profile seemed to mainly relate to the location of the fire rather than to fire type, for example, the Queensland samples, both forest and sugar cane, were dominated by OCDD, while the forest samples from Victoria and WA showed a homologue profile with substantial contributions from low chlorinated PCCDs and PCDFs (Figure 3.2). The three tests in NT were more variable. Sample S-NT-4 from Darwin was similar to the Queensland profiles with OCDD dominating, Sample S-NT-2 was similar to the Vic and WA patterns and sample S-NT-3 was dominated by TCDF and unique within our data set. Most of the toxic emissions came from the 2,3,7,8-Cl-substituted PCDDs, particularly the tetra- and penta-dioxins, and in the cane fires, 1,2,3,4,6,7,8-HpCDD. The only significant furan in terms of toxicity was 2,3,4,7,8-PeCDF (Figure 3.4).

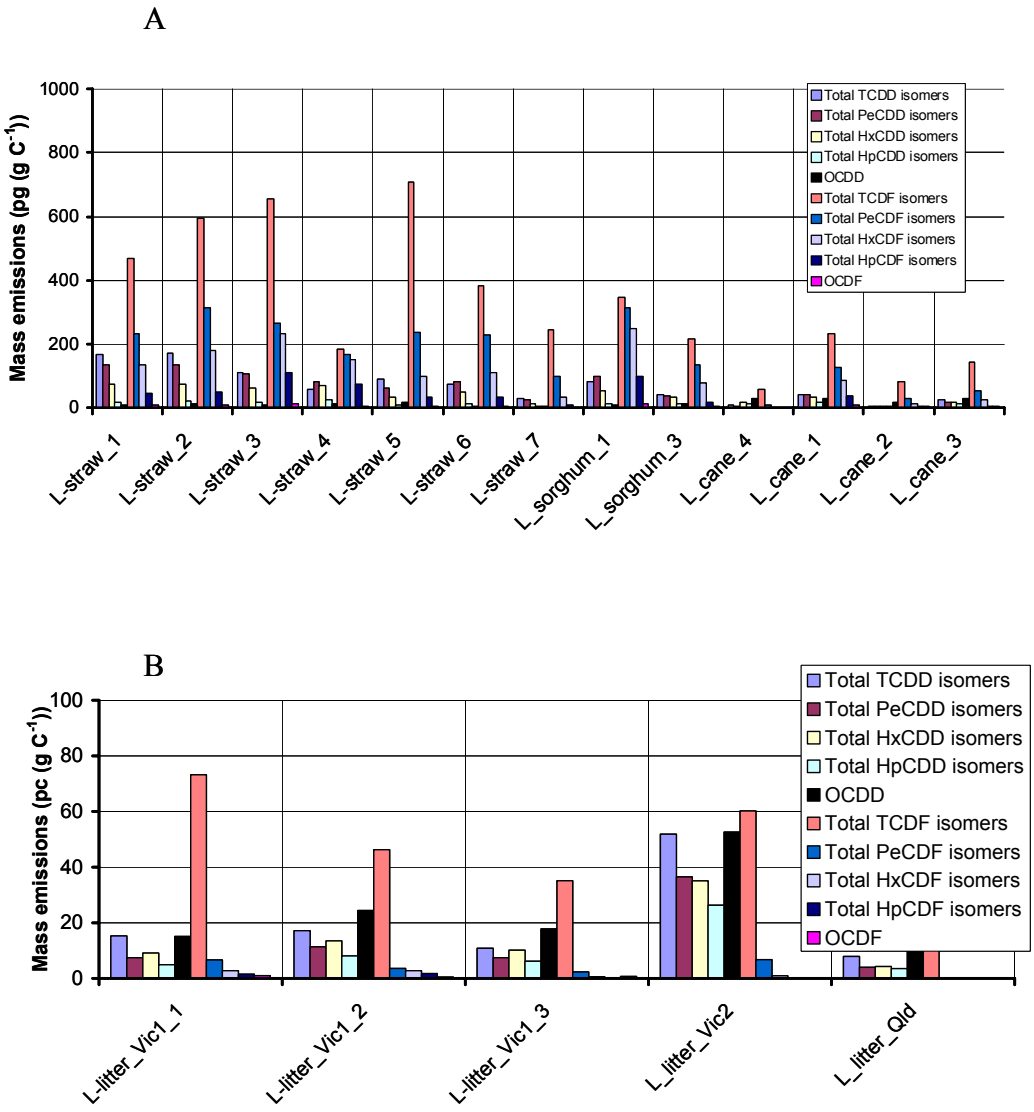

Figure 3.1. Mass emission rates of PCDD/PCDF homologue groups from laboratory burns.

A. Grass fuels
B. Fine forest fuels.

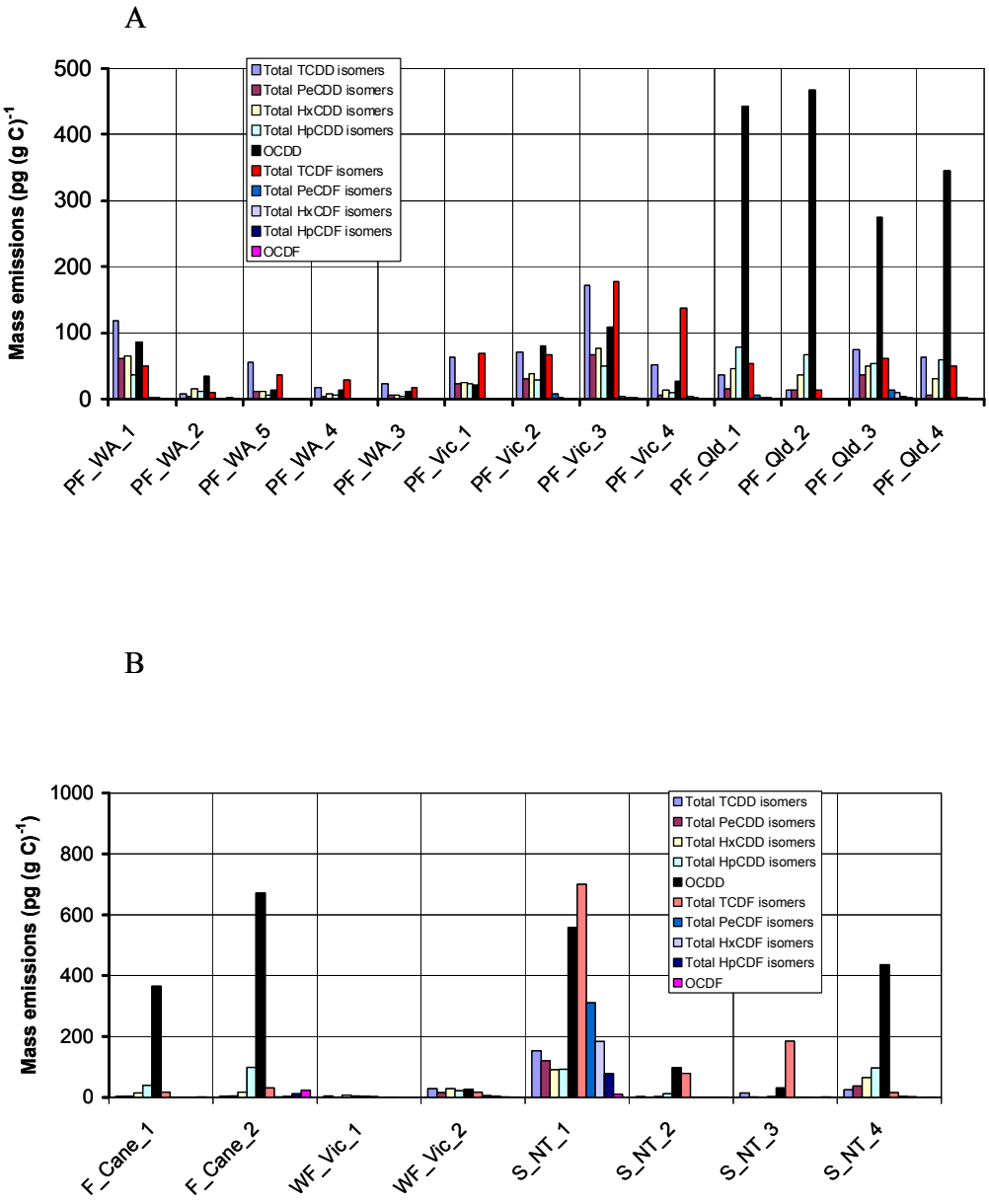

Figure 3.2. Mass emission rates of PCDD/PCDF homologue groups from field fires.

