Determination of the source and level of dioxin emissions from bushfires in Australia

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Executive summary

The National Dioxins Programme (NDP) bushfire study methodology (Meyer et al., 2004) applied to the latest inventory activity data (2005) predicts that Australia's emissions to the environment of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and dioxin-like polychlorinated biphenyls (dl-PCB) from bushfires and agricultural waste burning fall within the range of 50 g to 795 g WHO_{97}-TEQ with the best estimate of 233 g TEQ. Results of the current study lowers the estimate by 37% to 147 g TEQ and narrows the uncertainty range by 65% to 61 to 323 g TEQ. It is however possible that up to 30% of the emission is PCDD/PCDF and dl-PCB previously present in the soil and fuel and transferred to the smoke through the heat of the combustion. If so, then this component constitutes redistribution, not addition of new material to the environment and the amount of new PCDD/PCDF and dl-PCB added to environment lies within the range 36 g TEQ to 234 g TEQ with a best estimate of 104 g TEQ.

The extent of formation of PCDD/PCDF and dl-PCB during bushfires is an important issue for national emissions inventories because it can be argued that only formation constitutes release of new material to the environment. Previous studies were unable to distinguish between volatilisation of PCDD/PCDF and dl-PCB from soil and fuel, from formation during combustion and therefore were unable to determine the proportion of PCDD/PCDF and dl-PCB emitted in smoke that adds to the environmental burden. The objective of this study was to determine whether formation of PCDD/PCDF and dl-PCB can occur during bushfires, and if so how much they contribute to the national emissions.

Several experiments were designed to address the problem. The first addressed the potential for soil to release or form PCDD/PCDF and dl-PCBs in the absence of fire at elevated temperatures. The second assessed the potential for fuel to form PCDD/PCDF and dl-PCB during combustion when isolated from soil. The third compared the PCDD/PCDF and dl-PCB content of soil and fuel before combustion with the content of ash and smoke post combustion to determine the amount of new material produced during combustion.

The first experiment comprised a series of laboratory tests in which soil samples collected from field sites in central Victoria (Vic) and southern Queensland (Qld) were heated at 400 C in a quartz glass vessel for 30 minutes to simulate surface heating of soil during bushfires. There was no detectable emission of 2,3,7,8-Cl PCDD/PCDF congeners into the gas phase other than 1,2,3,4,6,7,8-HpCDD and OCDD, however there were large emissions of non-2,3,7,8-Cl congeners, particularly the more volatile, less chlorinated homologue groups TCDD and TCDF. Total emissions of these groups exceeded the original soil content indicating that some of this material was formed from combustion of soil organic carbon. Total emission of PCDD exceeded PCDF by more than a factor of two, which is similar to the congener patterns reported for Australian field measurements. Overall, the laboratory tests indicated that soil could be a significant source of PCDD/PCDF and dl-PCB during bushfires.

The second experiment showed that fuel burned over an inert surface released PCDD/PCDF and dl-PCB at rates which were only marginally lower than fuel combustion on a soil surface. This confirms that PCDD/PCDF and dl-PCB emission from combustion can also occur in the absence of soil and therefore that it is unlikely that soil is the sole source of PCDD detected in bushfire smoke.

The third experiment assessed whether the PCDD/PCDF and dl-PCB content of soil prior to combustion was sufficient to explain the PCDD content found in smoke and ash. There appears to be sufficient labile PCDD/PCDF and dl-PCB in soils and fuel to explain up to 75% of the PCDD/PCDF and dl-PCB content detected in smoke and ash. Emissions were weighted toward non-2,3,7,8-Cl PCDD/PCDF congeners, therefore a smaller proportion

(30%) of the TEF-weighted mass emissions could be explained by pre-combustion PCDD/PCDF and dl-PCB content. However, the study was not able to distinguish emission of PCDD/PCDF and dl-PCB from soil by physical processes (such as volatilisation) from chemical formation in the surface soil therefore these fractions indicate the upper limits of potential PCDD/PCDF and dl-PCB redistribution from pre-combustion sources.

Several studies and reviews have found there is significant risk of PCDD/PCDF and dl-PCB formation by artefacts unless particular care is taken during sampling. These artefacts are thought to arise through catalytic formation of PCDD at high temperature on metal surfaces. From their PCDD/PCDF congener patterns two test burns appeared to be impacted by formation artefacts. All other tests were comparable to the field measurements of the 2004 NDP bushfires study. Because the 2004 NDP field data are considered to be free from this class of artefact, the consistency between the two data sets is evidence that the current study has yielded valid measurements.

The *Inventory of Dioxin Emissions in Australia* currently reports bushfire PCDD/PCDF and dl-PCB emissions in four sub-categories; savanna fires, wildfires, prescribed fires and agricultural residue burning (cereal stubble and cane fires). Given the importance of the surface soil to PCDD emission rates and congener composition, fire class might not be the most appropriate stratification. This was confirmed by application of a cluster analysis to the combined field emission data from the 2004 NDP study and the current tests. The bushfire emissions data segregated naturally into two distinct groups; fires in tropical coastal areas and fires in inland and temperate forest, grassland and woodlands. This classification was incorporated into the emissions inventory methodology leading to substantially improved national emissions estimates. The revisions reduced the mean PCDD/PCDF and dl-PCB emission estimate for 2005 from 168 g TEQ for the fire-class stratification to 147 g TEQ for the regional stratification and reduced the estimate uncertainty by 51%. At least 104 g TEQ within an uncertainty range of 18 to 228 g TEQ is PCDD/PCDF and dl-PCB formed from fuel combustion. Fires in the savanna woodlands of Western Australia (WA), Cape York and Northern Territory (NT) comprise 85% of the total emissions and the arid grasslands of inland Australia comprise 5%. The remaining 10% is evenly divided between prescribed fires and wildfires in southern Qld, south-west WA, New South Wales (NSW), Vic and Tasmania (Tas), and agricultural burning; predominantly stubble fires.

This study also provided sufficient data on PCCD/PCDF/PCB content residual ash to allow an estimate on emissions to land. The combined average PCDD/PCDF and dl-PCB content measured in ash in this study and the 2004 NDP study is 2.2 pg TEQ (g ash)$^{-1}$ which is approximately 1% of the value indicated by the UNEP toolkit to be typical. Applying this emission factor to 2005 Australian activity data we estimate that 49 g TEQ PCCD/PCDF and dl-PCB was emitted to land from open burning in Australia. This is 8% of the emission estimated using the UNEP toolkit.

In conclusion, this study has found that soil is an important determinant of PCDD/PCDF and dl-PCB emissions from open burning, and is probably more significant than fire class. Emissions inventories based on soil classification (i.e. regionalisation) rather than fire class yield more accurate estimates of national emissions. It is possible that a significant proportion of total emissions, up to 75% of mass and 30% of TEQ, may derive from pre-combustion sources. However further investigations of PCDD/PCDF and dl-PCB formation processes are required to confirm this finding before a sound argument can be developed that national emissions estimates should be adjusted to account for PCDD/PCDF and dl-PCB redistribution from pre-combustion sources.

Glossary/abbreviations

Congeners: Closely related chemicals, derived from the same parent compound e.g. PCDD and PCDF.

Toxic equivalents: The toxicity of complex mixtures of congeners can be simply expressed using a single variable, the Toxic Equivalent (TEQ), which is derived by summing the product of the Toxic Equivalency Factor (TEF) for each congener with the mass of the congener (Van den Berg et al*.,* 1998*).* In this study we report WHO_{97}-TEQ WHO toxic equivalents, based on WHO_{97}-TEF WHO toxic equivalency factors. This system updates and expands the widely adopted system of International Toxic Equivalents Factors (I-TEFs and I-TEQs) proposed by the North Atlantic Treaty Organization. It includes dioxin-like-PCB (dl-PCB)and expands to TEFs for birds and fish. The issue was further reviewed by WHO in 2005 (Van den Berg et al., 2006), and some of the TEFs values were revised. For comparability with the 2004 NDP study (Meyer et al., 2004) the WHO_{97}-TEF values are used throughout this report unless specifically indicated.

ACT	Australian Capital Territory
CMAR	CSIRO Marine and Atmospheric Research
CO_2	Carbon dioxide
CO_2-C	Mass of carbon in CO_2
CSIRO	Commonwealth Scientific and Industrial Research Organization
CV	Coefficient of variance
DEW	Department of the Environment and Water Resources, Australia
dl-PCB	Dioxin-like polychlorinated biphenyls
EF	Emission factor
HpCB	heptachlorobiphenyl
HpCDD	heptachlorodibenzo-p-dioxin
HpCDF	heptachlorodibenzofuran
HxCB	hexachlorobiphenyl
HxCDD	hexachlorodibenzo-p-dioxin
HxCDF	hexachlorodibenzofuran
IPCC	Intergovernmental Panel on Climate Change
MDL	Minimum detection limit
NDP	National Dioxins Programme
NGGI	National Greenhouse Gas Inventory
NMI	National Measurement Institute
NRCET	National Research Centre for Environmental Toxicology
NSW	New South Wales
NT	Northern Territory
OCDD	octachlorodibenzo-p-dioxin
OCDF	octachlorodibenzofuran
PCA	Principal Component Analysis
PCDD	Polychlorinated dibenzo-*p* dioxins
PCDF	Polychlorinated dibenzofurans
PeCB	pentachlorobiphenyl
PeCDD	pentachlorodibenzo-p-dioxin
PeCDF	pentachlorodibenzofuran
PUF	Polyurethane Foam
Qld	Queensland
SA	South Australia

Tas	Tasmania
TCDD	tetrachlorodibenzo-p-dioxin
TCDF	tetrachlorodibenzofuran
TeCB	tetrachlorobiphenyl
TEF	World Health Organization toxic equivalency factor (WHO_{97}-TEF)
TEQ	World Health Organization toxic equivalent based on WHO_{97}-TEFs
Vic	Victoria
WA	Western Australia
WHO	World Health Organization

The samples collected during this study are identified in this report using a standard code:

<Sample type>-<Test burn location>-<Fuel source.-<Substrate>

e.g. A-GU-GU-S

Sample type codes are:

A	Air
L	Leaf litter
Ash	Ash and burned fuel residues
S	Soil

Test burn location codes are:

K	Redlands Bay, Qld
GU	Griffith University, Qld
Eb	Mt Barker, Qld
PT	Potter’s Tk, Vic
B	Blakeville, Vic
G	Guildford, Vic
As	Aspendale, Vic

Fuel source locations codes are:

D	Darwin, NT (native Sorghum spp)
GU	Griffith University, Qld
Eb	Mt Barker, Qld
PT	Potter’s Tk, Vic
B	Blakeville, Vic
G	Guildford, Vic
As	Aspendale, Vic

and substrate codes are:

S	Soil
B	Bricks

1 Introduction

The bushfire study conducted from 2002 to 2004 under the National Dioxins Program (NDP) aimed to provide a more accurate estimate of the emissions of PCDD from bushfires (Meyer et al., 2004). The study determined that the total emissions of PCDD, PCDF and dl-PCB from bushfires ranged from 0.05 to 2.9 pg TEQ/g of fuel. Based on these levels and the total area of land burnt each year in Australia, the total emissions of PCDD to air from bushfires was estimated to be 32 to 570 g TEQ per year of which savanna fires in northern Australia accounted for 83%. The 2004 inventory of dioxin emissions in Australia estimates that this accounts for 20 to 30% of total PCDD/PCDF and dl-PCB emissions to the environment (Bawden et al., 2004).

There are a number of uncertainties with the estimate including the extent that emissions are related to formation in the fire or represent the release of dioxin-like chemicals from fuel and soil due to heating in the combustion process. The NDP bushfire study did not include an examination of the fuel, soil and ash components, hence it could not clarify the origin of the PCDD/PCDF and dl-PCBs that were measured in the emissions. The bushfire study found:

- Congener profiles in smoke were similar to soil profiles suggesting that at least for some congeners re-emission may be an important pathway.
- A separate study by Prange et al. (2003) based on a few samples using a mass balance approach has suggested that re-emission from soil may explain the large proportion of the PCDD/PCDF and dl-PCBs that are emitted during bush fires.

These findings, while not conclusive, have major implications towards a successful inventory of PCDD/PCDF and dl-PCB emissions in Australia. If PCDD/PCDF and dl-PCBs detected in smoke are not newly-formed but are to some extent volatilised from the soil or fuel, then bushfires could be a means of redistribution rather than a primary source of PCDD/PCDF and dl-PCBs. In order to develop effective policies to reduce both the emissions and their impacts it is important to distinguish between the actual amount of new PCDD/PCDF and dl-PCB mass that is added to the environment from long-distance transport of old PCDD/PCDF and dl-PCB by smoke-plumes. If bushfire emissions were composed substantially of old PCDD/PCDF and dl-PCB rather than newly-formed material then the there could be a case for either reviewing the current inventory guidelines such as the UNEP toolkit, or for developing specific advice on their application.

The Department of the Environment and Water Resources contracted CSIRO Marine and Atmospheric Research to conduct an experimental program to assess this question, and specifically to address the following objectives:

1. Assess the extent to which PCDD/PCDF and dl-PCB releases could be the result of re-mobilisation of PCDD/PCDF and dl-PCB from the soil, ground litter or vegetation in contrast to new formation during the fire event.
2. Provide a more accurate estimation of the total emissions of PCDD/PCDF and dl-PCB from bushfires in Australia.

This report presents the progress towards answering these objectives.

2 Experimental design

The logic of the experimental design is encapsulated the following scientific questions.

The primary questions addressed in this study are:

1. Can soil emit PCDD/PCDF and dl-PCB when heated in the absence of fuel?
2. Can fuel combustion emit PCDD/PCDF and dl-PCB in the absence of soil?

If soil is not a source of PCDD/PCDF and dl-PCB then the question of redistribution disappears. If it is a source then the next questions are:

1. How much of the emission is sourced from fuel combustion?
2. How much of the soil emission is newly-formed or transformed PCDD/PCDF and dl-PCB?

Questions 3 and 4 present a major challenge. To quantitatively disaggregate the components of combustion chemistry from the physical processes of volatilisation and desorption is beyond the scope of a study of this size, however it may be possible to identify some limits.

To address these questions, the objectives were cast as a set of hypotheses that could be individually tested. The hypotheses are:

A. The PCDD/PCDF and dl-PCB observed in smoke are derived primarily from the heated soil layer.

B. At the extreme, all the PCDD/PCDF and dl-PCB in the smoke are volatilised from PCDD/PCDF and dl-PCB already present in the soil and the fire is a component of a natural redistribution mechanism rather than the process by which new PCDD/PCDF and dl-PCB is formed.

Several experiments were designed to test these hypotheses:

I. A direct approach was to measure in the laboratory the emissions from soil samples subjected to a heating pulse similar to that produced in surface soil in the field by a fuel reduction burn. The PCDD/PCDF and dl-PCB release could occur by volatilisation from the existing pool or formation in the soil matrix of new PCDD/PCDF and dl-PCB. From this it can be determined whether, in the absence of fuel combustion, the soil pool releases sufficient PCDD/PCDF and dl-PCB to explain the concentration previously observed in smoke.