A. Prescribed fuel reduction burns in forest
B. Cane fires, wildfires and savanna fires.

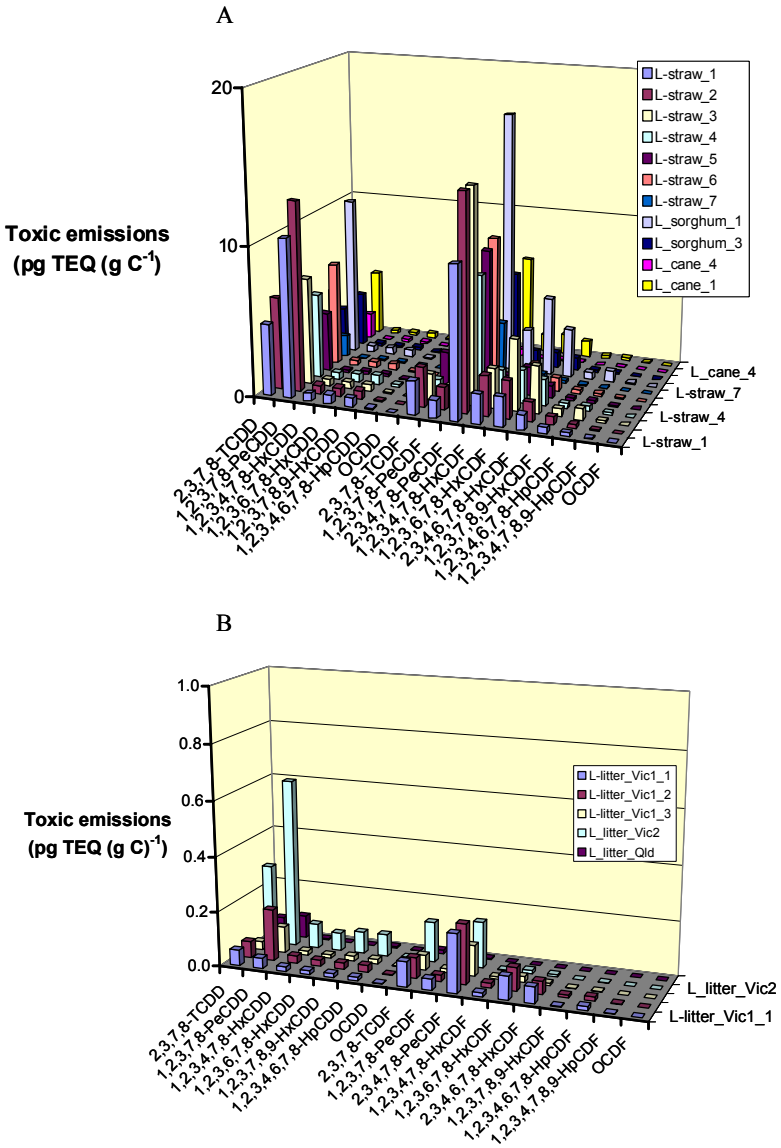

Figure 3.3. Emission rates in terms of toxicity for congeners from laboratory burns.

A. Grass fuels
B. Fine forest fuels.

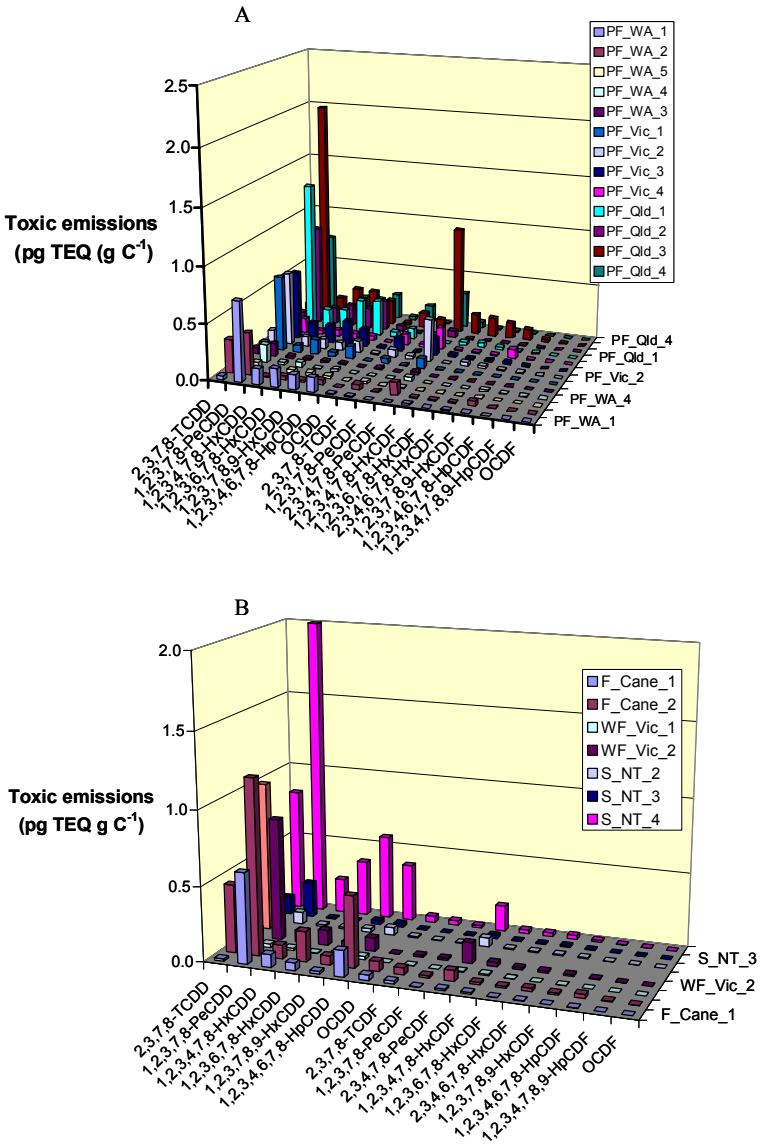

Figure 3.4. Emission rates in terms of toxicity for congeners from field fires.

A. Prescribed fuel reduction burns in forest
B. Cane fires, wildfires and savanna fires.

One sample, S-NT1, stands out as an outlier among the field samples. The total PCDD/PCDF emission rate is 10 fold larger than the next largest field sample, and the congener profile is similar to the laboratory burns but totally dissimilar to all other field burns. This sample was analysed with a batch of laboratory samples one of which was lost during extraction (L-sorghum-2). We suspect that there may have been a labelling error introduced between sample collection and analysis and that the sample analysed as S-NT-1 could be in fact L-Sorghum_2. Applying the sample volume and trapped carbon for L-Sorghum_2 to the analysis results of S-NT_1 gives an emission factor of 20.4 pg TEQ $(g\ C)^{-1}$, which is very similar to the value of 18.2 for L-Sorghum_3. The

congener patterns of both samples are also very similar congener pattern. Given this suspicion we have removed S-NT-1 from the subsequent analyses.

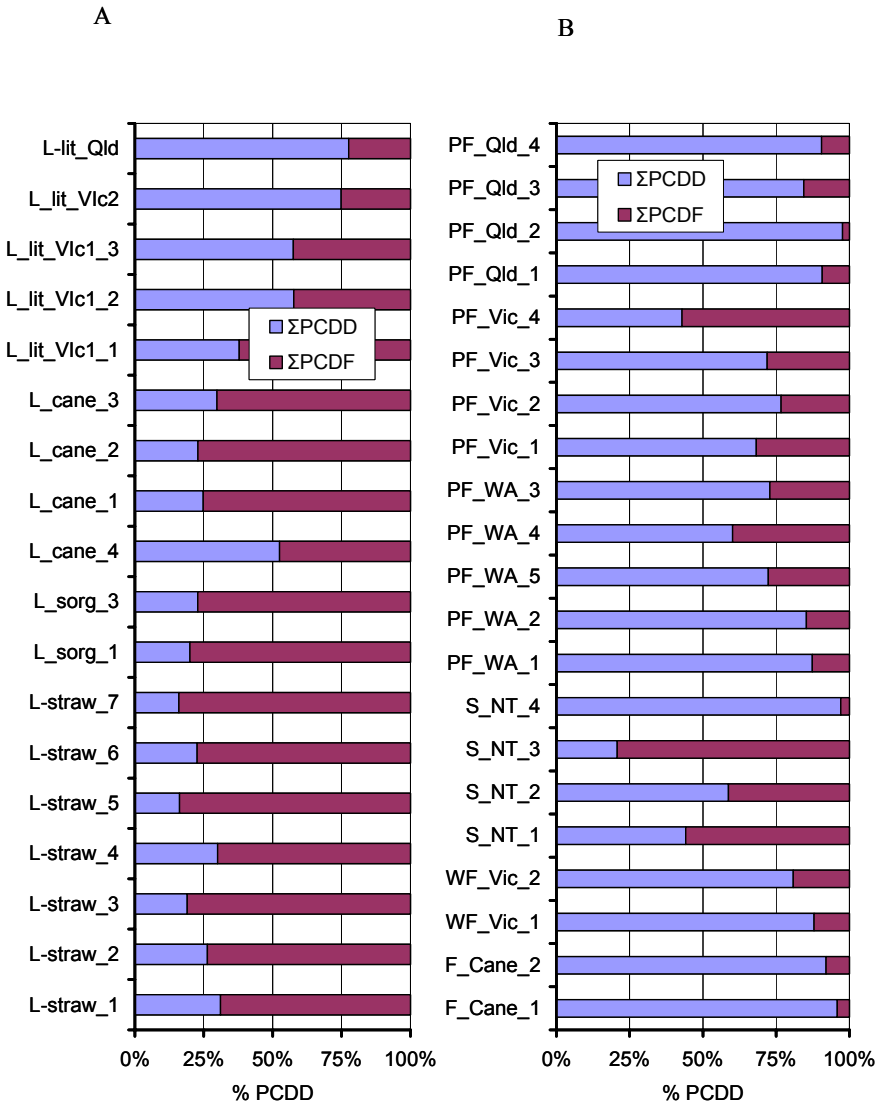

Figure 3.5. The relative contribution of PCDD to total PCDD/PCDF mass.