II. Whether PCDD/PCDF and dl-PCB is released directly from fuel combustion or whether PCDD/PCDF and dl-PCB is released from soil by the heat of fuel combustion can be tested by measuring the PCDD/PCDF and dl-PCB content of smoke from fuel burned in the field directly on soil or on an inert surface (e.g. vitrified bricks). If the PCDD/PCDF and dl-PCB originates from the soil, then the PCDD/PCDF and dl-PCB concentration in smoke from fuel burned on an inert surface should be minimal.

III. A mass balance of PCDD/PCDF and dl-PCB content in soil and fuel prior to combustion and smoke and ash following combustion should indicate the amount of new PCDD/PCDF and dl-PCB formed during combustion.

IV. If the PCDD/PCDF and dl-PCB is primarily of soil origin, then PCDD/PCDF and dl-PCB content in smoke should be dependent on the soil properties and independent of the fuel type. Therefore, if subsamples of fuel from a uniform batch are burned on a range of soils with contrasting PCDD/PCDF and dl-PCB content and congener pattern, then the PCDD/PCDF and dl-PCB content of the smoke will be highly correlated with PCDD/PCDF and dl-PCB content of the soil.

The experiments are described in detail in the following sections.

3 Methodology

3.1 Sampling locations, soils and fuels

The experimental design required measured PCDD/PCDF and dl-PCB emissions from test burns at selected locations in Australia. This section describes the test locations and their characteristics.

Meyer et al. (2004) suggested that the primary factor determining the clustering of PCDD/PCDF and dl-PCB emissions profiles was location. There were two main clusters:

1. temperate forest areas in southwest and southeast Australia and inland NT
2. coastal tropical regions in Qld and NT.

Therefore, this study concentrated on three regions: (1) central highland forests in Vic that are representative of the temperate southeast and southwest forests, (2) the coastal region near Brisbane characterised by soils with very high OCDD content which is representative of the coastal tropical region, and (3) the region approximately 50km inland of Brisbane where OCDD concentrations are 2 to 3 orders of magnitude lower, which is representative of the inland tropical region.

The three locations selected in Qld were:

1. Redland Bay in cleared grazing land (site K, tropical coastal)
2. Coastal forest on the Griffith University campus (site GU, tropical coastal)
3. Mt Barker, an inland site approximately 50km west of Brisbane (site Eb, tropical inland).

Sites 2 and 3 were relatively undisturbed sites over soils that previous studies had shown contained substantially different concentrations of PCDD/PCDF and dl-PCBs in the surface soil. Redland Bay was chosen for its suitability for safely conducting experimental burns of the selected fuels over an inert surface.

Three sites were selected in messmate/stringy-bark forests in central Vic:

1. Potter’s Tk, 5km northwest of Blackwood (site PT)
2. Blakeville (Site B)
3. Rusconis Road, 8km south of Guildford (site G).

All are representative of temperate southeast forests.

The locations of these sites are shown in Figure 3-1

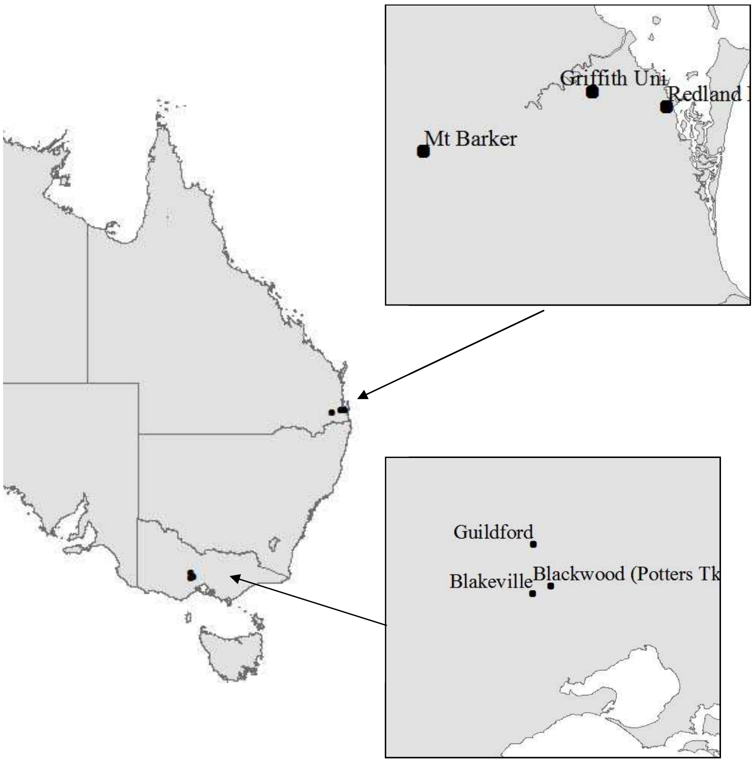

Figure 3-1 Locations of the field sites

Fuels

The fuels used in this study were: (1) the natural forest litter at the Griffith University forest site, (2) the native tussock grass at the Mt Barker site, and (3) the fine fuels, mostly comprising leaf litter with a small (~10%) humus content, on the forest floor at Guildford, Blackwood (Potter's Tk) and Blakeville in central Vic. In addition to forest fuels it was decided also to include native annual sorghum harvested commercially in the NT. This fuel is representative of tropical savanna woodland fuels.

3.2 Field measurements

Experiments II, III and IV involved analysis of PCDD/PCDF and dl-PCB emissions from combustion of natural fuels over undisturbed soil or over an inert surface. Experiment II compared emissions over soil with emissions from identical fuel over an inert surface. Experiment III compared the PCDD/PCDF and dl-PCB concentrations in each of the pre-combustion and post-combustion pools and Experiment IV compared the congener patterns observed when fuels from low PCDD/PCDF and dl-PCB regions were burned over high PCDD/PCDF and dl-PCB soils and the reverse. The three experiments were designed around a common set of field emissions data and required the development of high volume smoke samplers which could collect smoke from small area test sites so that all components contributing to the emission (soil, fuel, smoke and ash residue) could be sampled for PCDD/PCDF and dl-PCB content.

3.2.1 Field test design

The study comprised a series of controlled test burns at the Vic and Qld locations described above. Each test burn comprised an area of approximately 10 m by 10 m from which soil, fuel, smoke and ash samples were collected for analysis. Specifically the samples were:

- 1 pre-burn soil sample
- 1 or 2 fuel samples

- 1 smoke sample
- 1 background air sample
- 1 ash sample
- 1 smoke sample from fuel burned over the inert surface.

Samples of surface soil and litter were collected before combustion to determine the pre-combustions PCDD/PCDF and dl-PCB pool size. Surface soil (0 to 3 cm) is the zone that is affected by the combustion process (Tomkins et al., 1991 Tolhurst, 1995). Each sample comprised 18 soil cores collected on a uniform grid within the burn site, which were bulked and homogenised for analysis. The litter sample comprised fine fuel (<6 mm) and where relevant coarse woody fuel (>6 mm). Samples were ground using a Wiley mill to pass a 2 mm mesh.

During combustion a smoke sample containing 50 to 100 g carbon in the form of CO_2 (CO_2-C) was collected using the high volume sampler described in the next section. Each sample comprises both burning-phase and smouldering-phase combustion. Sampling specifically was not biased towards the cooler smouldering-phase combustion.

Following combustion, representative ash samples were collected from each test site, and bulked for analysis.

A second test was conducted over an inert surface of fired paving bricks using fuels collected at each of the sites. The purpose of this second burn was to measure PCDD/PCDF and dl-PCB concentration in smoke from combustion of fuel in the absence of soil. These data are required by Experiment II.

In the tests conducted in Qld each fuel type was burned over soil in each of the locations and over bricks at Redland Bay. This gives an orthogonal experiment (Experiment IV) in which all combinations of fuel and soil were tested.

The Vic tests concentrated on prescribed burns with defined fuel loads. The tests conducted at Potter's Tk and Blakeville were routine operational burns on undisturbed fuel conducted by the Department of Sustainability and Environment (DSE), Vic. In the Guildford test an artificially high fuel load of 35 t ha^{-1} was produced by adding fine fuel collected from an adjacent area.

The test burn schedule and the labels for the smoke and air samples are shown in Table 3-1. The fuel, soil and ash samples are listed in Table 3-2.

Table 3-1 Locations, details of test burns and sample labels

Test	Date	Location	Fuel	Surface	Smoke sample	Background air sample
1	19/8/2005	Redland Bay	Griffith Uni	Soil	A-K-GU-S	-
2	13/9/2005	Redland Bay	Mt Barker	Bricks	A-K-Eb-B	-
3	15/9/2005	Redland Bay	Griffith Uni	Bricks	A-K-GU-B	-
4	22/9/2005	Mt Barker	Mt Barker	Soil	A-Eb-Eb-S	-
5	29/9/2005	Griffith Uni	Griffith Uni	Soil	A-GU-GU-S	-
6	28/10/2005	Redland Bay	Darwin (Sorghum)	Bricks	A-K-D-B	-
7	28/10/2005	Redland Bay	Darwin (Sorghum)	Soil	A-K-D-S	A-Bkd-K
8	3/11/2005	Mt Barker	Darwin (Sorghum)	Soil	A-Eb-D-S	-
9	3/11/2005	Mt Barker	Griffith Uni	Soil	A-Eb-GU-S	A-Bkd-Eb
10	17/11/2005	Potter’s Tk	Potter’s Tk	Soil	A-PT-PT-S	-
11	18/11/2005	Blakeville	Blakeville	Soil	A-B-B-S	-
12	28/11/2005	Guildford	Guildford	Soil	A-G-G-S	-
13	12/12/2005	Aspendale	Guildford	Bricks	A-As-G-B	-
14	13/12/2005	Aspendale	Blakeville	Bricks	A-As-B-B	A-Bkd-B
15	5/4/2006	Aspendale	Potter’s Tk	Bricks	A-As-PT-B	A-Bkd-Asp

Table 3-2 Locations where fuel, soil and ash samples were collected, and sample labels

Test	Location	Fine Fuel	Coarse Fuel	Soil sample	Ash
1	Redland Bay	-	-	S-K	-
4	Mt Barker	L-Eb	-	S-Eb	Ash-Eb-Eb
5	Griffith Uni	L-GU-F	L-GU-C	S-GU	Ash-GU-GU
7	Redland Bay	L-D	-	-	Ash-D-K
9	Mt Barker	-	-	-	Ash-GU-Eb
10	Potter’s Tk	L-PT	-	S-PT	Ash-PT-PT
11	Blakeville	L-B	-	S-B	Ash-B-B
12	Guildford	L-G	-	S-G	Ash-G

3.2.2 High volume PCDD/PCDF and dl-PCB field sampler

The design of the high volume smoke samplers was based on the design developed for the 2004 NDP study (Meyer et al., 2004). Each unit consisted of a hood (0.8 m by 0.8 m) that could be positioned approximately 0.5 to 2 m above the combustion zone to collect the smoke. The smoke was then drawn at high flow rate (0.5 to 1 m^3 min^{-1}) though a sample line 6 m long by 100 mm diameter, a 10 by 8 inch quartz filter and a 130 mm diameter XAD2/PUF trap. The air pumps used were either a centrifugal air blower (GAST, SDR5, USA) powered by an 8 HP Honda petrol motor, or a carbon vane pump powered by a petrol driven 5 kVA generator. In order to control the trap temperature and humidity the smoke sample could be diluted with ambient air at a controlled and measured flow rate upstream of the trap. The dilution rate was measured using an orifice plate. Air flow through the trap was measured with an annubar-type flow meter and total sample volume was measured with a high-volume gas meter. The hood and sample tubes were constructed from 316 stainless steel. The filter housing, filter holder and the XAD2 trap cartridges were constructed from anodised aluminium.

A small sample of air was drawn upstream of the filter and trap in order to monitor the CO_2 concentration in the smoke during sample collection. In order to ensure that the CO_2 concentration in this sub-sample remained within range of the analyser, the sample was diluted with CO_2 free air. The split ratio was set to approximately 1 in 5 and accurately measured with a bubble flow meter before and after each test. During each test a second air sample was drawn using a Teflon diaphragm pump from the main sample line upstream of the filter and accumulated into a 60 litre Tedlar bag. The average sample CO_2 concentration during sampling was calculated either directly from the accumulated gas sample in this Tedlar bag or from the CO_2 concentrations measured continuously during sampling. A schematic diagram of this system is shown in Figure 3-2.

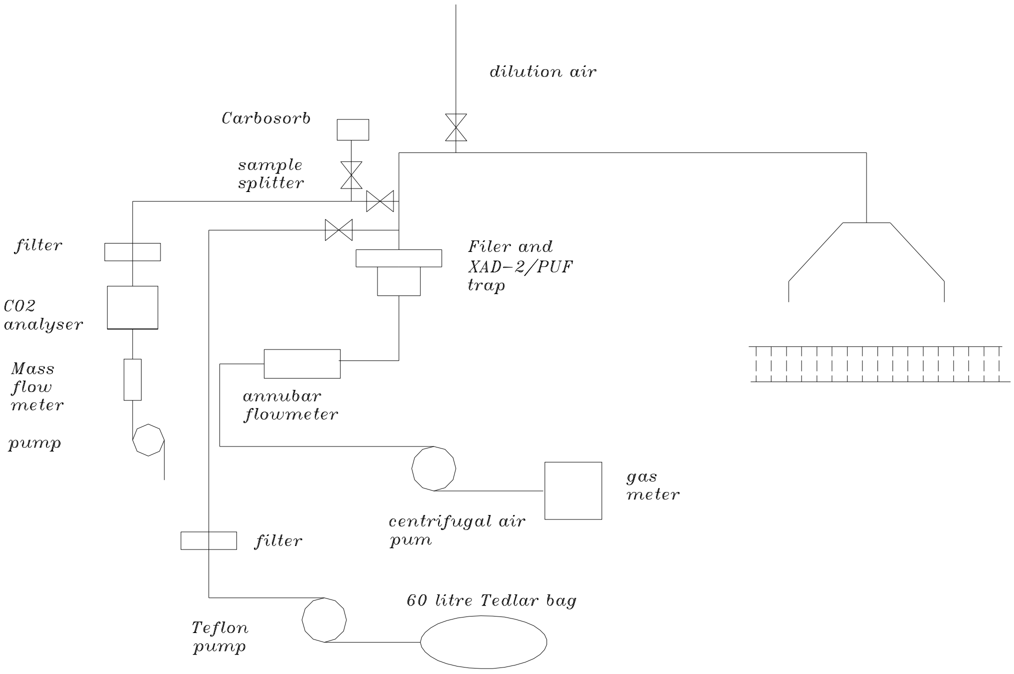

Figure 3-2 Schematic diagram of smoke sampler

The units were fitted with twenty Type K thermocouples, sheathed in 1/16 inch stainless steel; eight were used to measure the soil surface temperature at the interface between the fuel and the humus layer, eight were used to measure soils temperature at 10 mm depth, and the remaining thermocouples measured air temperature at the hood inlet, hood surface temperature and XAD2 trap temperature. The control/logger unit block layout is shown in Figure 3-3.

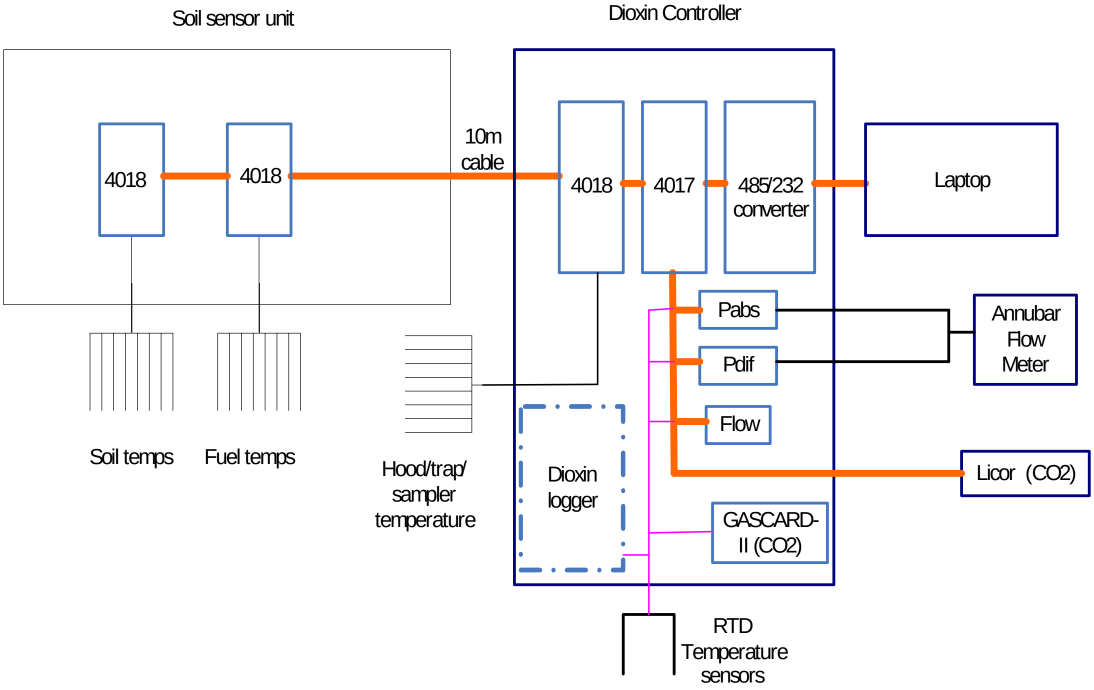

Figure 3-3 Schematic diagram of system logger/controller

The PCDD/PCDF and dl-PCB sampling head comprised an open face filter for trapping the condensed phase (10 by 8 inch pure quartz fibre filters, Pall 10 by 8 QAT-UP), backed up by PUF-XAD2-PUF sandwich gas traps. Traps are constructed from medium-density PUF (polyurethane foam) plugs (nominal density 0.02 to 0.03 g cm^{-3}, 130 mm diameter, 25 mm and 50 mm thickness) with 40 g of XAD-2 resin per charge.

The Victorian sampler was mounted on a small trailer, for ease of access to the field sites. It could be quickly assembled and deployed, and manoeuvred around the fire area. It is shown in operation in Figure 3-4.

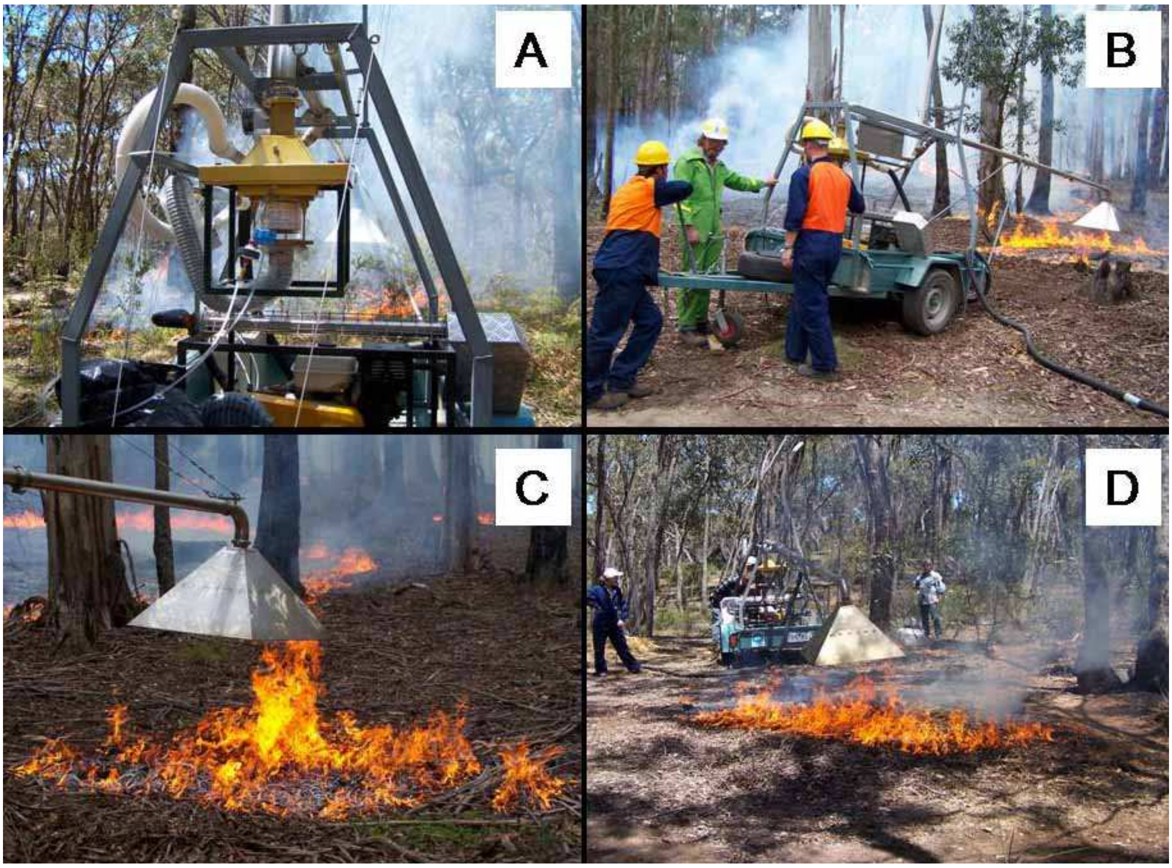

Figure 3-4 Victorian sampler in operation at (a) Potter's Tk near Blackwood; (b),(c), at Blakeville; and (d) at Guildford.

The Brisbane unit was designed for operation from a flat-tray truck equipped with a small crane. The hood, sample tube and trap were suspended from the crane and connected to the main pump and gas meter by flexible polyethylene ducting. This unit is shown in operation in Figure 3-5.

The height of the sample hood above the combustion zone was continually adjusted to maintain the CO_2 concentration of the sample air within the range of the CO_2 sensor while also keeping the temperature of the sample gas below 200 ^{o}C.

Figure 3-5 Queensland sampler in operation at Griffith University. (a) Manoeuvring the hood over the combustion zone, (b) proximity of hood to combustion area.

3.3 Laboratory measurements of PCDD/PCDF and dl-PCB emission directly from soil

The laboratory tests required by Experiment I were conducted on each of the soils from the field sites to determine their PCDD/PCDF and dl-PCB emissions in the absence of fuel combustion. In these tests a soil sample was placed in a quartz cell and heated for 30 minutes in a tube furnace thermostated at 400 ^{o}C. The cell was purged with a constant flow of zero grade air; the airstream then passed through a 25 mm quartz filter and PCDD/PCDF and dl-PCB trap consisting of XAD-2 resin sandwiched between two PUF plugs. The system is shown schematically in Figure 3-6.

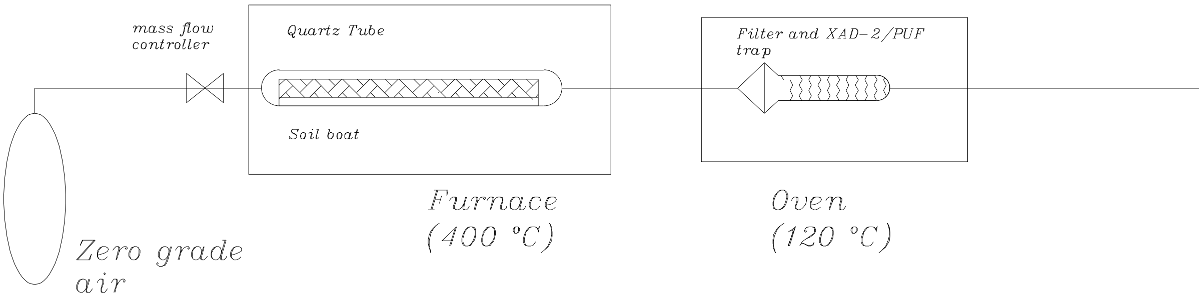

Figure 3-6 Diagram of the trapping system for PCDD/PCDF and dl-PCB emissions from soil

The soil samples used in the laboratory tests were collected at the field sites prior to the field test burns. Each soil sample comprised 18 cores of the top 3 cm of soil, which were bulked, ground, homogenised and frozen until required. A sample of approximately 100 g soil was used for each test providing sufficient sample for a layer 2 to 5 mm thick on the bottom of the quartz tube within the heated zone. The XAD-2/PUF trap was maintained at 120 ^{o}C in a temperature controlled chamber to avoid condensation of water and semi-volatile organics. The transfer lines in the air gap between the tube furnace and the oven were heated with a heat gun to prevent condensation.

The zero air flow rate was set to 2 SLPM. The air pressure at the inlet to the quartz tube was maintained near ambient pressure by balancing the pump flow rate to the zero air delivery rate of the mass flow controller. Excess air from the mass flow controller was vented upstream of the sample tube. Its flow was monitored and maintained at less than 50 mL min^{-1} by minor adjustments to the pump flow. Amongst other things this ensured all points downstream of the inlet were below ambient pressure and therefore any air leaks downstream of the soil sample would be inward and would not result in loss of sample gas.

In each test soil was heated for 30 minutes at approximately 400 ^{o}C. Typically, when the quartz tube containing the soil was inserted into the tube furnace and the gas lines were connected, furnace temperature dropped to approximately 350 ^{o}C then slowly increased to the 400 ^{o}C set point during the subsequent 5 to 10 minutes. The soil water content was evaporated in a pulse during the first few minutes, which was also the period in which most of the organic material was emitted. At the end of each test, the soil was reweighed.

The schedule for the 5 laboratory tests is shown in Table 3-3.

Table 3-3 Laboratory tests soil samples used and smoke sample labels

Test	Ambient air	Soil	Label
1	-	Mt Barker, S-Eb	Lab-Eb
2	-	Griffith Uni, S-GU	Lab-GU
3	-	Guildford, S-G	Lab-G
4	-	Potter's Tk, S-PT	Lab-PT
5	-	Blakeville, S-B	Lab-B
6	Lab air	-	Lab-air

3.4 Analysis

Samples of ambient air, smoke, fuel, soil and ash residues were analysed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for all 2,3,7,8-chlorinated PCDD (seven) and PCDF (ten) congeners, the 12 dl-PCB congeners assigned a TEF by WHO, and total PCDD/PCDF homologue concentration for the 4-Cl to 8-Cl PCDD/PCDFs. The analytical methodology for the determination of PCDD/PCDF and dl-PCBs are based on USEPA methods 1613B and 1668A, respectively. A detailed description of the analysis method is given in Section 8.1.

All sample analyses data are listed in Section 8.2.

4 Results

4.1 Emission of PCDD/PCDF and dl-PCB from combustion in the field

The field emission tests provided the data for Experiments II, III and IV.

4.1.1 Emission factors

PCDD/PCDF and dl-PCB emission rates are presented in this study as emission factors. The emission factor is usually defined as the amount of the chemical species emitted by the combustion per unit mass of fuel. To measure this directly requires sampling all the smoke produced from combustion of a known mass of fuel usually in a cone calorimeter, a dilution tunnel (e.g. the Australian Standard 4013 test for combustion heaters) or a combustion room (e.g. Gullett and Touati, 2002, 2003a, 2003b). It is not possible to achieve this in the field. An alternative method, which is suitable for field measurement, is based on the fact that total fuel carbon is a conserved quantity. The approach has been used in many field campaigns over more than 25 years (e.g. Hurst et al., 1994; Andreae and Merlet, 2001).

The combustion of forest fuel first converts the fuel into smoke compounds. About 50% of fuel mass is carbon, and the carbon-based chemical species formed during combustion are the gaseous compounds comprising CO_2, carbon monoxide (CO), methane (CH_4), and the volatile organic compounds (VOCs), and semi volatile and non-volatile compounds that condense into fine particles. Collectively these combustion products are termed “volatilised carbon”. The exact species composition may vary but the mass of carbon is conserved and, therefore, if 1 kg of fuel with a carbon content of 50% is burned then the smoke produced will contain a total of 500 g of volatilised carbon. The smoke mixes with ambient air, diluting some species, and adding to the concentrations of other species already present in the ambient air. The dilution ratio is usually not known, however, assuming that no further chemical transformation occurs and that loss by deposition to the ground surface is negligible in the time between combustion and sampling, then the mass ratio of each combustion product to total volatilised carbon in the raw smoke remains unchanged by this dilution. Therefore, to determine the mass of a specific combustion product from combustion of a known mass of fuel of known carbon content, we only need measure the concentrations of the trace species and the total volatilised carbon in each smoke sample and in the background air. CO_2 comprises more than 90% of the total volatilised carbon (Andreae and Merlet, 2001), and therefore CO_2 is an easily measured and effective surrogate for total emitted carbon.

The derivation of emission factors is presented in detail in Meyer et al. (2004). In brief, emission factors (EF) of PCDD/PCDDF relative to emitted CO_2-C are calculated as:

$$EF= ([X] – [X_{amb}])/([CO_2]- [CO_2]_{amb})$$

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.

The ratio of CO_2 to total carbon on average varies from approximately 0.92 in forests to 0.95 in savannas, grasslands and agricultural waste fires (Andreae and Merlet, 2001), therefore, at worst, the emission factors calculated relative to CO_2-C are 8% larger than emission factors expressed relative to total emitted carbon.

To calculate emission factors, the congener concentrations in each smoke sample are first corrected for the relevant background content air concentration. The corrections are less than 1% of total PCDD/PCDF and dl-PCB mass and less than 2% of TEQ in all samples. These concentrations are further corrected for the total mass of CO_2-C above ambient background that had passed through the XAD-2 trap to give the emission factor. Unless otherwise indicated congeners present at levels below the detection limit are assigned the concentration of 0 pg or lower bound values.