A. Laboratory fire samples
B. Field samples.

If there is a single feature on which to group the samples then the total dioxin/furan ratio would be a good candidate. The laboratory grass samples (and S-NT-1) form one group with furan content of about >50%, mostly near 75% (Figure 3.5). The field samples form a second group with furan content <50% mostly near 25%. The laboratory litter burns form a third and intermediate group with furan content <60% down to 25%.

Figures 3.6, 3.7 and 3.8 present the average congener patterns of samples grouped by fire class. These are consistent with the patterns observed in the individual samples, and

further emphasis the differences between lab tests and field burns. Direct comparisons can be made for cane and forest litter, which were measured in both sets of burns.

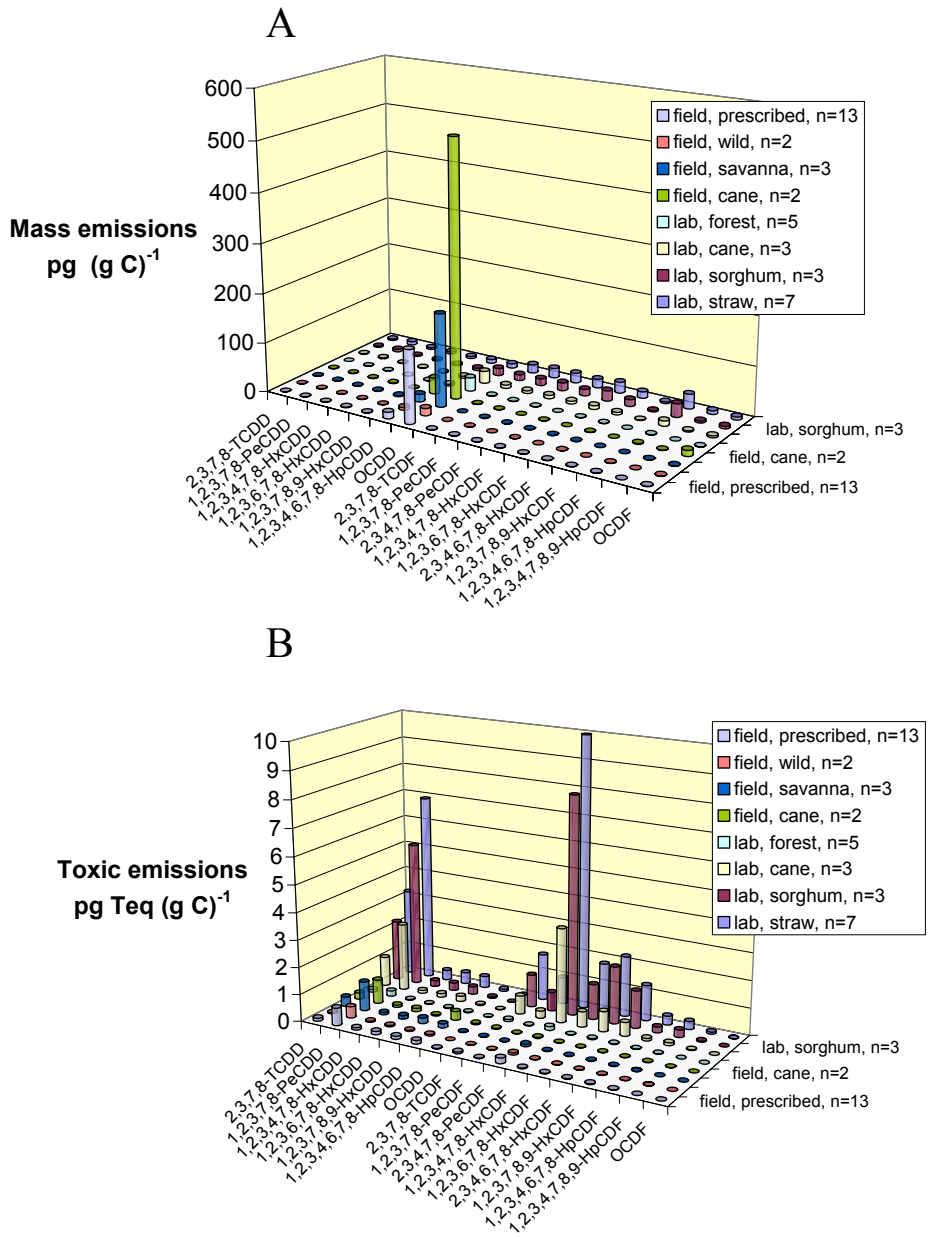

Figure 3.6. Mean emission rates of 2,3,7,8 PCDD/PCDF congeners from laboratory and field fire classes.

A. Mass emission rates
B. Toxic equivalent emission rates.

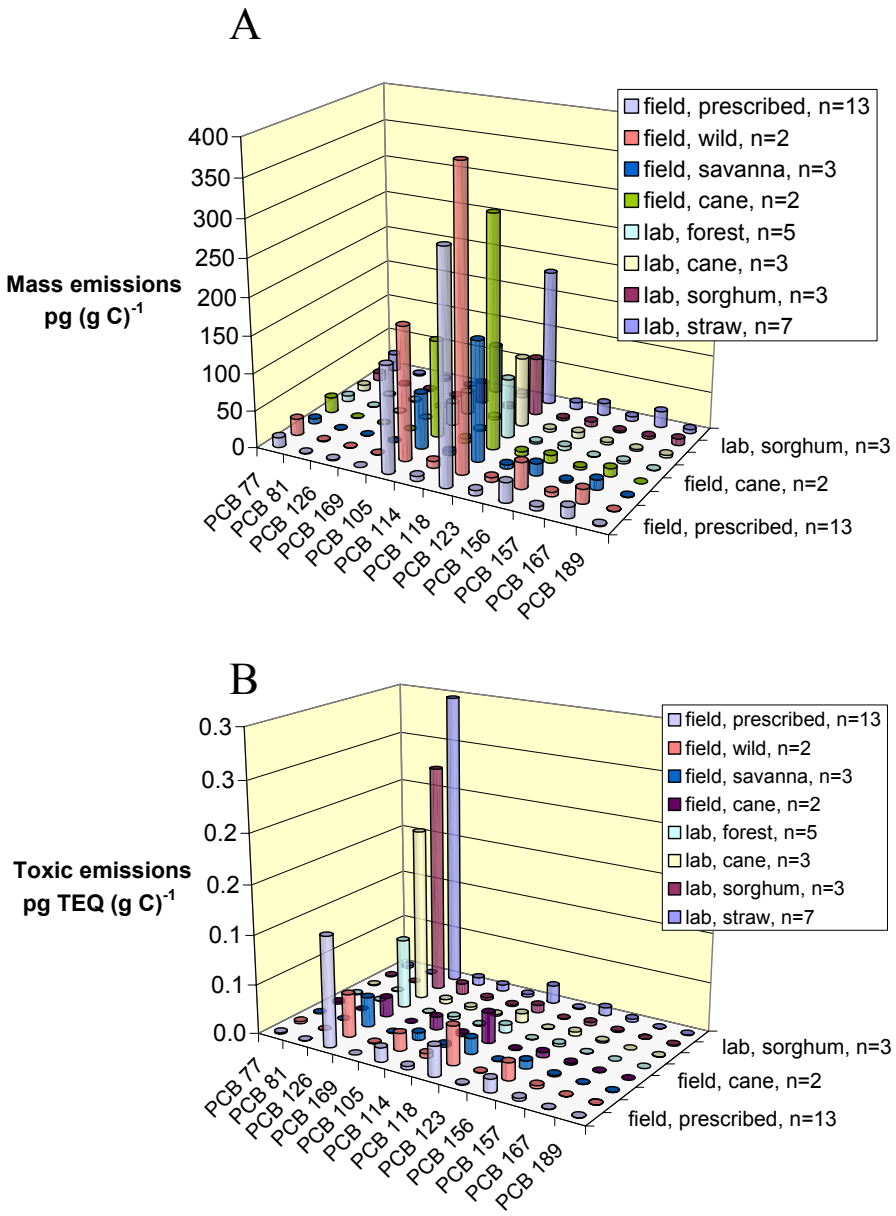

Figure 3.7. Mean emission rates of coplanar PCBs for laboratory and field fire classes.

A. Mass emission rates
B. Toxic equivalent emission rates.

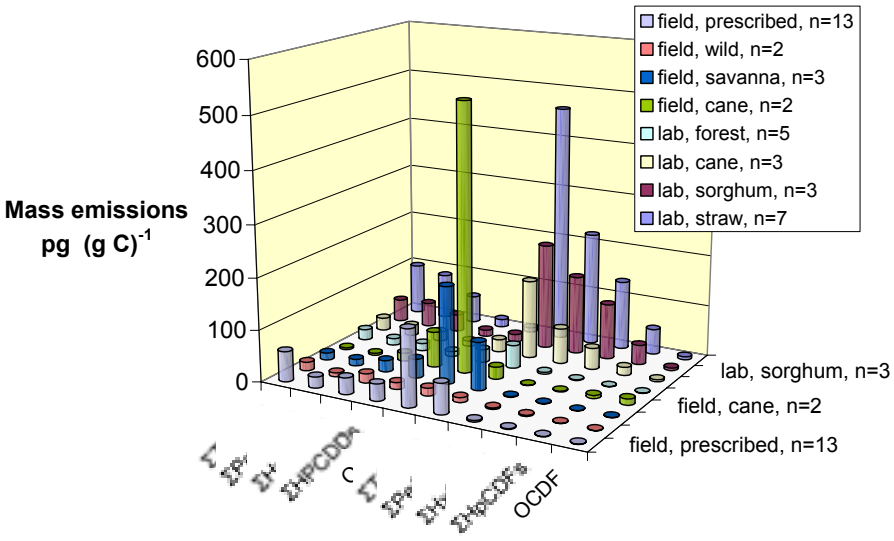

Figure 3.8. Mean mass emission rates PCDD/PCDF monologue groups for laboratory and field fire classes.

Table 3.1. Total suspended particle concentration in smoke samples.

Laboratory burns			Field burns		
Label	µg m^{-3}	mg $(g\ C)^{-1}$	Label	µg m^{-3}	mg $(g\ C)^{-1}$
L-straw_1	10746	25.8	F_Cane_1	1181	7.6
L-straw_2	15812	32.7	F_Cane_2	255	1.0
L-straw_3	5031	8.9	WF_Vic_1	1010	31.0
L-straw_4	4713	9.6	WF_Vic_2	2302	48.5
L-straw_5	20209	8.5	PF_WA_1	na	
L-straw_6	20480	8.9	PF_WA_2	2340	78.2
L-straw_7	25227	5.2	PF_WA_5	5055	125.4
L_sorghum_1	19087	38.2	PF_WA_4	1729	22.2
L_sorghum_3	16316	21.8	PF_WA_3	5551	43.2
L_sorghum_2	18626	33.7	PF_Vic_1	869	25.7
L_cane_1	15097	38.4	PF_Vic_2	861	39.3
L_cane_2	14727	36.5	PF_Vic_3	2668	87.9
L_cane_3	8576	14.6	PF_Vic_4	2998	75.0
L_cane_4	18571	33.1	PF_Qld_1	3533	31.5
L-litter_Vic1_1	9437	33.3	PF_Qld_2	4363	17.3
L-litter_Vic1_2	10667	29.0	PF_Qld_3	4466	25.5
L-litter_Vic1_3	16053	36.7	PF_Qld_4	3589	98.7
L_litter_Vic2	11281	33.4	S_NT_1	3542	46.6
L_litter_Qld	14584	31.3	S_NT_2	na	
			S_NT_3	na	
			S_NT_4	5088	25.9

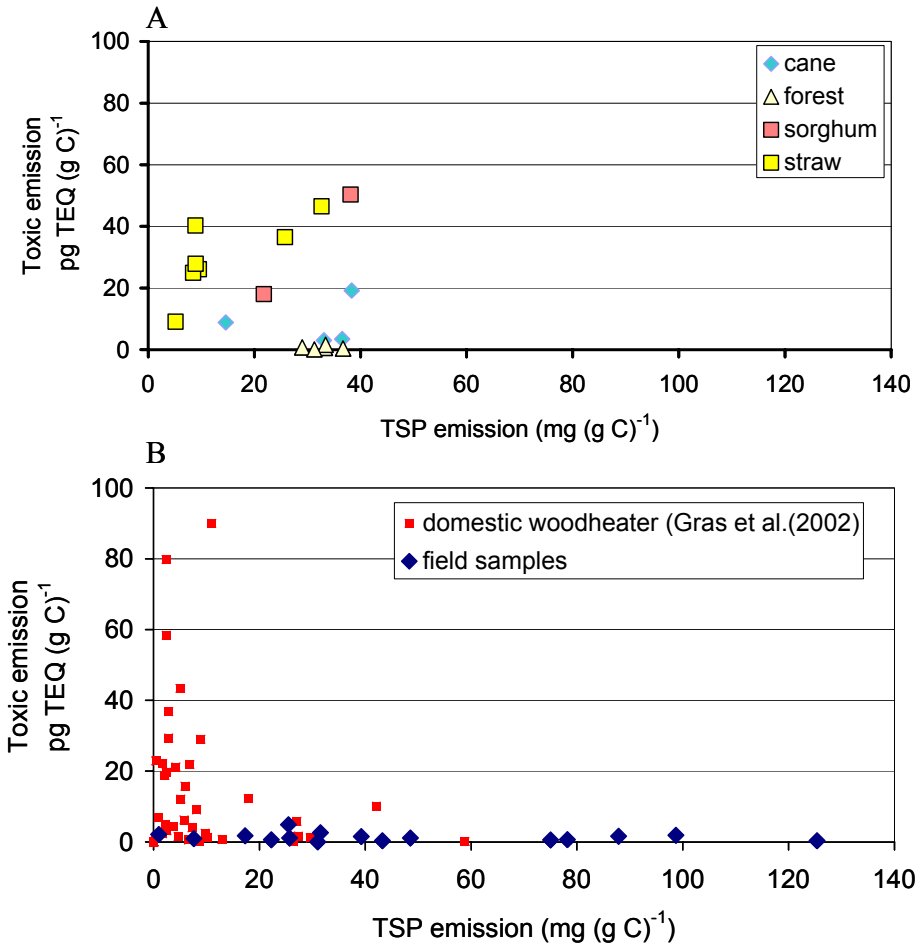

Figure 3.9. Relation between particulate emissions and total 2,3,7,8 PCDD/PCDF and PCB emissions.

A. Laboratory burns
B. Field burns.

Sugar cane burned in the laboratory test emitted large quantities of furans, which accounted for most of the mass of toxic and non-toxic species, most of the mass of the 2,3,7,8 congeners and most of the toxicity. In contrast, field sugar cane fires emitted mostly OCDD and most of the toxicity was derived from 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD. The laboratory litter burns were characterized by their mass and TEQ emission rates, which were lower than field burns.