4.1.2 Combustion characteristics of the field test

The fifteen tests were performed mostly as single burns although in four cases, two or three burns were performed to increase the total carbon sample passing through the XAD-2 trap. Most burns were performed over an area typically 10 m in diameter with the exception of the three Victorian burns over a small brick hearth 1 m^2 in area. Each burn was completed within 15 to 30 minutes. Surface temperature and soil temperature at approximately 1 to 2 cm depth were each measured at eight points within the test area and recorded at 1 second intervals. Additionally, thermocouples were located at the top of the hood approximately 5 cm respectively below the entrance to the sampling tube, and in the sample plenum chamber 5 cm above the main filter to measure sample gas temperature prior to collection and trap temperature.

Two contrasting examples of the time course of the temperatures are shown for the prescribed burn at Blakeville in Vic (A-B-B-S, Figure 4-1) where the surface fine fuel load was14 t ha^{-1} and in the test burn at Guildford (A-G-G-S, Figure 4-2) in which the fuel load was increased to 35 t ha^{-1} by the addition of litter from areas adjacent to the burn site. In both tests maximum soil surface temperatures were similar, however the duration of the surface heating increased with fuel load. At Blakeville, the soil surface temperature remained above 200 ^oC for approximately 3 to 4 minutes compared to the Guildford test in which this state was maintained on average for 13 minutes. The difference in heating duration was particularly apparent at 10 mm depth in the soil. At Blakeville, with one exception the heat pulse was barely detected at 10 mm depth, while at Guildford, the soil heating of 5 to 50 ^oC was observed. However in neither case were 10 mm temperatures sufficient to have any effect of PCDD/PCDF and dl-PCB formation or volatilisation.

The minimum temperature at which heterogeneous PCDD/PCDF and dl-PCB formation is thought to occur is 200 °C, (Stanmore, 2004) therefore the operational objectives were to maximise sample CO_2-C collection at a sampling temperature below 200 °C. Because the temperature and CO_2 are correlated, this posed a challenge that was rarely achieved. In both cases illustrated above, sample air temperatures in excess of 200 °C in the hood were encountered, although at Guildford (Figure 3-1) high temperatures persisted for a significant proportion of the burn duration. The sample air temperature observed in the plenum chamber was always less than 50 °C, increasing slowly from ambient temperature to a maximum near the end of the sampling period.

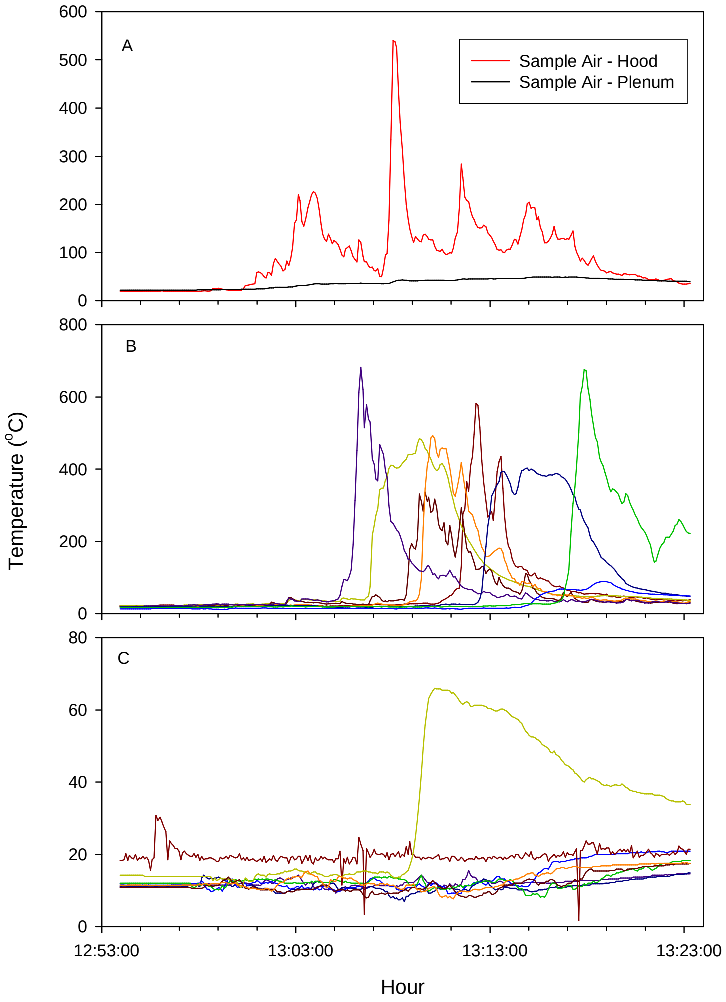

Figure 4-1 Time-course of temperatures at Blakeville, Vic (a) sample air temperature, (b) soil surface temperature and (c) soil temperature at 10 mm depth. For clarity replicate thermocouples are distinguished by colour.

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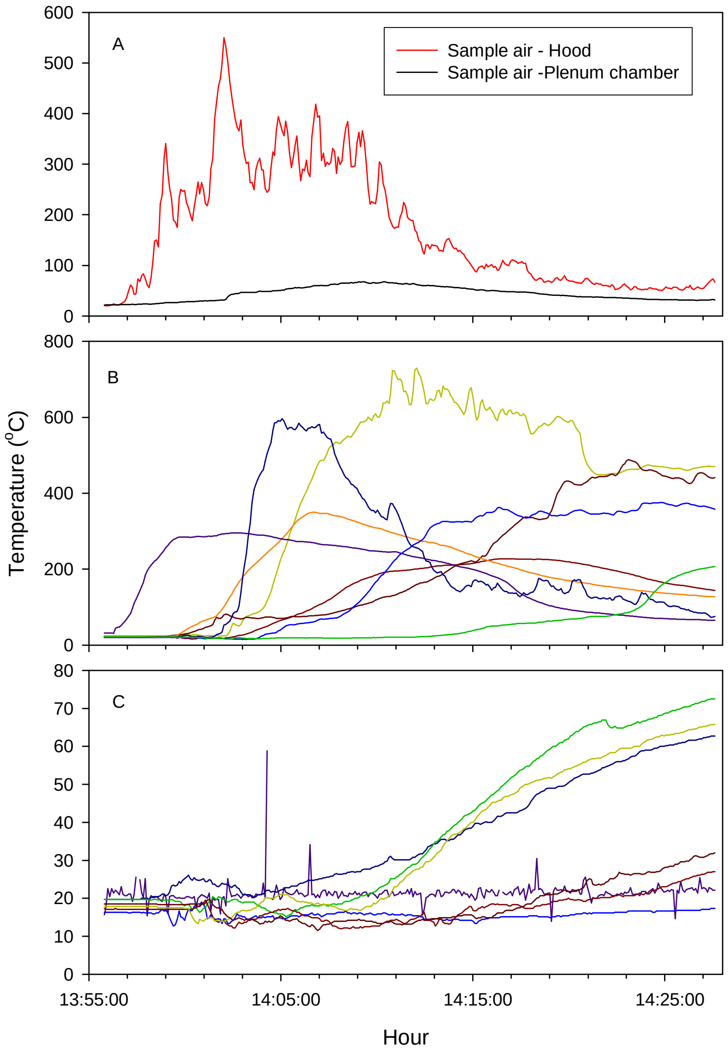

Figure 4-2 Time-course of temperatures at Guildford, Vic. (a) sample air temperature, (b) soil surface temperature and (c) soil at 10 mm depth. For clarity replicate thermocouples are distinguished by colour.

In the final three tests, thermocouples were clamped to the surface of the hood, halfway up and on opposite sides, to monitor the time-course of the hood temperature (Figure 4-3). Although the sample air temperature exceeded 400 ^{o}C, the fluctuations were strongly damped and hood temperature increased to a peak at approximately 200 ^{o}C. The hood was constructed of 0.6 mm stainless steel sheet and therefore, despite the poor thermal conduction of the material, it would be expected that temperature gradients across the thickness of the material would be small, and that the thermocouples would register a good approximation of hood surface temperature. Nevertheless, all thermocouples have significant heat capacity and it is possible that we did not measure the detailed dynamics of the surface temperatures and, therefore, underestimated the short-term maxima.

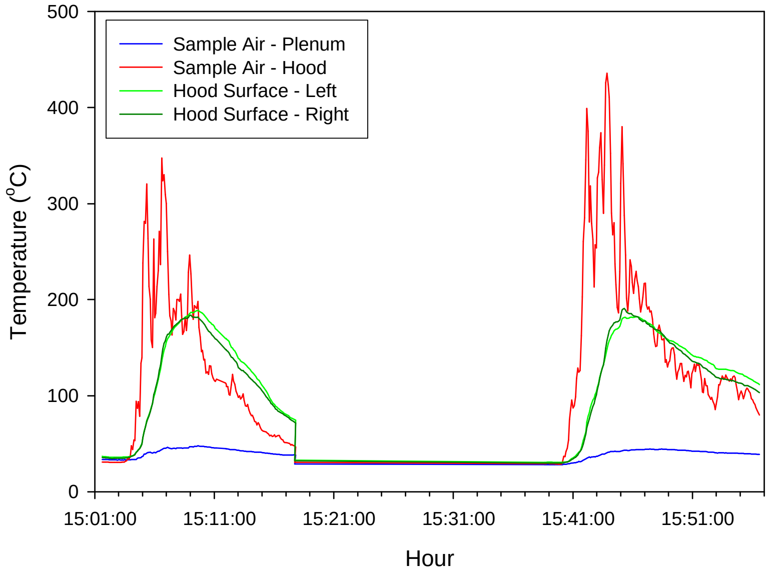

Figure 4-3 Time-course of sample air temperature and hood surface temperature during testing of Guildford fuel over fired bricks at Aspendale (A-As-G-B)

Broadly similar time-courses were observed in all field tests. These are summarised in Table 4-1. Most of the heating activity occurs at the soil surface with virtually no penetration even to 10 mm depth. Soil surface temperature is very high, peaking between 375 °C and 700 °C and within the temperature range that PCDD/PCDF chemistry occurs (> 200 °C) averages between 320 °C and 500 °C (Table 4-2). Therefore there is a high probability of complex PCDD/PCDF/PCB mobilisation, production and transformation at or near the soil surface.

Table 4-1 Average sample gas and soil temperatures, and their ranges (in brackets) recorded during field tests

Label	Sample gas (hood)		Sample gas (plenum)		Soil-surface[1]		Soil 1cm depth	
A-K-GU-S	82	(14 – 293)	34	(16 – 57)	236	(19 – 454)	32	(13 – 63)
A-K-Eb-B	-	-	-	-	196	(15 – 375)	-	-
A-K-GU-B	153	(94 – 381)	35	(22 – 57)	164	(25 – 499)	-	-
A-Eb-Eb-S	87	(13 – 241)	34	(13 – 47)	185	(11 – 528)	17	(12 – 24)
A-GU-GU-S	166	(66 – 401)	33	(18 – 49)	151	(17 – 408)	73	(18 – 342)
A-K-D-B	137	(77 – 435)	36	(25 – 51)	245	(27 – 664)	-	-
A-Eb-D-S	182	(21 – 522)	48	(3 – 72)	159	(22 – 536)	29	(23 - 35)
A-Eb-GU-S	190	(74 – 467)	58	(39 – 83)	141	(31 – 517)	32	(25 – 45)
A-PT-PT-S	102	(20 – 600)	-	-	147	(19 – 454)	14	(9 – 18)
A-B-B-S	95	(19 – 540)	36	(22 – 49)	168	(18 – 468)	16	(8 – 25)
A-G-G-S	170	(20 – 550)	44	(22 – 68)	242	(21 – 409)	28	(15 – 72)
A-As-G-B	104	(29 – 436)	37	(28 – 48)	223	(29 – 541)	-	-
A-As-B-B	131	(19 – 421)	32	(19 – 42)	275	(25 – 622)	-	-
A-As-PT-B	175	(18 – 578)	18	(17 – 19)	318	(18 – 789)	-	-

1. Mean temperature following passage of fire front when T> 40 °C

Table 4-2 Sample collection properties for all tests and emission factors of total PCDD/PCDF and dl-PCB mass and TEF-weighted PCDD/PCDF and dl-PCB mass.

Label	% burn time when sample temp >200	Mean temp when sample temp>200	% of sample-CO_2 collected when sample temp>200	% burn time when soil temp>200	Mean soil temp when soil temp >200	EF (pg TEQ (g CO_2-C)$^{-1}$)	EF (pg (g CO_2-C)$^{-1}$)
A-K-GU-S	7.1	244	26.5	39.2	366	2.9	491
A-K-Eb-B	0.0	200	0.0	3.4	326	0.6	66
A-K-GU-B	13.7	243	29.3	20.6	330	5.2	896
A-Eb-Eb-S	8.0	221	12.0	9.6	358	0.6	33
A-GU-GU-S	34.1	254	65.4	8.0	377	7.0	1557
A-K-D-B	12.5	254	20.6	47.5	369	2.0	151
A-Eb-D-S	48.4	316	83.5	14.5	399	52.3	1698
A-Eb-GU-S	34.5	313	61.5	16.6	360	8.8	869
A-PT-PT-S	11.7	313	46.7	7.3	382	1.1	217
A-B-B-S	7.5	288	18.5	11.0	355	0.4	127
A-G-G-S	36.8	313	77.3	41.5	330	18.7	1131
A-As-G-B	19.0	275	43.3	32.0	425	0.4	122
A-As-B-B	21.1	288	45.3	43.6	433	1.1	214
A-As-PT-B	36.2	280	62.9	47.9	504	1.9	69

Sample air temperature, while high in the hood, cools very rapidly in the two seconds taken for the air to pass to the trap. Therefore there is little possibility of significant PCDD/PCDF transformations within the sampler. However, when sample air at temperatures in excess of 200 ^{o}C contacts a metal surface there is a risk that PCDD/PCDF and dl-PCB formation may occur. Formation by this path is a sampling artefact and it is likely that the risk of it occurring increases the longer the high temperature sampling state persists. The fraction of the time when sample air temperature was above 200 ^{o}C and the fraction of sample CO_2-C collected when sample air was greater than 200 ^{o}C in the hood was calculated for each test (Table 4-2). In some tests a substantial fraction of the sample was collected at temperatures above 200 ^{o}C which raises the issue of whether PCDD/PCDF and dl-PCB formation during sampling could have introduced artefacts into the data.

4.1.3 Emission rates and artefacts

The 2004 NDP study (Meyer et al., 2004) found that there was potential for PCDD/PCDF and dl-PCB formation through sampling artefacts when sample gas could react with surfaces at high temperature, and when the residence time of high temperature gases was protracted. In the 2004 field campaign the smoke emitted from combustion was very rapidly cooled by dilution with ambient air, and therefore was unreactive when it was sampled. The sampler used in the current study collected smoke at much higher temperatures, and although the residence time in sample hood was short, and cooling of sample gas in the sample tube was very rapid, there is a higher risk of artefacts than in the previous study.

Figure 4-4 shows the relationship between the TEF-weighted EFs from all the field burns and the fraction of sample CO_2-C collected when sample gas was above 200 ^{o}C in the hood. The tests with the two highest emission rates (A-G-G-S and A-Eb-D-S), which were also the samples taken at the highest temperature, are clearly anomalous; these emission factors are respectively 7 and 20-fold larger than the average of all the other tests.

The picture is less clear in the total PCDD/PCDF and dl-PCB mass emission rates. In Figure 4-4A there appear to be three distinct groupings:

1. Group 1 comprised samples A-G-G-S and A-Eb-D-S which rank respectively, 1 and 3 in emission rate and 1 and 2 in sample collection temperature.
2. Group 2 comprised all the tests using fuel collected at the GU (Griffith University) conducted on 4 different substrates (brick, and over soil as GU, Mt Barker and Redlands Bay).
3. All other tests.

The PCDD/PCDF homologue group emission rates from the Griffith University fuel tests are between 4 and 12 times larger than the nine tests in group 3 which include the three Vic fuels, Darwin sorghum and fine fuel from Mt Barker. The EFs for Group 1 and Group 2 also appear to be correlated with sampling temperature.

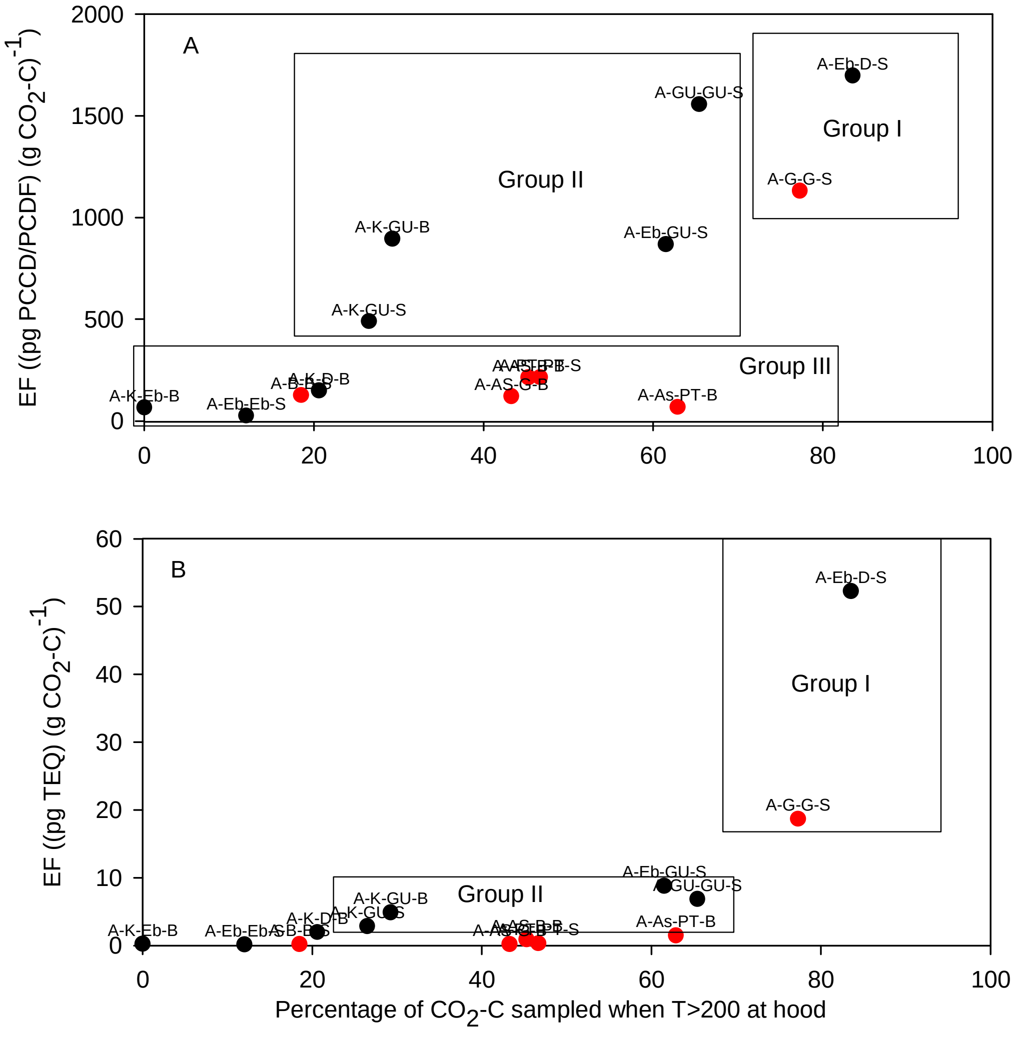

Figure 4-4 Effect of sample temperature in the sampler hood on emission factors. A, PCDD/PCDF homologue groups; B, TEF-weighted EFs for 2,3,7,8-Cl PCDD/PCDF and dl-PCBs. Black points are from the Qld tests, red points are from the Vic tests.

These groupings were further examined with a principal component analysis (PCA) as follows. First, the set of principal component weights were determined from a PCA on the EFs of the 2,3,7,8 PCDD/PCDF congeners and tetra to octa PCDD/PCDF homologue groups and dl-PCBs. The component weights, presented in Table 4-3, show that the homologue groups and PCB 118 are the main determinants, particularly OCDD and the TCDD group. Plotted in PCA space (Figure 4-5), Group 3 (low in OCDD and TCDF) clusters near the origin, Group 2 (low in PCDF and higher in OCDD) clusters on a trajectory to the left while Group 1 (high in TCDF) lies to the trajectory to the right. The Group 1 sample A-Eb-D-S unequivocally is an outlier, sample A-G-G-S is less so.

The PCA component weightings were also applied to mass PCDD/PCDF and PCB EFs from the laboratory and field measurements in the 2004 study. When these are overlaid onto the PCA predictions from the current study, Group 2 and Group 3 align closely with the field measurements from the 2004 study. Group 1 aligns more closely with the laboratory measurements. The 2004 study concluded that the laboratory results were significantly compromised by artefacts from PCDD/PCDF and dl-PCB formation in the combustion chamber. Group 1 aligns with the high PCDF, low OCDD laboratory tests that we considered were suspect.

In summary, based on their similarity with the 2004 NDP data set, it appears that group 2 and group 3 samples are likely to be reliable, but that group 1 could be compromised by PCDD/ PCDF formation artefacts produced in the sampler. Therefore we have excluded the two Group 1 samples from the subsequent analyses and discussion.

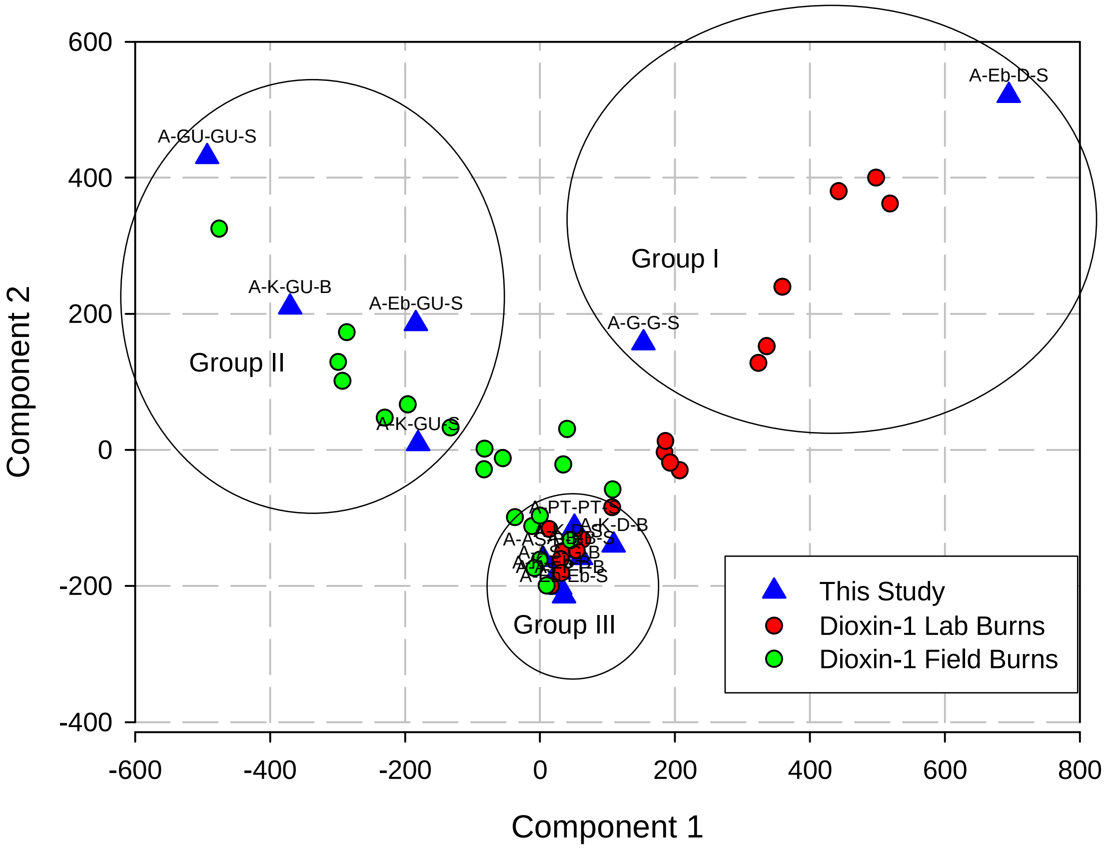

Figure 4-5 Principal component analysis. The PCA loadings derived from the current study were applied to the field burns and the lab burns reported in Meyer et al. (2004). The individual burns from the current study are explicitly identified.

Table 4-3 Weightings for first two principal components for PCA of the mass EFs of 2,3,7,8-Cl PCDD/PCDF congeners, PCDD/PCDF homologue groups and dl-PCBs.

Congener	Component 1	Component 2
Total TCDF isomers	0.663	0.641
Total TCDD isomers		0.111
Total PeCDF isomers	0.205	0.206
Total PeCDD isomers		0.13
Total HxCDF isomers	0.121	0.125
Total HxCDD isomers	-0.122	0.202
Total HpCDF isomers		
OCDD	-0.678	0.641
PCB 118	-0.119	0.165
Cumulative variance explained	**0.528**	**0.972**

4.2 Emission of PCDD/PCDF and dl-PCB from soil in the absence of surface combustion: Experiment I

The laboratory experiment (Experiment I) tested whether surface soils, when heated to temperatures that occur in fuel beds during bushfire, emit PCDD/PCDF and dl-PCB. Previous studies (e.g. Müller et al., 2004) have shown that the soil PCDD/PCDF and dl-PCB concentration in some Australian soils is large, leading to the questions:

- How much of the soil pool of PCDD/PCDF and dl-PCB is labile?
- Can the emission rates explain the EFs measured in the field?

Surface soil is not an inert matrix on which chemicals such as PCDD/PCDF are adsorbed but complex mixture of organic residues from litter decay, bacteria, fungi and other micro biota, and inorganic material. Emissions of PCDD/PCDF and dl-PCB could arise through physical desorption from the matrix, volatilisation, chemical formation during pyrolysis of soil organic material and transformation of PCDD/PCDF and dl-PCB congeners by chlorination or dechlorination. Destruction of PCDD/PCDF and dl-PCB congeners could also occur. Emission rates and relative recoveries of individual congeners may give some indication of the emission processes. For example, recoveries greater than 100% can only be explained by chemical formation of new PCDD/PCDF and dl-PCB congeners. However if recoveries are less than 100% and physical processes dominate, the emission rate of individual congeners should be proportional to their gas-phase concentration in the soil air spaces, i.e. to their vapour pressure.

Each test in this experiment measured the amount of PCDD/PCDF and dl-PCB emitted from a soil sample heated to 400 ^{o}C for 30 minutes, which is in the upper range of temperatures measured in fuel beds during bushfires, and the surface temperatures observed in the field tests (Table 4-1). The soil samples were collected at the field burn sites prior to the field tests, in order that the laboratory emission rates can be compared directly with field emissions (described in Section 4.1). The Victorian soils (Potter's Tk, Blakeville and Guildford) and the inland Queensland soil (Mt Barker) had low concentrations of PCDD/PCDF and dl-PCB averaging 170 pg (g soil)$^{-1}$ in contrast to the Queensland coastal site (Griffith Uni) which had a PCDD/PCDF content of 27000 pg (g soil)$^{-1}$.

Table 4-4 and Table 4-5 show the emissions and recoveries of PCDD/PCDF and dl-PCB congeners in the five tests. Recoveries were calculated only for those congeners present in soil at concentrations above the detection limit, however, setting non-detect concentrations to half MDL made little difference to the results. The emissions were mostly PCDD, with TCDD homologues contributing the greatest amount (Table 4-4). The exception was the GU soil, which had an OCDD content 2 to 3 orders of magnitude higher than the other soils tested and emitted mostly OCDD. TCDF was the only furan homologue group emitted in substantial quantities. Among the 2,3,7,8-Cl PCDD/PCDF congeners only 1,2,3,4,6,7,8-HpCDD and OCDD were emitted in significant quantities. There were larger emissions of dl-PCBs however the patterns were not consistent between tests.

Table 4-4 PCDD/PCDF homologue group mass recovered from the air stream after purging for 30 minutes at 400 °C. Number in brackets is the percentage of the initial soil content recovered from the air stream.

	Emission (pg (g soil)$^{-1}$)				
Homologue Group	Potter's Tk	Blakeville	Guildford	Mt Barker[1]	Griffith Uni[1]
TCDF	21 (115)	18 (163)	162 (953)	0.9 (8)	6.2 (74)
TCDD	28 (314)	24 (887)	380 (2237)	1.8 (53)	15 (115)
PeCDF	0.3 (nd)	nd	nd	nd	nd
PeCDD	3.2 (139)	2.7 (nd)	23 (962)	nd	2.8 (14)
HxCDF	0.1 (20)	0.1 (19)	0.6 (55)	nd	0.2 (16)
HxCDD	3.7 (102)	2.8 (164)	17 (460)	0.1 (3)	3.5 (4)
HpCDF	nd	0.1 (30)	nd	nd	0.1 (4)
HpCDD	2.1 (35)	3.0 (65)	13 (180)	0.0 (0)	13 (3)
OCDF	nd	nd	nd	nd	nd
OCDD	5.4 (13)	6.4 (8)	23 (44)	0.0 (0)	311 (1)

[1] Soil concentrations are the mean of two analyses

nd: concentrations less than detection limit

Table 4-5 Mass of 2,3,7,8-Cl PCDD/PCDF and PCB recovered from the air stream after purging for 30 minutes at 400 °C. Number in brackets is the percentage of the initial soil content recovered from the air stream.