The profiles of coplanar PCBs are shown in Figure 3.7.The patterns were relatively uniform across all classes with PCBs 105 and 118 the main dominant species with respect to mass and PCB 126 the main source of toxicity supplemented by PCB 118. In

the laboratory burns the emissions were strongly weighted towards PCB 126. In the field burns, other species such as PCBs 105, 118 and 156 were also significant

This study measured total suspended particle mass (TSP) emission (Table 3.1). In the laboratory tests particle emissions ranged up to a maximum of about 38 mg $(g\ C)^{-1}$ with lower rates for the hotter grass fuel burns. In the field emissions were more variable ranging from 1 to 125 mg $(g\ C)^{-1}$ from a high-temperature cane fire to a smouldering prescribed burn in forest. There was no correlation between TSP and PCDD/PCDF emissions in the laboratory tests, and no clear correlation in the field burns, although the pattern was consistent with other studies (Figure 3.9). Gras et al. (2002) found that a scatter plot of PCDD/PCDF versus TSP was bounded by un upper envelope where high TSP emissions (>were always accompanied by low PCDD/PCDF emissions and the high PCDD/PCDF emissions always occurred at low TSP emissions. Finally, fuel and ash from some lab burns and one field burn were analysed to test whether PCDD/PCDF following combustion was the result of synthesis during combustion or revolatilisation from the fuel. The mass balance of PCDD/PCDF/PCB remaining after combustion is given in Eq. 3.3.

$$Emitted + residue = source + synthesised \qquad \text{Eq. 3.3}$$

where

$$source = [PCDD/PCDDF]_{fuel} \quad (g\ (g\ fuel)^{-1}) \qquad \text{Eq. 3.4}$$

$$residue = [PCDD/PCDF]_{ash}(1 - C_{eff}) \quad (g\ (g\ fuel)^{-1}) \qquad \text{Eq. 3.5}$$

$$emitted = \frac{[PCDD/PCDF]_{smoke} - [PCDD/PCDF]_{ambient}}{[CO_2]_{smoke} - [CO_2]_{anb}} * \frac{[CO_2]_{smoke} - [CO_s]_{amb}}{[C]_{smoke} - [C]_{amb}}$$

$$(g\ (volatilised\ C)^{-1}) \qquad \text{Eq. 3.6}$$

$[PCDD/PCDF]_{fuel}$, $[PCDD/PCDF]_{ash}$, and C_{eff} are respectively the mass concentrations $(pg\ g^{-1})$ of fuel and ash and burning efficiency, and $[CO_2]_{smoke}$, $[C]_{smoke}$, $[CO_2]_{amb}$, $[C]_{amb}$ are the concentrations of CO_2 and total carbon in smoke and ambient air

To relate volatilised carbon to fuel mass we need a mass balance for fuel carbon

$$C_{volatilised} = C_{fuel} - C_{ask} \qquad \text{Eq. 3.7}$$

where $C_{volatilised}$, C_{ash} and C_{fuel} are the masses of carbon volatilised, in the ash residue and the fuel respectively, which can be related to fuel mass (M_{fuel}) by the carbon content of the fuel and the ash (Cc_{fuel} and Cc_{ash})

$$C_{volatilised} = (M_{fuel} CC_{fuel}) - M_{fuel}(1 - C_{eff}) CC_{ash} \qquad \text{Eq. 3.8}$$

Depending on the extent of combustion, ash contains non volatile minerals and varying amounts of charred fuel. Mineral ash content of fuel is typically about 1% of fuel dry weight, and the remainder of the ash from field fires is typically high in charcoal.

We want to calculate the proportion of PCDD/PCDF emerging from combustion ($F_{produced}$) that was synthesised (or destroyed) during combustion. From Eq. 3.3.

$$F_{produced} = \frac{emitted - source + residue}{emitted + residue}$$

Eq. 3.9

Equation 3.7 can be evaluated using Eq. 3.4 to 3.8. Burning efficiency is given in Table 2.3 and the emitted CO_2/emitted C ratio is approximated by combustion efficiency (Table 2.4).

The fractions of dioxin released from combustion of straw, cane residue and forest litter in the laboratory tests, and a savanna fire at Berrimah, Darwin are given in Table 3.2. In many cases the concentrations of PCDD/PCDF species in fuel ash and air was below the limit of detection (LOD. To allow for this, $F_{product}$ was calculated for all PCDD/PCDDF homologue groups and 2,3,7,8- PCCD/PCDF with non detects set successively at 0, half LOD and LOD, and the results were reported as a range. A large range indicates measured PCDD/PCDF concentrations near or below detection limits in fuel, ash or smoke. Negative values of $F_{product}$ occur when there is less PCDD/PCDDF in ash residue and smoke than in the unburned fuel, presumably due to destruction during combustion.

In general, the mass balance indicated most (>90%) of the emitted PCDD/PDCF species were synthesised during combustion. The exception was sugar cane combustion in the laboratory in which a large proportion of the OCDD present in the fuel was not detected in ash or smoke although total PCDD/PCDF mass present in smoke and ash was largely accounted for in the fuel.

Table 3.2. Proportion of PCDD/PCDF present in smoke and ash after combustion.

Congener	% PCDD/PCDF produced during combustion				
	Lab straw_5	Lab straw_7	Lab cane_4	Lab litter_Vic2	Field NT_4
2,3,7,8-TCDD	93 to 100	96 to 100	77 to 100	83 to 100	90 to 100
Total TCDD isomers	100	100	92	98	98
1,2,3,7,8-PeCDD	94 to 100	94 to 100	66 to 100	91 to 100	97 to 100
Total PeCDD isomers	98 to 100	98 to 100	56 to 100	98 to 100	99 to 100
1,2,3,4,7,8-HxCDD	79 to 100	90 to 100	19 to 100	85 to 100	95 to 100
1,2,3,6,7,8-HxCDD	87 to 100	96 to 100	69 to 71	83 to 100	97 to 100
1,2,3,7,8,9-HxCDD	84 to 100	94 to 100	57 to 60	87 to 100	98 to 100
Total HxCDD isomers	96 to 100	99 to 100	32	98 to 100	98
1,2,3,4,6,7,8-HpCDD	94 to 100	96 to 100	-29 to -2	96 to 100	96
Total HpCDD isomers	97 to 100	97	-1	97	96
OCDD	86 to 100	38 to 100	-295	90 to 100	86
2,3,7,8-TCDF	100	100	78	91 to 100	72
Total TCDF isomers	100	100	93	99	94 to 100
1,2,3,7,8-PeCDF	100	100	46	90 to 100	87 to 100
2,3,4,7,8-PeCDF	100	100	55	87 to 100	83 to 100
Total PeCDF isomers	100	100	63	97	86 to 100
1,2,3,4,7,8-HxCDF	98 to 100	99 to 100	34 to 41	83 to 88	85 to 100
1,2,3,6,7,8-HxCDF	99 to 100	99 to 100	73 to 100	87 to 100	77 to 100
2,3,4,6,7,8-HxCDF	97 to 100	98 to 100	71 to 100	76 to 100	79 to 100
1,2,3,7,8,9-HxCDF	81 to 100	94 to 100	32 to 100	-74 to -48	69 to 100
Total HxCDF isomers	99 to 100	99 to 100	45	74 to 100	74 to 100
1,2,3,4,6,7,8-HpCDF	100	98 to 100	44 to 100	71 to 100	82
1,2,3,4,7,8,9-HpCDF	92 to 100	94 to 100	55 to 100	-86	-67 to 100
Total HpCDF isomers	98 to 100	98 to 100	21 to 32	35	74
OCDF	64 to 100	91 to 100	-3 to 59	59 to 100	79 to 100
Total PCCD	97 to 100	92 to 100	-92 to -91	95 to 99	90
Total PCDF	0 to 100	100	87 to 88	97 to 99	90 to 100
Total	94 to 100	98 to 100	5	96 to 99	90

3.2 Discussion

In 1998 Environment Australia published a review Sources of Dioxins and Furans in Australia: Air Emissions. This was revised in 2002 to include up-to-date data from the cement industry. This review (Environment Australia, 2002) concluded that the best estimates that were available for predicting emissions from biomass burning in the field ranged from 0.5-10 μg TEQ t^{-1} for agricultural waste, prescribed fires in forests and fires in savanna and grasslands and 0.5-28 μg TEQ t^{-1} for wildfires. None of these emission estimates were based on measurements of fires in the field, but they were derived from laboratory tests or combustion of wood in domestic heaters where at the least the fuel was the same as in the field even if the combustion process was not. The dangers in assuming that difference in combustion was not an issue was recognised and discussed, and the resulting emission estimates were highly qualified, with no indication of where in the range the mean, or best estimate might be found. The reviewers were implying that the probability distribution was uniform. The current study has explicitly addressed this assumption and has produced some clear conclusions.

The measured emission factors for field forest fires (prescribed and wildfires) and savanna fires fall at the lower end of the range suggested by the review averaging 1 ±0.5 pg TEQ (g C)$^{-1}$ which translates to approximately 0.5 μg t^{-1}. These data were consistent across 20 measurements at different sites across Australia.

Total emission factors[1] ranged from 0.05 to 2.9 pg TEQ (g fuel)$^{-1}$ as observed in the field burns for total polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF) and polychlorinated biphenyls (PCBs), with means of 0.9, 1.2, 0.5 and 1.1 pg TEQ (g fuel)$^{-1}$ for total PCDD/PCDF for prescribed fire, savanna fires, wildfires, and sugar cane fires, respectively. These are comparable to the values of 0.5 to 30 pg TEQ (g fuel)$^{-1}$ comprising the minimum of the previous estimates. Dioxin was the major component (70%) with furans and PCB contributing a further 20 and 10%, respectively. The congener patterns were not uniform across all states. Emissions from cane fires and prescribed forest fires in Queensland were dominated by OCDD; in Victoria, WA and, to some extent NT, the lower chlorinated homologue groups were equally important. The main furan homologue group was TCDF and the main toxic congeners were 1,2,7,8-TCDF and 1,2,3,7,8-PeCDF. 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 dioxin emitters.