	Emission (pg (g soil)$^{-1}$)				
Congener	Potter's Tk	Blakeville	Guildford	Mt Barker[1]	Griffith Uni[1]
1,2,3,4,7,8-HxCDD	nd	nd	0.3 (nd)	nd	0.1 (3)
1,2,3,6,7,8-HxCDD	0.1 (nd)	0.1 (nd)	0.7 (nd)	0.1 (5)	0.2 (3)
1,2,3,7,8,9-HxCDD	nd	0.1 (nd)	nd	nd	nd
1,2,3,4,6,7,8-HpCDF	nd	0.1 (23)	nd	nd	0.1 (7)
1,2,3,4,6,7,8-HpCDD	0.8 (28)	0.6 (25)	4.1 (128)	nd	5.3 (3)
OCDD	5.4 (13)	6.4 (8)	23 (44)	0.0 (0)	311 (1)
PCB 77	2.1 (32)	0.8 (16)	3.2 (40)	nd	4.9 (69)
PCB 81	0.0 (18)	nd	nd	nd	0.2 (5)
PCB 126	nd	nd	0.4 (45)	nd	0.3 (4)
PCB 169	0.5 (nd)	nd	nd	nd	nd
PCB 105	0.0 (0)	0.0 (0)	2.6 (8)	0.0 (0)	50 (323)
PCB 114	0.0 (0)	0.0 (0)	0.3 (18)	nd	4.1 (nd)
PCB 118	0.0 (0)	0.0 (0)	4.9 (6)	0.0 (0)	192 (599)
PCB 123	nd	nd	0.1 (9)	nd	3.3 (364)
PCB 156	nd	1.4 (16)	2.3 (21)	nd	15 (289)
PCB 157	0.2 (19)	0.3 (16)	nd	nd	1.6 (106)
PCB 167	0.4 (16)	0.7 (20)	1.4 (35)	nd	5.2 (198)
PCB 189	nd	nd	nd	nd	0.6 (25)

[1] Soil concentrations are the mean of two analyses

nd: initial soil concentration less than detection limit

What can we conclude from these measurements?

1. All of the soils tested emitted a significant fraction of their PCDD/PCDF content. From the soil temperature measurements in the field we know that soil heating is extremely shallow, with almost no penetration to 10 mm depth. If we assume, as a first approximation, that in the field the top 5mm of soil is heated to surface temperature and all CO_2-C is produced by fuel combustion, then observed PCDD/PCDF and dl-PCB emissions from soil could explain most of the emissions measured in the field at Guildford, Potter's Tk and Blakeville and approximately

50% of the emissions observed at Mt Barker and Griffith University (Table 4-6). They are also sufficient to explain the TEF-weighted PCDD/PCDF and dl-PCB emissions for the Mt Barker and Blakeville soils, and about 25% of the emission factors measured at the other sites. Therefore we can conclude that soil has the potential to be a substantial source of PCDD/PCDF and dl-PCB under a suitably intense fire.

2. For many of the PCDD/PCDF congeners recoveries were greater than 100% particularly for the less chlorinated groups which indicates that chemical formation was occurring. Somewhat similar patterns have been reported for municipal solid waste (MSW) ash (e.g. Vogg et al., 1987) with MSW ash, peak formation rates occurred near 300 ^{o}C favouring penta and hexa PCDD and tetra and penta PCDF We can conclude that significant amounts of PCDD/PCDF were newly-formed or transformed from other congeners during soil pyrolysis.
3. The soil temperature approached the boiling points of the less chlorinated congeners. The recoveries were inversely correlated with boiling point (Table 4-7). To a degree, this was broadly true also for the emissions however there were significant variations from the expected correlation such as the GU soil for which the emission was highest for OCDD. If emission was largely caused by volatilisation then emission rate would be directly correlated with vapour pressure and hence inversely correlated with boiling point.

Undoubtedly, volatilisation occurred in these tests, but clearly it was not the sole emission process. However it is possible to calculate an upper limit that could be explained by volatilisation. If we assume that the emission due to volatilisation cannot exceed 100% of the initial soil content and that only PCDD/PCDF and dl-PCB in excess of the initial soil content is newly-formed, this sets an upper limit for the emission that could potentially be due to volatilisation. This limit still accounts for a large fraction of the emission factor measured in the field (Table 4-6).

Table 4-6 Comparison of observed emission factors with the emission factors explained by the emission rates from the laboratory tests. Assumed soil depth = 5 mm

Soil Emission test	Potter's Tk A-PT-PT-S	Blakeville A-B-B-S	Guildford A-G-G-S	Mt Barker A-Eb-Eb-S	Griffith Uni. A-GU-GU-S
PCDD/PCDF homologue emission (pg (g CO_2-C)$^{-1}$)					
Total soil emission	295	321	1415	15	702
Measured EF	217	127	1131	33	1557
Upper limit of volatilised component of EF	295	321	244	15	702
TEF weighted PCDD/PCDF emission (pg TEQ (g CO_2-C)$^{-1}$)					
Total soil emission	0.31	0.32	1.29	0.60	0.55
Measured EF	1.14	0.36	18.7	0.58	6.8
Upper limit of volatilised component of EF	0.29	0.32	1.11	0.6	0.52

Therefore, the laboratory experiment answers Question 1: soil, heated in the absence of surface fuel combustion, has the potential to explain a substantial fraction of the emissions observed in the field.

Table 4-7 Boiling point and vapour pressures (at 25 °C) of selected 2,3,7,8-Cl PCDD/PCDF congeners (from McKay et al., 1992)

Compound	Boiling point (°C)	**Vapour Pressure** (atm)
2,3,7,8-TCDD	446.5	2.00×10^{-7}
1,2,3,4,7-PeCDD	464.7	8.80×10^{-8}
1,2,3,4,7,8-HxDD	487.7	5.10×10^{-9}
1,2,3,4,6,7,8-HpCDD	507.2	7.50×10^{-10}
OCDD	510	1.10×10^{-10}
2,3,7,8-TCDF	438.3	2.00×10^{-6}
2,3,4,7,8-PeCDF	464.7	3.50×10^{-7}
1,2,3,4,7,8-HxCDF	487.7	3.20×10^{-8}
1,2,3,4,6,7,8-HpCDF	507.2	4.70×10^{-9}
OCDF	537	5.0×10^{-10}

4.3 Volatilisation and formation of PDCC/PCDF during combustion

The laboratory tests showed that PCDD/PCDF and dl-PCB can be emitted from soil in the absence of fuel combustion, possibly through volatilisation of soil PCDD/PCDF and dl-PCB, and possibly through formation from combustion of soil organic matter. The field experiments were designed to determine whether these processes occur in practice, i.e. whether PCDD/PCDF and dl-PCB emissions are determined by the soil, the fuel or both.

The three experiments (II, III and IV) were:

- comparing the emissions from combustion on a soil surface to combustion of the same fuel on an inert surface (bricks)
- determining from a mass balance, whether there was more or less PCDD, PCDF and PCB present following combustion than was available for emission prior to combustion
- determining if the congener distribution of emitted PCDD, PCDF and PCB is influenced or determined by the congener distribution in the soil.

Each experiment has its advantages and weaknesses but in combination they should shed some light on Questions 2 and 3.

Before describing the results of Experiments II, III and IV, it is important to clarify what they are designed to test, and equally importantly, what they do not test. The underlying conceptual model is that there are two sources of PCDD/PCDF and dl-PCB:

1. a PCDD/PCDF and dl-PCB pool present in the fuel and in the soil
2. a combustion zone in which new PCDD/PCDF and dl-PCB is formed from simpler precursors and pyrolysis products.

This model assumes that PCDD/PCDF and dl-PCB, once formed, is transported to the smoke plume without further transformation. Clearly, this is not reality. The chemistry of the combustion zone is extremely complex. As reviewed by Stanmore, 2004, PCDD/PCDFs are formed from precursors, chlorination and dechlorination transforms congeners between homologue groups, and PCDD/PCDFs are destroyed in the combustion zone. These processes take place at rates that depend on temperature, substrates and catalysts. The extent to which they progress depends on the residence time of the reactants in an unconfined combustion zone. What the model tests is whether, in the absence of any chemical transformation, the initial PCDD/PCDF and dl-PCB pool is large enough to play a significant role in the emissions we measure in the smoke. The experiments are not designed to partition the PCDD/PCDF and dl-PCB observed in smoke between all the potential sources and chemical pathways, i.e. to quantify the reality, but to assess whether the fuel and soil PCCD/PCDF pools are large enough to play a role in bushfire emissions without further chemical transformation.

4.4 Combustion of fuel in the absence of soil: Experiment II

Experiment II tests whether PCDD/PCDF formation occurs in the absence of soil from combustion of Australian forest litter.

Emission rates from six burns conducted over bricks ranged from 0.3 to 5.03 pg TEQ (g CO_2-g)$^{-1}$ and averaged 1.74 pg TEQ (g CO_2-g)$^{-1}$. In comparison the emissions from the complementary burns conducted over soil ranged from 0.3 to 8.8 pg TEQ (g CO_2-g)$^{-1}$ averaging 3.4 pg TEQ (g CO_2-g)$^{-1}$. The equivalent mass emission factors were 90 to 1200 pg (g CO_2-C)$^{-1}$ with a mean of 332 pg (g CO_2-C)$^{-1}$ over bricks and 74 to 1900 pg (g CO_2-C)$^{-1}$ with a mean of 596 pg (g CO_2-C)$^{-1}$ over soil.

The first conclusion to be drawn is that PCDD/PCDF and dl-PCB formation can occur during combustion of fuel in the absence of soil. This answers Question 2 and complements Experiment I (Section 4.2), leading to Question 3: in practice how much can the soil contribute to emissions in the field?

The mass PCDD/PCDF and dl-PCB EFs for all tests are shown in Figure 4-6. For soils with low PCDD/PCDF and dl-PCB concentrations the EFs for the test pairs are similar; in some cases the over-bricks emission factor exceeds the complementary test over soil, in others the reverse occurs. The test conducted over soils of high PCDD/PCDF and dl-PCB concentration show greater emission over soil than over bricks. A similar result is observed for TEF weighted emissions of 2,3,7,8-chlorinated PCDD/PCDF congeners (Figure 4-6B). Interestingly, the EFs for the sorghum and GU fuel, both of which come from regions of high soil PCDD/PCDF, appear to produce higher EFs on both soil and bricks than fuels from regions of low soil PCDD/PCDF (Mt Barker, and the Victorian fuels).

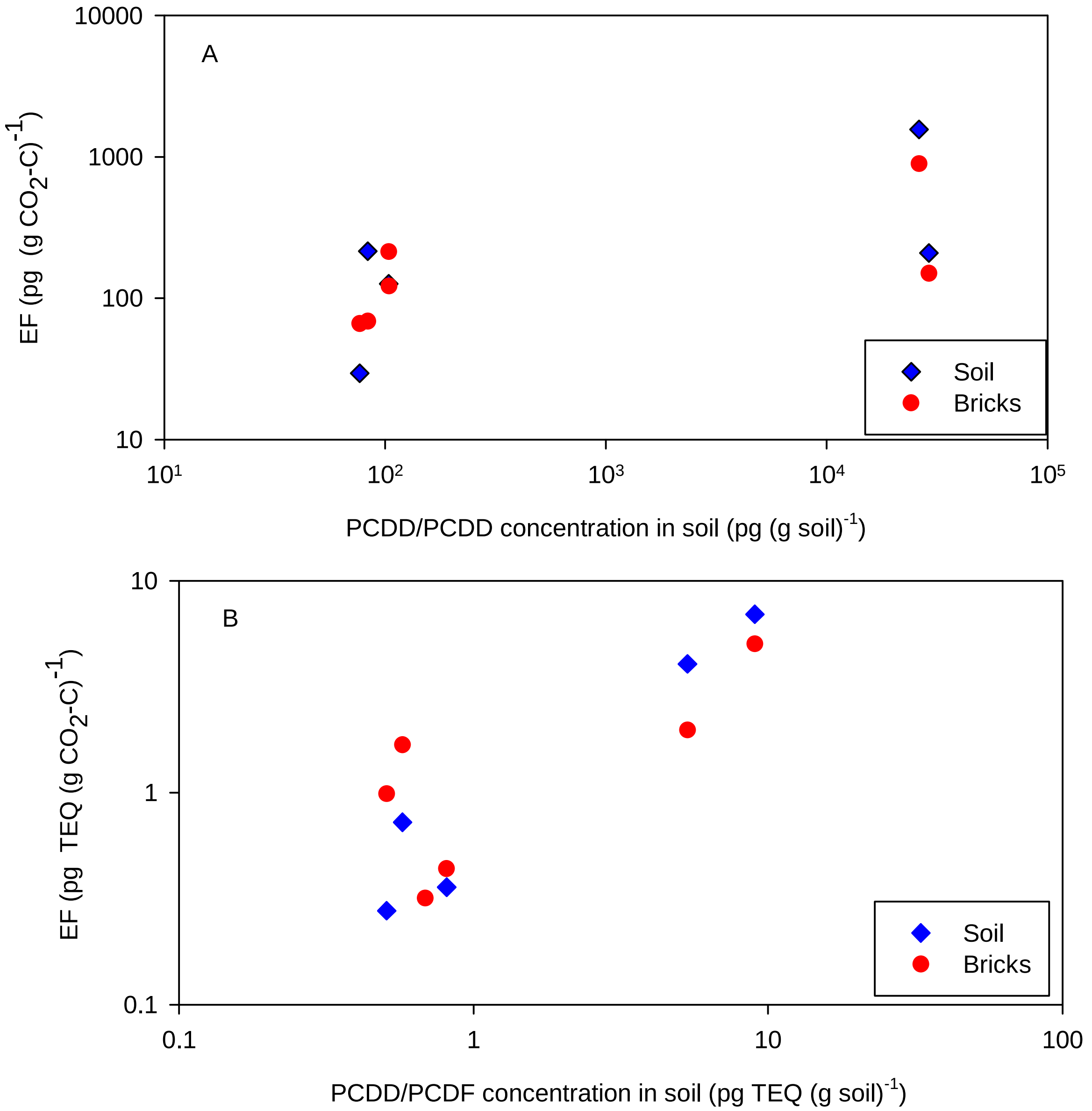

Figure 4-6 Emission factors measured over soil (◊) and brick (●) surfaces. A. Total mass of PCDD/PCDF homologue groups and B. TEF weighted 2,3,7,8-Cl PCDD/PCDF congeners and dl-PCBs.

The EFs for tests over soil are presented in Tables 4.4 and 4.5. For all samples TDCF homologue group mass accounted for more than 80% of furans and 2,3,7,8-TCDF contributed more than 60% of 2,3,7,8-Cl PCDF mass. PCDD accounted for 65-95% of total homologue mass emitted from the high PCDD/PCDF soils and 37% to 55% of homologue mass from the low PCDD/PCDF soils. OCDD accounted for most of the 2,3,7,8-Cl PCDD emitted. The TEF-weighted emissions were mostly PCDD. These congener patterns are similar to the field data from the 2004 NDP study.

When the over-soil emission factor exceeds the over-bricks emission factor, the additional contribution that might be attributable to the soil is calculated as

$$\% \text{ additional} = 100^{*}\ (E_{soil}-E_{brick})/E_{soil}$$

In soils of high PCDD/PCDF and dl-PCB content, 30% to 50% of the TEF weighted mass was derived from the soil (Table 4-9). Soil also appeared to contribute significantly to total PCDD/PCDF homologue mass emission when EFs were greater than 200 pg (g CO_2-C)$^{-1}$.

In soils of low PCDD/PCDF and dl-PCB content, over-soil emissions were not significantly different from over-brick emissions and random variation masked any treatment effects.

Therefore, Experiment II unequivocally confirms that formation of PCDD/PCDF occurs during combustion of fine fuel. However, processes at the soil/fuel interface may also contribute significantly to PCDD/PCDF emissions, at least over soils of high PCDD/PCDF content.

Table 4-8 Emissions of PCCD/PCDF over soil. The number in brackets is the fraction (%) of the emission over soil that is additional to the emission observed over bricks.

Congener	Location				
	Potter's Tk	Blakeville	Mt Barker	Redlands Bay-Sorghum	Griffith Uni
Soil					
TEF-weighted 2,3,7,8– Cl PCDD/PCDF (pg TEQ (g soil)$^{-1}$)	0.57	0.51	0.81	5.33	9.02
Homologues (pg (g soil)$^{-1}$)	83	104	77	29000	26200
	Emission (pg (g CO_2-C)$^{-1}$)				
2,3,7,8 – Cl PCDD/PCDF					
2,3,7,8-TCDF	1.2 (22)	0.3 (100)	0.3 (0)	3.7 (0)	1.2 (55)
2,3,7,8-TCDD	nd	nd	nd	1.1 (77)	Nd
1,2,3,7,8-PeCDF	nd	nd	nd	0.8 (0)	0.1 (100)
2,3,4,7,8-PeCDF	nd	nd	nd	0.5 (0)	0.5 (100)
1,2,3,7,8-PeCDD	nd	0.1 (0)	nd	1.7 (94)	3.5 (28)
1,2,3,4,7,8-HxCDF	nd	nd	nd	0.1 (0)	0.4 (100)
1,2,3,6,7,8-HxCDF	nd	0.0 (28)	nd	0.1 (0)	0.1 (39)
2,3,4,6,7,8-HxCDF	nd	nd	nd	0.1 (0)	0.1 (100)
1,2,3,7,8,9-HxCDF	nd	nd	nd	nd	Nd
1,2,3,4,7,8-HxCDD	nd	0.1 (0)	nd	1.0 (97)	6.2 (24)
1,2,3,6,7,8-HxCDD	0.5 (0)	0.1 (0)	0.4 (32)	2.1 (97)	4.7 (17)
1,2,3,7,8,9-HxCDD	0.5 (0)	0.2 (0)	0.4 (26)	1.7 (100)	6.1 (10)
1,2,3,4,6,7,8-HpCDF	0.2 (0)	0.1 (0)	nd	0.1 (0)	0.4 (61)
1,2,3,4,7,8,9-HpCDF	nd	nd	nd	nd	0.0 (100)
1,2,3,4,6,7,8-HpCDD	3.9 (21)	1.3 (0)	0.9 (0)	11.1 (97)	73.6 (26)
OCDF	nd	nd	nd	nd	1.1 (0)
OCDD	31.7 (62)	11.8 (0)	nd	40.9 (91)	761.4 (27)
Homologue groups					
TCDF	94.1 (81)	73.4 (64)	14.7 (0)	66.4 (0)	80.6 (69)
TCDD	55.8 (85)	30.8 (0)	2.1 (18)	20.5 (85)	102.5 (70)
PeCDF	1.5 (0)	0.4 (6)	3.0 (56)	5.3 (0)	5.5 (66)
PeCDD	4.6 (0)	2.9 (0)	0.7 (0)	17.7 (95)	146.4 (75)
HxCDF	1.2 (0)	0.2 (0)	1.0 (46)	0.8 (0)	5.9 (84)
HxCDD	14.7 (52)	3.3 (0)	2.2 (0)	30.5 (97)	227.5 (53)
HpCDF	0.2 (0)	0.1 (0)	nd	0.1 (0)	0.6 (64)
HpCDD	10.8 (43)	3.3 (0)	2.1 (0)	26.8 (98)	225.5 (41)

nd: concentrations less than detection limit

Table 4-9 Emissions over soil of PCDD/PCDFs and dl-PCBs. The number in brackets is the fraction (%) of the emission over soil that is additional to the emission observed over bricks.

Congener	Emission (pg (g CO_2-C)$^{-1}$)				
	Potter's Tk	Blakeville	Mt Barker	Redlands Bay-Sorghum	Griffith Uni
Homologue groups					
PCDF	96.9 (70)	74.2 (62)	18.7 (0)	72.6 (0)	93.7 (68)
PCDD	117.6 (67)	52.1 (0)	7.2 (0)	136.4 (94)	1463.3 (41)
Total	214.6 (68)	126.3 (0)	25.9 (0)	209.1 (29)	1557.0 (42)
TEF weighted 2,3,7,8-PCDD/PCDF and PCBs					
PCDF	0.1 (0)	0.0 (77)	nd	0.7 (0)	0.4 (85)
PCDD	0.2 (0)	0.1 (0)	0.1 (0)	3.4 (90)	6.0 (25)
PCB	0.0 (82)	0.0 (95)	0.0 (93)	0.0 (0)	0.4 (23)
Total	0.3 (0)	0.2 (0)	0.1 (0)	4.0 (51)	6.8 (28)

nd: concentrations less than detection limit

4.5 Mass balance of combustion sources and products: Experiment III

A mass balance is the most direct method of comprehensive analysing the relative contributions of soil and fuel to the measured EFs. A complete mass balance would quantify the pools of all congeners and trace the transformations between congeners and the formation of PCDD/PCDF from precursor compounds. However, as described in section 4.3 this is beyond the scope of the current project, however, a partial mass balance should provide some insight into the emission processes. In this we assume, for simplicity, that there are no transformations from one congener to another, only volatilisation, formation or destruction. Additionally we do not explicitly measure the change in the soil pool, but estimate it from the laboratory incubations (Experiment 1). There are two reasons for this; (1) the soil is heated at the fuel-air interface and is therefore not heated uniformly, which makes it impossible to define precisely the thickness of the heated soil layer; (2) for many congeners the initial soil pool size is likely to be large in comparison to expected changes and therefore uncertainties in congener concentration associated with sampling and analysis are likely to mask the changes in concentration due to combustion processes.

The initial PCDD/PCDF and dl-PCB pools are soil and fuel and the post-combustion post combustion pools of soil, air and ash (strictly speaking ash plus partially combusted fuel residues). The mass balance is formalised as follows:

A	is area of fire (m^2)
FL	is fuel load (g dwt m^{-2})
CC	is fuel carbon content (g C in fuel (g dwt)$^{-1}$)
BEF	is burning efficiency ((1-g ash)(g fuel)$^{-1}$)
EF	is emission factor ((g PCDD/PCDF and dl-PCB) (g CO_2-C)$^{-1}$)
D_{fuel}	is PCDD/PCDF and dl-PCB content of fuel (g (g dwt)$^{-1}$)
D_{ash}	is PCDD/PCDF and dl-PCB content of ash (g (g dwt)$^{-1}$)
D_{soil}	is PCDD/PCDF and dl-PCB content of soil (g (g dwt)$^{-1}$)
BD	is bulk density of soil (g cm^{-3})
T_{soil}	is depth of heated soil (cm)
F_{soil}	is fraction of PCDD, PCDF or PCB in the heated layer that is emitted

Then from area A, the PCDD/PCDF and dl-PCB mass in each of the major pools comprising fuel (E_{fuel}), smoke (E_{smoke}), ash (E_{ash}) and labile PCDD/PCDF and dl-PCB in soil (E_{soil}) is determined as:

$$\begin{aligned} E_{fuel} &= A*FL*BEF*D_{fuel} \\ E_{smoke} &= A*FL*CC*BEF*EF \\ E_{ash} &= A*FL*(1\text{-}BEF)*D_{ash} \\ E_{soil} &= A*T_{soil}*BD*D_{soil}*F_{soil} \end{aligned}$$

The PCDD, PCDF and PCB pool, prior to combustion is the content of the fuel and the labile component of the soil, i.e.

$$\text{Source} = E_{fuel} + E_{soil}$$

Non-labile PCDD/PCDF and dl-PCB in the soil does not contribute to the balance because it is present both before and after combustion. The PCDD, PCDF and PCB pool after combustion is the mass in the smoke and in the ash, i.e.

$$\text{Final} = E_{smoke} + E_{ash}$$

Therefore, the change in mass of PCDD/PCDF and dl-PCB as a result of the combustion is:

$$\begin{aligned} \Delta\text{mass} &= \text{Final} - \text{Source.} \\ &= E_{smoke} + E_{ash} - E_{fuel} - E_{soil} \end{aligned}$$

If Δmass >0, then there has been net formation of PCDD/PCDF and dl-PCB. The percentage of the emitted (i.e. final) mass that was initially present in the fuel and labile soil pool, i.e. the pre-combustion pool is

$$\% precombustion = \left(1 - \frac{\Delta mass}{E_{smoke} + E_{ash}}\right) \times 100$$

The fuel loads and burning efficiencies used in the mass balance calculations for Potter's Tk, Blakeville and Guildford were directly measured on site at the time of the test (Table 4-10). The fuel loads of the Brisbane burns were estimated from the mass of fuel added to the burn site. The fuel carbon content and surface soil bulk density are standard average values. The fraction of soil congener content emitted by volatilisation (F_{soil}) is taken from the laboratory tests (Table 4-5) unless the values exceed 1, in which case it is assumed to be 1. This is likely to be an overestimate because the duration and possibly also the temperature were greater than observed in the field; it is however useful for establishing an upper limit to the potentially labile soil pool. The depth of the heated soil layer (T_{soil}) has not been measured with confidence, however we can put some limits on its value. It is well documented that the heat pulse is unlikely to penetrate to 10 mm (Table 4-1, Meyer, et al., 1997), therefore initially we set the value of T_{soil} to 5 mm. The sensitivity of the results were assessed by recalculating the mass balances for T_{soil} = 2 mm and T_{soil} = 10 mm.

Table 4-10 Parameter values used in the mass balance calculations

Congener	Location				
	Potter's Tk	Blakeville	Mt Barker	Redlands Bay-sorghum	Griffith Uni.
FL (t ha $^{-1}$)	13.3	15.7	15	15	37
BEF	0.82	0.85	0.82	0,.82	0.82
CC	0.5	0.5	0.5	0.5	0.5
BD (g cm^{-3})	0.8	0.8	0.8	0.8	0.8

The contribution of the pre-combustion pool to PCDD/PCDF and dl-PCB emissions for each of the test burns are given in Table 4-11, Table 4-12 and Table 4-13. In these tables each congener, homologue group or aggregation (i.e. total) is treated as a discrete pool. For the low PCDD/PCDD soils (Potter's Tk, Blakeville and Mt Barker) the mass balance indicates that the 2,3,7,8-Cl PCDF and the tetra, penta and hexachlorinated 2,3,7,8-Cl congeners are probably entirely synthesised during combustion, while 1,2,3,4,6,7,8-HpCDD and OCDD emission might be explained by mobilisation from pre-combustion pools (Table 4-11). The pre-combustion pools might also contribute a significant fraction of hexachlorinated 2,3,7,8-PCDDs emissions in burns on the high PCDD/PCDF and dl-PCB soils (Redlands Bay and Griffith Uni). Virtually all the homologue group mass appeared to be derived from pre-combustion sources for Potter's Tk and Blakeville tests but not in the Mt Barker test, while for the high PCDD/PCDF and dl-PCB soils, the tetra and pentachlorinated groups were predominantly newly formed. Most of the PCB emissions were sourced from pre-combustion pools (Table 4-12).

Because many congeners are close to or below the detection limit, the picture can change when the groups are aggregated. In aggregate, total homologue mass emission could be explained largely by pre-combustion pools (Table 4-13) and TEF-weighted PCDD/PCDF and dl-PCB mass appeared to be predominantly newly produced. The pre-combustion pool also appeared to be a larger potential source for PCDD than for PCDF both for total mass emissions and TEF-weighted emissions.

The sensitivity of the analysis to soil depth and MDL is explored in Table 4-14. Because heated depth defines the size of the soil pool, the results are highly sensitive to this parameter, particularly for TEF-weighted emissions. Detection limit was not a major source of error for the homologue group mass, which was well within precision. It was more of an issue for TEF-weighted emissions because 2,3,7,8-TCDD and 2,3,7,8-TCDF, congeners with very high TEFs, occurred in all soils at concentrations near or below MDL.