The laboratory tests produced similar emission rates for the forest fuels, but much higher rates for the grass fuels, than were found in the field. Of this, the congener profiles were distinctly different from the field burns. The implication is that the laboratory tests do not adequately simulate the combustion processes occurring in the field. The literature supports this conclusion. The high furan/dioxin ratio is reported routinely for emissions from wood combustion in furnaces and domestic heaters (e.g. Gras et al., 2002), while the only measurement of field combustion published to data

[1] To obtain estimates in terms of mass of fuel, we assume that the carbon content of the fuel is exactly 50%.

(Prange et al., 2003) report low furan/dioxin ratios similar to the field burns in this study. This issue requires detailed examination.

The dioxin and furan emissions from the laboratory tests were substantially different to the field measurements. The laboratory burns were conducted on cereal straw, native sorghum, sugar cane trash and forest leaf litter in the test corridor at the CSIRO fire-testing laboratory. Fuel of known provenance was laid on the floor of the corridor to a loading of either 20 or 30 t ha^{-1}. Emission rates for the grass fuels of straw, sorghum and sugar cane were high, averaging 17, 35 and 5 pg TEQ $(g\ fuel)^{-1}$, respectively, and ranged from 1.5 to 59 TEQ $(g\ fuel)^{-1}$. These rates are 10-times higher than the field measurements but comparable to previously reported estimates from laboratory tests. In contrast to the field burns, the PCDD homologue groups contributed less than 30% of total mass emissions and 35 to 40% of the TEQ emissions. The most abundant homologue groups were TCDF and TCDD. Emission rates from leaf litter combustion in the laboratory ranged from 0.1 to 0.9 pg TEQ $(g\ fuel)^{-1}$ and averaged less than a third of the field observations. Congener profiles for leaf litter burns in the laboratory were weighted toward furans.

The congener profiles observed in the laboratory tests were consistent with profiles observed in emissions from wood combustion in domestic heaters and small industrial furnaces. The field measurements particularly from SE Queensland were consistent with published field measurements from prescribed fires and soil congener profiles. The key difference between these and laboratory emissions may be the duration for which the smoke plume remains at high temperature. In field burns, air entrained into the smoke plume rapidly cools to temperatures that will not support the heterogeneous reactions required for dioxin synthesis. In wood combustion appliances, where the combustion gases are confined within the appliance or flue, they remain at temperatures suitable for dioxin synthesis. A similar situation probably occurs during laboratory tests with grass fuel combustion, when the corridor temperatures remained above 200 ºC for the duration of the fire. However, the slower combustion rate of leaf litter produces a thermal environment intermediate between the extremes of confined grass burns and open field burns resulting in intermediate congener profiles.

The current understanding of the chemistry of dioxin formation and redistribution has been extensively reviewed by Stanmore (2004). There are thought to be two pathways by which dioxins are synthesized during combustion; gas phase reactions occurring in a temperature window of 500 to700 ºC and heterogeneous reactions, which occur on particle surfaces in thermal window between 200 and 400 ºC. In field fires, while the flame temperature are typically 600 to 1,000 ºC (Gould et al., 2003) the smoke plume rapidly entrains surrounding air and cools so that the residence time for gas or particles in either window is very short probably of the order of a few seconds. In the laboratory burns the flame temperatures are 600 to700 ºC, however, the smoke is retained in the combustion room and, therefore, the residence time for particles in the 200 to 400 ºC window is considerable (see Figures 2.23, 2.25 and 2.27). In the grass fuel tests in the current study the combustion chamber remained within the 200 to 400 ºC thermal window for the full duration of the test. The residence time for smoke within the combustion chamber was probably of the order of a minute rather than seconds. However, in the forest litter fuel tests, while flame temperature was 600 to 700 ºC the combustion chamber temperature was well below 200 ºC, too cool to support dioxin synthesis. The congener profiles from these litter burns were also somewhat "field-

like". Therefore, it is extremely likely that the high emission rates observed in the grass burns are the result of heterogeneous chemistry within the combustion chamber and does occur to a much lesser extent in the field. Laboratory tests of open burns, in which the smoke plume entrains ambient air and is immediately cooled, produce congener profiles with high dioxin to furan ratios similar to the field burns of our study.

To date there are only two studies reporting emission factors for agricultural and field fires. Gullett and Touati (2003a) report emission factors for wheat and rice stubble combustion of 0.5 µg TEQ (t fuel)$^{-1}$ which is similar to the cane fires in Australia (0.8 µg TEQ (t fuel)$^{-1}$), although the dioxin to furan ratios were more similar to the forest litter burns in the laboratory tests than our field measurements. Gullett and Touati (2003b) also reported emission factors for pine litter in simulated forest fires ranging from 1 to 56 µg TEQ (t fuel)$^{-1}$, which is entirely different from our findings for Australian fires. There are two possible explanations: (1) the fuels are different; and (2) because the measurements were conducted in a combustion room the combustion chemistry of the tests was different from that which occur in the field. Gullett and Touati report substantial differences between the -forest fuels they investigated, and suggest that the provenance of the fuel is a significant determinant of emission characteristics. However, the congener patterns from their tests are unlike any observed in our field measurements, which could indicate difference in combustion properties. Given the differences in fuels and measurement method between their study and ours we doubt that these emission factors can be applied to Australian fires.

The difference between our laboratory and field tests is an important issue and is the subject of ongoing studies by the team. The question to address in the current report is which set of measurements are appropriate for calculating National PCDD/PCDF emissions from biomass burning in the field. Clearly there is no uncertainty about the combustion characteristics of the field burns because the smoke samples were "the real thing". However, the results from the laboratory burns can only be used for inventory purposes if we accept that they adequately reproduce the combustion characteristics of the field burns, and, clearly, this is questionable. Therefore, we have taken a conservative approach and have used only the field data to estimate National PCDD/PCDF emissions.

There are two final points that need to be discussed. One interesting outcome is that all the field burns from Queensland had congener profiles dominated by OCDD. This feature has been reported previously by Prange et al. (2003) in fire emission studies. The feature also appears in soils of the region (Prange et al., 2002) and has led to speculation that the presence of high concentration of OCDD in smoke might be due to revolatilisation from OCDD present in the fuel and soil. The mass balances of PCDD/PCDF from the laboratory tests strongly indicated that most of the PCDD/PCDF in smoke and ash was formed during combustion. This was also indicated from the substantial shift in congener pattern from the dominance of OCDD the fuel to the dominance PCDFs in smoke and ash. The mass balance the field burn S-NT-4 also strongly suggested that concentrations of PCDD/PCDF in the fuel could not explain the concentrations measured in the smoke. However, Prange et al, (2003) found that the soil surface layer to be a major component of their mass balance and the soil component was not included in our analysis. Therefore, we cannot rule out the possibility that revolatilisation is important, and if it is a general phenomenon in the field, then emission factors should be stratified by both region and fire class.

The second point is that the emission factors observed for the two wildfires were very low and at variance with previous speculation that high temperature fires might be large emitters of dioxins. The measurements were made in the dense smoke plume during the fires in NE Victoria in January 2003. The smoke plume from this region extended to Boroolite, one of the ambient air monitoring sites Dioxins in Ambient Air in Australia Project under the National Dioxins Program, and persisted for a significant proportion of the monthly sample although the TSP measurement confirmed that the samplers had been exposed to high smoke concentrations. Particle mass and the biomass tracer, non sea salt potassium were observed in high concentrations at Boroolite in the integrated weekly samples from late January and early February 2003 peaking at 30 and 25 times the ambient concentrations in the weeks preceding the fires (Figure 3.10a). In contrast, the integrated monthly PCDD/PCDF concentration for February was 0.31 fg TEQ m^{-3} which was marginally lower than the monthly concentration reported for December 2002 (0.31 fg TEQ m^{-3}). The Boroolite data, therefore, supports our field measurements and confirms that these extensive and highly intense wildfires did not produce substantial emissions of PCDD/PCDF in smoke plumes impacting the region at ground level.

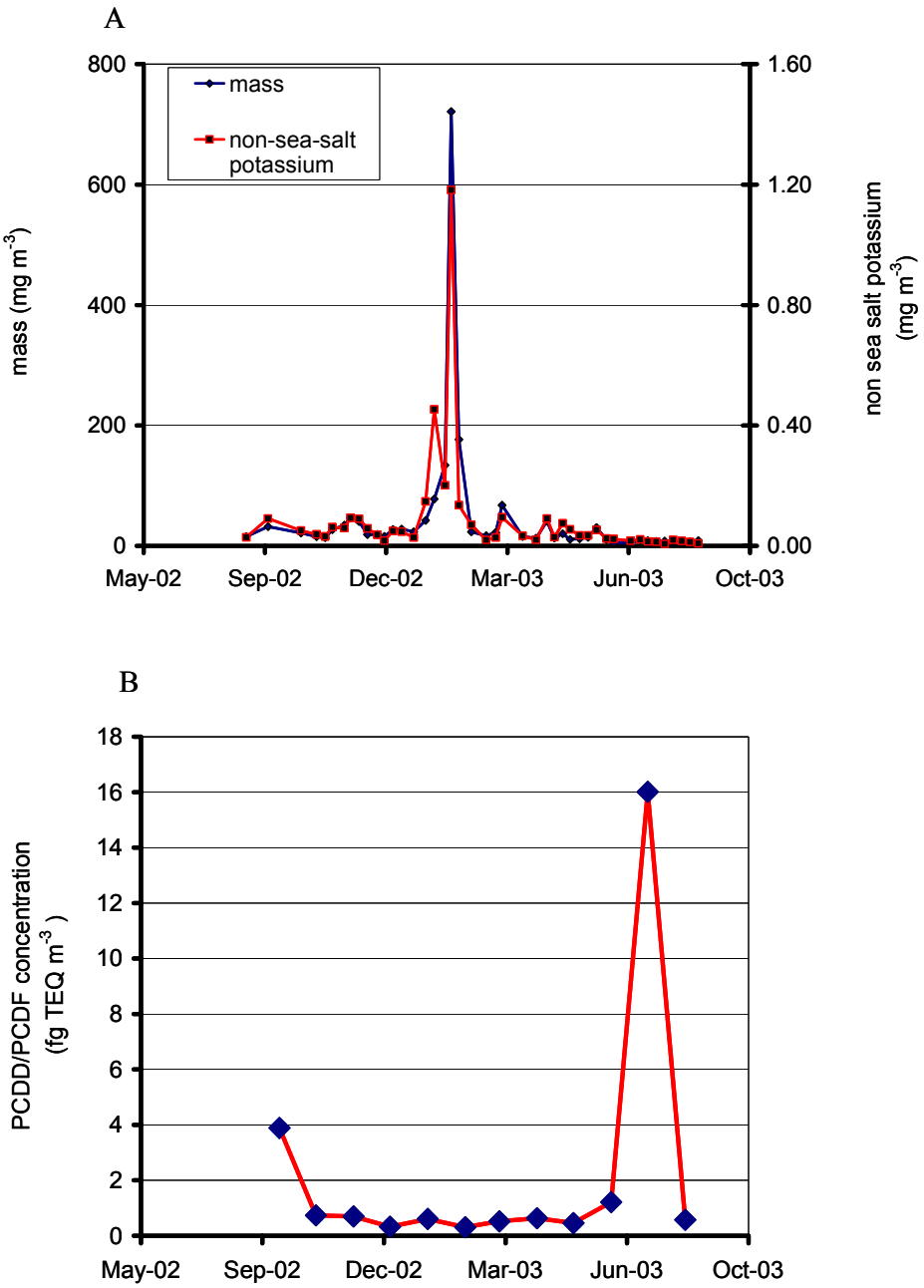

Figure 3.10. Seasonal variation in particle and PCDD/PCDF concentrations in ambient air at Boroolite Vic.

A. Integrated weekly particle mass and non sea salt potassium
B. Integrated monthly PCDD/PCDF concentration. (From the Ambient study, Gras 2004).

The field measurements have produced a set of emission factors that can be used directly to estimate national PCDD/PCDF emissions. The laboratory tests produced emission factor estimates that on occasions can be misleading and are do not reflect the emission rates in the field.

The objectives of this study were to:

1. consolidate the current state of knowledge on dioxin emissions from wildfires and prescribed burns in Australia
2. derive an estimated inventory of wildfire and prescribed burn activity in Australia
3. gain a greater understanding of dioxin emissions from wildfires and prescribed burns by either direct sampling or by carrying out laboratory-controlled experiments or by both.

The first and the third objectives have been met, as summarised above. The inventory calculations are given in Appendix 3 and Appendix 4. The review, Sources of Dioxins and Furans in Australia: Air Emissions 1998, previously estimated the total emission of dioxins and furans to air from prescribed burns and bushfires to be 72 to 1,700 g TEQ per year. Using the measured field emission rates from the current study the total emission of dioxins, furans and dioxin-like PCBs to air is estimated to be 32-494 g TEQ per year, 70% lower than the previous estimate.

3.3 Comparison of results

The results for the field trials are consistent with reports from other forest trials (Gabos et al., 2001; Gullet et al., 2003b; Prange et al., 2003). Martinez et al. (2000) report on soil samples from Spanish forest fires and find low PCDD/PCDF concentrations in soil. Kim et al. (2003) investigated soil and ash samples from Korean forest fires, and found higher levels of PCDD/PCDF in the burnt soil than in the unburnt soil. Green et al (2004) examined archived soil samples from around the world to conclude that most PCDD/PCDF found in the soil is of natural (rather than anthropogenic) origin.

If one assumes that all of the I-TEQ is present on the particles, an estimate of its concentration in the ash can be made. The I-TEQs reported in these trials ranged from 0.1-6 (pg I-TEQ) $(g\ C)^{-1}$. Assuming that the biomass was 50% carbon, the ash content was 0.5% by weight and the effective toxicity factor was 0.02, then the PCDD/PCDF concentrations range from 0.5 to 30 (ng PCDD/PCDF) $(g_{ash})^{-1}$. Most values reported in the literature for the free combustion of wood fall in this range (Tame et al., 2003; Wunderli et al., 2000)

The gas phase (resin) and solid phase (filter) components of the samples were not analysed separately, so it was impossible to identify the phase distribution of the PCDD/PCDF. However, Figure 3.9 provides an indication because it depicts the relationship between the TEQ of the samples and the TSP. For the laboratory burns plotted in Figure 3.9a, there is an approximately linear relationship between the two variables for cane, straw and sorghum, suggesting that the greater part of the TEQ was present on particles. This is typical of the situation for wood combustion and solid waste incineration (Stanmore, 2004). No conclusion can be drawn for forest leaf litter because of the low TEQ values.

The field burns as shown in Figure 3.9b demonstrate no correlation between the PCDD/PCDF and the ash content. This suggests that a significant part of the PCDD/PCDF is present in the gas phase, reflecting the rapid cooling of the ash under field conditions.

3.4 Uncertainty analysis

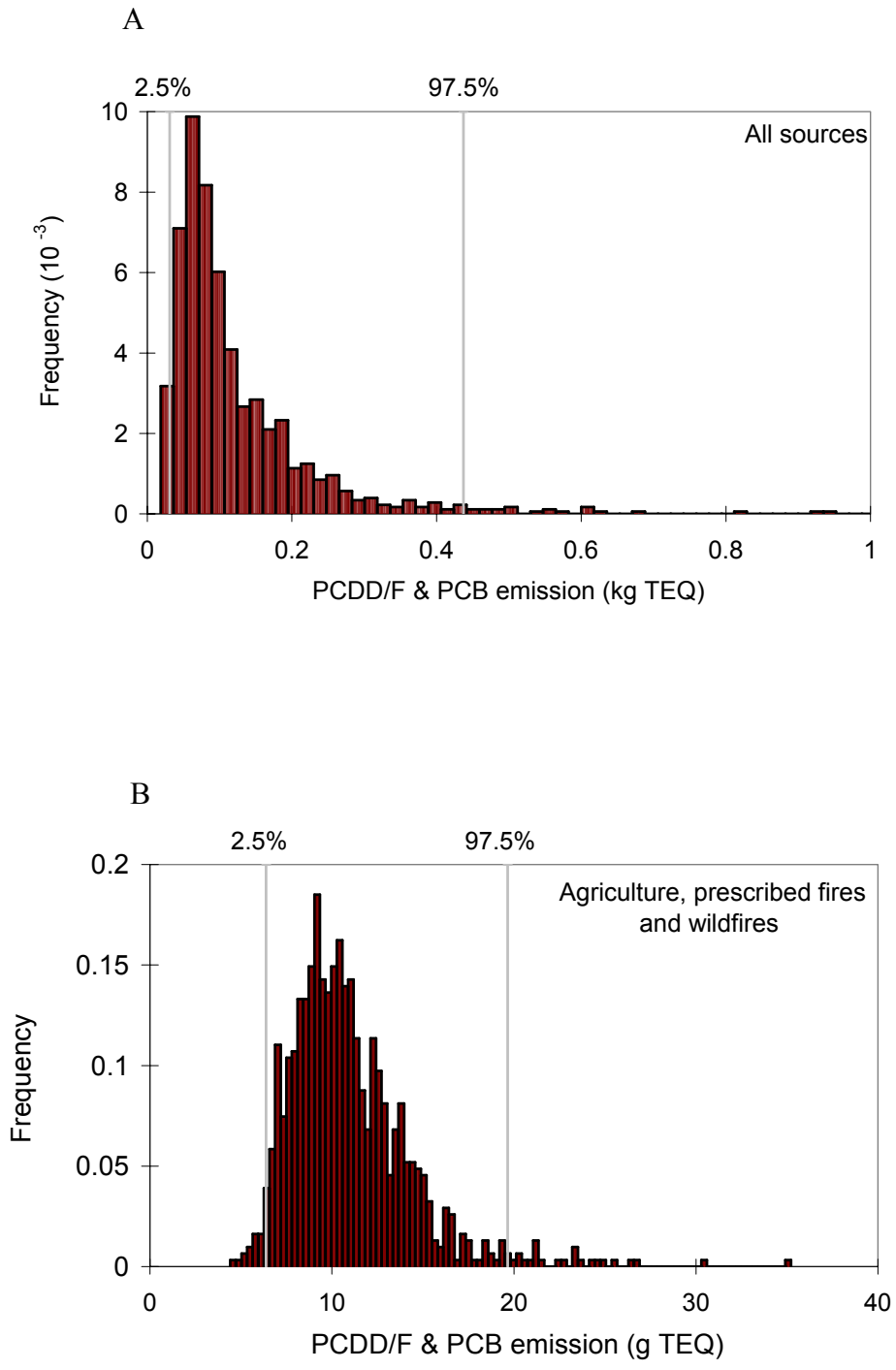

Figure 3.11. Probability distribution of PCDD/PCDF and PCB TEQ emissions.

A. All fire-types
B. Agriculture, prescribed fires and wildfires in 1994.

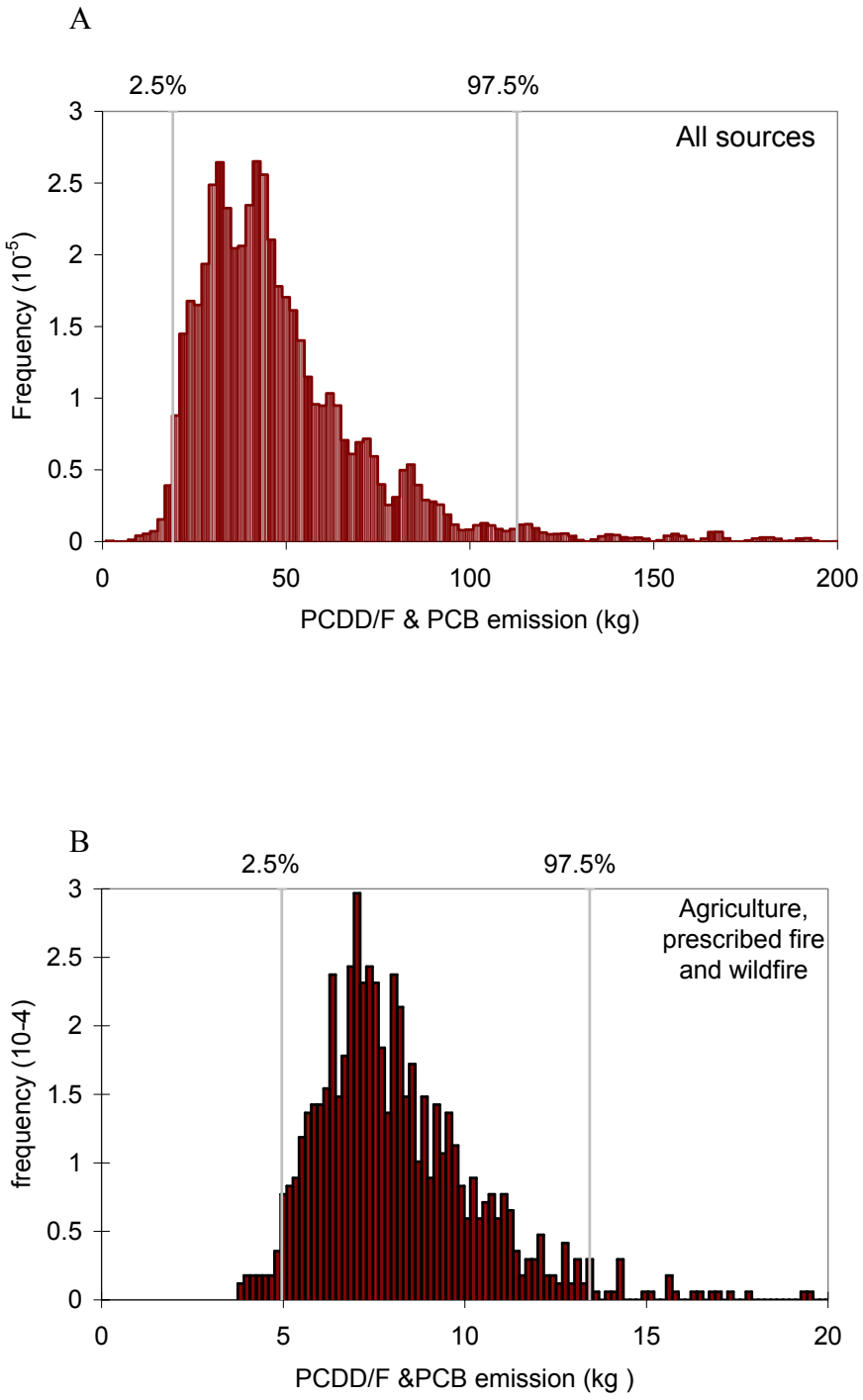

Figure 3.12. Probability distribution of PCDD/PCDF and PCB mass emissions.

A. All fire-type
B. Agriculture, prescribed fires and wildfires in 1994.

In the previous estimate for dioxin emissions (Environment Australia, 2002), the range was derived solely from the range in observed or assumed emission factors. In this study, uncertainties are estimated from the observed variability in emission factors and assessed uncertainty in activity data aggregated correctly from region and sector to national totals. The estimated probability distributions of the total emissions and emission from agriculture and forestry are shown in Figures 3.11 and 3.12.

The main purpose for illustrating the probability distributions of the emission estimates is to emphasise that by using measured emission factors we are now able to indicate where within the potential range the most likely emission estimate occurs. Previously, this was not possible and all values in the range were considered equally probable. The upper limit of the previous range was equally probable to all others. The current study has been able to reduce the most likely estimate of Australia's emission from 1,708 g TEQ to 152 g TEQ.

4 Summary of findings

This report details findings from a study of dioxins, furans and dioxin-like PCBs in Australian bushfires across a wide range of locations. There are five major findings.

Firstly, the dioxin emissions from wildfires were much lower than expected.

Secondly, laboratory tests cannot be used to infer emissions from fires in the field. Both the congener profiles and the emission factors differ. As illustrated in Figures 3.3 and 3.4, the congener profiles of field fires and laboratory burns are sufficiently different that laboratory burns cannot be used to infer dioxin emission profiles. The differences are less marked when examining mass emission rates (Figures 3.1 and 3.2) but there are still sufficient differences to imply that laboratory burns should also not be used to infer dioxin emission rates.

Thirdly, there are marked regional differences in dioxin emission factors and congener profiles. This is shown in Figure 3.2. In Queensland, dioxin emissions from forest fires are dominated by OCDD, but this is not the case in Western Australia or Victoria where no single congener dominates.

Fourthly, our uncertainty analysis enabled us to determine the probability distribution of expected dioxin and furan emissions, and thus to calculate a mean value. The current study has been able to reduce the most likely estimate of Australia's emission from 1,708 to 152 g TEQ y^{-1}.

Finally, the estimated emissions of dioxins from fires in Australia from this study (31-495 g TEQ y^{-1}) is substantially lower (>70%) than was previously estimated (72 to 1,700 g TEQ y^{-1}). This study also found that emissions from wildfires, 4.9 g TEQ y^{-1} (range 1.5 to 15 g TEQ y^{-1}) were substantially less than the previous estimate of 7 to 400 g TEQ y^{-1} (EA, 2002). However, our estimate of the mean value for savanna fire emissions is within the uncertainty bounds estimated by Environment Australia (2002). Most significantly, this study was able to determine a probability distribution for PCDD/PCDF emissions from bushfire, which should be valuable for the analysis of the environmental risk posed by this major air toxic.

Table 4.1. Emission estimates for PCB, dioxins, and furans.

Species	Crop residue	Prescribed fires	Wildfire	Savanna	All
PCB	0.1	0.4	0.7	3.9	5.1
PCDD/PCDF	3.1	3.3	4.2	127	138
Total	**3.2**	**3.6**	**4.9**	**130**	**142**
	(1.8-5.6)*	**(1.4-7.9)**	**(1.2-15.2)**	**(20-476)**	**(31-494)**
EA, 2002			7-400	62-1,240	72-1,700

* 95% ranges in parentheses.

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