Table 4-11 The fraction of emitted PCDD/PCDF congeners derived from pre-combustion pools if heated soil depth = 5 mm

Congener	Emission fraction (%) explained by pre-combustion content				
	Potter's Tk	Blakeville	Mt Barker	Redlands Bay-sorghum	Griffith Uni
2,3,7,8-Cl congeners					
2,3,7,8-TCDF	0	0	0	0	0
2,3,7,8-TCDD	nd	nd	0	Nd	Nd
1,2,3,7,8-PeCDF	nd	nd	0	0	0
2,3,4,7,8-PeCDF	nd	nd	nd	0	0
1,2,3,7,8-PeCDD	nd	0	0	0	0
1,2,3,4,7,8-HxCDF	nd	nd	nd	0	0
1,2,3,6,7,8-HxCDF	nd	0	0	0	0
2,3,4,6,7,8-HxCDF	nd	nd	0	0	0
1,2,3,7,8,9-HxCDF	nd	nd	nd	0	Nd
1,2,3,4,7,8-HxCDD	0	0	0	55	5
1,2,3,6,7,8-HxCDD	0	0	9	29	9
1,2,3,7,8,9-HxCDD	0	0	0	0	0
1,2,3,4,6,7,8-HpCDF	0	100	0	100	100
1,2,3,4,7,8,9-HpCDF	nd	nd	nd	Nd	0
1,2,3,4,6,7,8-HpCDD	100	100	0	100	32
OCDF	nd	nd	nd	Nd	0
OCDD	100	100	6	100	100
Homologue groups					
TCDF isomers	100	100	13	15	25
TCDD isomers	100	60	72	43	12
PeCDF isomers	0	0	0	0	0
PeCDD isomers	100	0	0	34	7
HxCDF isomers	53	100	0	0	26
HxCDD isomers	100	100	2	62	8
HpCDF isomers	0	100	0	100	100
HpCDD isomers	100	100	2	100	25

nd: concentrations less than detection limit

Table 4-12 The fraction of emitted dl-PCBs derived from pre-combustion pools if heated soil depth = 5 mm mass

Congener	Emission fraction (%) explained by pre-combustion content				
	Potter's Tk	Blakeville	Mt Barker	Redlands Bay-sorghum	Griffith Uni
PCB 77	62	100	100	100	100
PCB 81	5	nd	0	0	100
PCB 126	12	49	0	Nd	100
PCB 169	nd	nd	0	Nd	Nd
PCB 105	98	100	100	100	100
PCB 114	0	100	0	0	100
PCB 118	100	100	100	Nd	100
PCB 123	nd	nd	0	Nd	92
PCB 156	100	100	0	Nd	100
PCB 157	74	58	0	Nd	100
PCB 167	77	100	nd	Nd	100
PCB 189	nd	0	nd	Nd	100

Table 4-13 The fraction of emitted total PCDD/PCDF mass derived from pre-combustion pools if heated soil depth = 5 mm

Congener	Emission fraction (%) explained by pre-combustion content				
	Potter's Tk	Blakeville	Mt Barker	Redlands Bay-sorghum	Griffith Uni
Homologues					
PCDF pool	100	100	10	37	26
PCDD pool	100	100	6	100	92
Total PCDD/PCDF pool	100	100	6	100	88
TEF-weighted mass (pg TEQ (g CO_2-C)$^{-1}$)					
PCDF pool	31	80	0	3	2
PCDD pool	100	100	1	20	7
Total PCDD/PCDF pool	90	100	1	16	7
dl-PCB pool	17	72	8	100	100
Total PCDD/PCDF/dl-PCB pool	30	86	1	23	30

Table 4-14 The sensitivity to soil depth and analytical sensitivity (MDL) of the fraction of emitted PCDD/PCF and dl-PCB emission derived from pre-combustion pools

Congener	Emission fraction (%) explained by pre-combustion content			
	2mm,	5mm	10mm	5mm, nd=MDL
Homologues				
PCDF pool	27	67	67	61
PCDD pool	73	80	81	80
Total PCDD/PCDFpool	68	79	82	80
TEF-weighted mass (pg TEQ (g CO_2-C)$^{-1}$)				
PCDF pool	11	23	34	52
PCDD pool	25	46	51	57
Total PCDD/PCDF pool	22	43	49	56
dl-PCB pool	57	59	63	70
Total PCDD/PCDF/dl-PCB pool	23	34	46	59

Assuming the heated depth is between 2 mm and 5 mm, which our measurements of field observation show is most likely to be the active zone, Experiment III predicts that between 23% and 34% of TEF-weighted emission and from 70% to 80% of total PCDD/PCDF and dl-PCB mass might be emitted from existing pools (Table 4-14). This is a similar picture to Experiment II, although it suggests that the pre-combustion pool could be a larger contributor of total PCDD/PCDF and dl-PCB mass.

Therefore, Experiment III gives a picture qualitatively similar to Experiment II suggesting that pre-combustion sources might account for slightly less than half the TEF weighted PCDD/PCDF and dl-PCB emission and slightly more than half of homologue group mass emitted during prescribed burning tests.

4.6 Combustion over contrasting soils: Experiment IV

Experiment IV compares the emissions from a single fuel class burned on soils of contrasting PCDD/PCDF composition. If soil PCDD/PCDF content is a major source of the PCDD/PCDF found in emitted smoke, then the observed congener pattern observed in the smoke should match the soil's congener pattern rather than the fuel's.

Two fuels, sorghum sourced from Darwin and fine fuel collected from the Griffith University Campus were each burned at the experimental sites at Redland Bay and at Mt Barker. The soil at Redland Bay has total PCDD/PCDF homologue concentration of 29000 pg g^{-1}, 99% of which is OCDD. The Mt Barker soil contains 90 pg g^{-1} PCDD/PCDF of which 50 pg g^{-1} is OCDD (Table 4-15). Despite this difference, total PCDD/PCDF emissions from Griffith University fuel were similar at both sites. Therefore, although the soils differed in PCDD/PCDF content by a factor of 320, the emissions differed by a factor of 0.3. A valid comparison cannot be made between the two sorghum tests because, as discussed in 4.1.3, the congener pattern of the Redland Bay test indicated the presence of sampling artefacts.

There was a weak correlation between the congener patterns in soil and smoke in both the 2,3,7,8-Cl congeners and the homologue groups; GU fuel burned on the coastal soil with high OCDD and low TCDF content emitted proportionally more OCDD and less TCDF/TDDD than the same fuel burned at Mt Barker where the soil has a low content of OCDD and proportionally higher TCDD/F content. This is consistent with the hypothesis that the soil affects the PCDD/PCDF emissions. However, the importance of fuel in determining PCDD/PCDF emissions is also evidenced from the substantial difference between congener patterns in smoke from the Griffith University and the sorghum fuels burned at Redland Bay.

The apparent inconsistency between the correlation in congener patterns and the total mass emissions might be explained by the difference in volatility between the different homologue groups. OCDD has low volatility, however its concentration in soil at both sites is very large in comparison to the emitted mass. Therefore if even a small fraction was emitted, its impact on the congener pattern of the smoke would be large and a correlation between the congener patterns of soil and smoke would occur despite small differences in emission rate.

Table 4-15 Relative composition of 2,3,7,8-Cl PCDD/PCDF and dl-PCB congeners and homologue groups in soil and smoke collected from tests with Griffith University litter and sorghum

	Redland Bay			Mt Barker	
	Soil	Griffith Uni. fuel	Sorghum	Soil	Griffith Uni. Fuel
PCDD+PCDF Emission factor (pg (g CO2-C)$^{-1}$)	-	529	80.5	-	774
Concentration of PCDD+PCDF (pg g^{-1})	29037	-	-	90	-
2,3,7,8-Cl congeners					
2,3,7,8-TCDF	0.0%	0.1%	5.6%	0.2%	2.1%
2,3,7,8-TCDD	0.0%	0.0%	1.6%	0.0%	0.1%
1,2,3,7,8-PeCDF	0.0%	0.0%	1.2%	0.5%	0.5%
2,3,4,7,8-PeCDF	0.0%	0.1%	0.8%	0.1%	0.6%
1,2,3,7,8-PeCDD	0.0%	0.4%	2.6%	0.2%	0.6%
1,2,3,4,7,8-HxCDF	0.0%	0.0%	0.2%	0.1%	0.6%
1,2,3,6,7,8-HxCDF	0.0%	0.0%	0.2%	0.5%	0.3%
2,3,4,6,7,8-HxCDF	0.0%	0.1%	0.1%	0.1%	0.3%
1,2,3,7,8,9-HxCDF	0.0%	0.0%	0.0%	2.3%	0.0%
1,2,3,4,7,8-HxCDD	0.0%	0.5%	1.6%	0.1%	0.6%
1,2,3,6,7,8-HxCDD	0.0%	0.6%	3.2%	2.4%	0.7%
1,2,3,7,8,9-HxCDD	0.0%	0.9%	2.6%	3.5%	1.0%
1,2,3,4,6,7,8-HpCDF	0.0%	0.2%	0.1%	0.5%	1.3%
1,2,3,4,7,8,9-HpCDF	0.0%	0.0%	0.0%	0.1%	0.1%
1,2,3,4,6,7,8-HpCDD	0.3%	8.2%	17.1%	5.3%	8.4%
OCDF	0.0%	0.0%	0.0%	0.0%	1.2%
OCDD	99.6%	88.9%	63.0%	84.1%	81.6%
Homologue groups					
TCDF isomers	0.0%	2.6%	31.8%	15.7%	15.0%
TCDD isomers	0.0%	2.0%	9.8%	4.5%	4.9%
PeCDF isomers	0.0%	3.9%	2.5%	0.9%	3.9%
PeCDD isomers	0.0%	3.1%	8.5%	0.3%	4.0%
HxCDF isomers	0.0%	2.4%	0.4%	2.2%	2.1%
HxCDD isomers	0.1%	8.6%	14.6%	6.9%	10.1%
HpCDF isomers	0.0%	0.2%	0.0%	0.5%	0.9%
HpCDD isomers	1.0%	16.3%	12.8%	8.8%	11.8%
OCDF	0.0%	0.0%	0.0%	0.0%	0.7%
OCDD	98.8%	60.8%	19.6%	60.3%	46.8%
PCBs					
PCB 77	0.0%	7.7%	35.6%	0.0%	11.6%
PCB 81	0.0%	0.3%	4.2%	0.0%	0.6%
PCB 126	0.0%	0.8%	0.0%	1.9%	1.6%
PCB 169	0.0%	0.0%	0.0%	0.0%	0.2%
PCB 105	0.0%	26.2%	56.5%	25.6%	20.1%
PCB 114	0.0%	0.9%	3.8%	0.0%	0.8%
PCB 118	0.0%	51.8%	0.0%	59.1%	55.0%
PCB 123	0.0%	4.0%	0.0%	0.0%	0.8%
PCB 156	0.0%	4.1%	0.0%	9.5%	4.9%
PCB 157	0.0%	1.0%	0.0%	0.0%	1.4%
PCB 167	100.0%	2.5%	0.0%	3.9%	2.5%
PCB 189	0.0%	0.4%	0.0%	0.0%	0.6%

In summary, Experiment IV supports the conclusions of Experiments II and III that the composition of the soil over which the burn occurs affects the composition of the smoke.

5 Discussion

These experiments show:

1. Soil has the capacity to emit PCDD and PCDF in quantities comparable to observed emissions in smoke, i.e. hot soil can emit PCDD and PCDF, particularly the more volatile congeners.
2. PCDD and PCDF formation can occur during the combustion of fine fuel in the absence of soil.
3. The pre-combustion pool of labile PCDD/PCDF and dl-PCB, particularly the higher chlorinated congeners might contribute significantly to the smoke content.

This answers three of the four questions cast at the beginning of the project.

Before discussing them in detail we should revisit the question of how valid are the measured emission factors. Meyer et al. (2004) concluded that laboratory-based combustion experiments had the potential to generate substantial artefacts. These conclusions were based on the distinctly different congener patterns measured in the laboratory tests compared to field measurements (Figure 4-5). In the commentary attached to their recent publication, Gullett et al. (2006) propose that the congener pattern observed in our 2004 field measurements, in which PCDD was the dominant component, could occur if there was fractionation of the smoke in the field such that the ground-level concentrations were dominated by smouldering phase emissions, low in total emissions and weighted towards PCDD, while flaming combustion emissions high in PCDD/PCDF and dl-PCB content were dispersed in the rising smoke plume. To date, the fractionation hypothesis remains untested, however both field observations and analysis of combustion physics suggest that fractionation is not substantial. For example, the emission factors for total particle mass measured at ground level in the field in the 2004 NDP study (21 g (kg fuel)$^{-1}$ are close to the average for temperate forests (17 g (kg fuel)$^{-1}$) reported by Andreae and Merlet (2002) in their review of all published data. It is also pertinent that in the 2004 study, the difference between the laboratory and the field measurements was principally the 2,3,7,8-Cl PCDD/PCDF congener distribution, not the total PCDD/PCDF homologue mass emissions. Specifically, the homologue mass emission factor from sugar cane and forest litter measured in the laboratory, were actually lower than those observed in the field; there were no field measurements for straw or sorghum to compare with the laboratory tests. These observations are not consistent with the fractionation hypothesis.

In the current study bias toward smouldering combustion was highly improbable. The sampler was designed to collect both flaming and smouldering phase emissions (Figure 3-4, Figure 3-5). The measurement protocols were explicitly designed to avoid this kind of bias to smouldering combustion yet the emission factors and congener profiles of the current study are remarkably consistent with those reported in the 2004 study (Figure 5-1).

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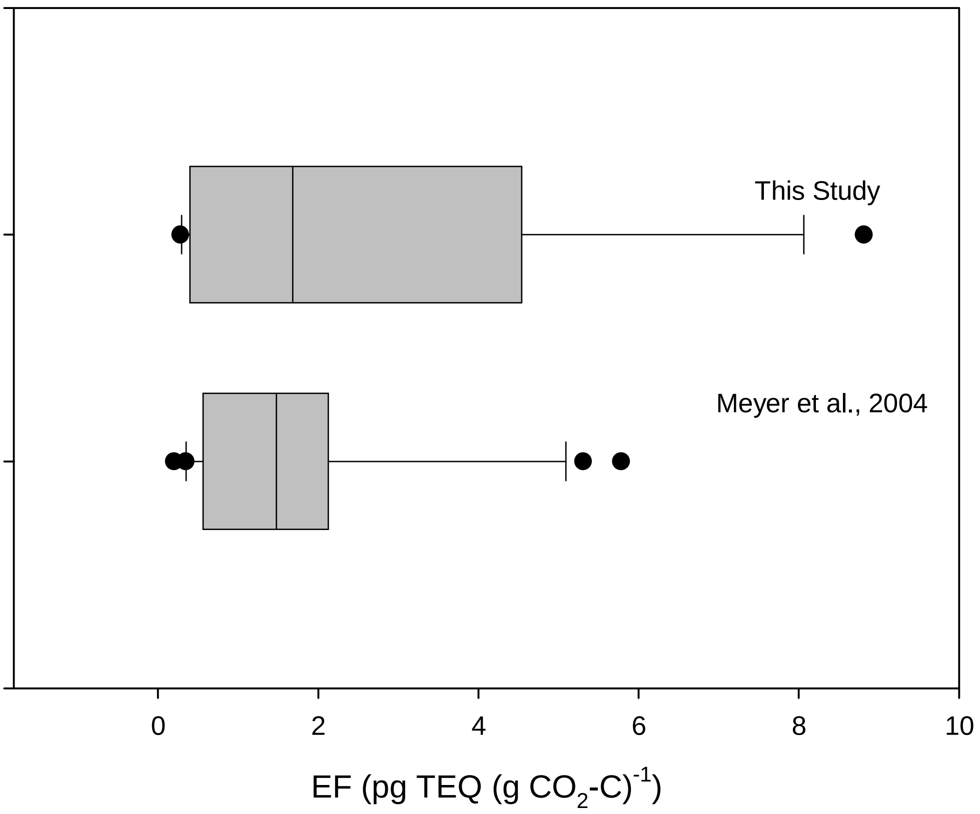

Figure 5-1 Comparison of the emission measurements over soil and bricks from this study (upper plot) against the EFs measured in the field from Meyer et al., 2004 (lower plot). The shaded boxes cover the 25th to the 75th percentiles, the bars show the 10th and 90th percentile range and the points are outliers.

While most of the internationally published data from the USA and Europe also lie within the range of the Australia studies of 1 to 10 pg TEQ (g-C)$^{-1}$, there are a number of outliers (Figure 5-2). The highest of these is a measurement of 252 pg TEQ (g-C)$^{-1}$ from sugar cane leaves sourced from Hawaii conducted in the burn hut facility of the USEPA. The mean and median of all data published to date are, respectively, 9.8 and 1.7 pg TEQ (g-C)$^{-1}$.

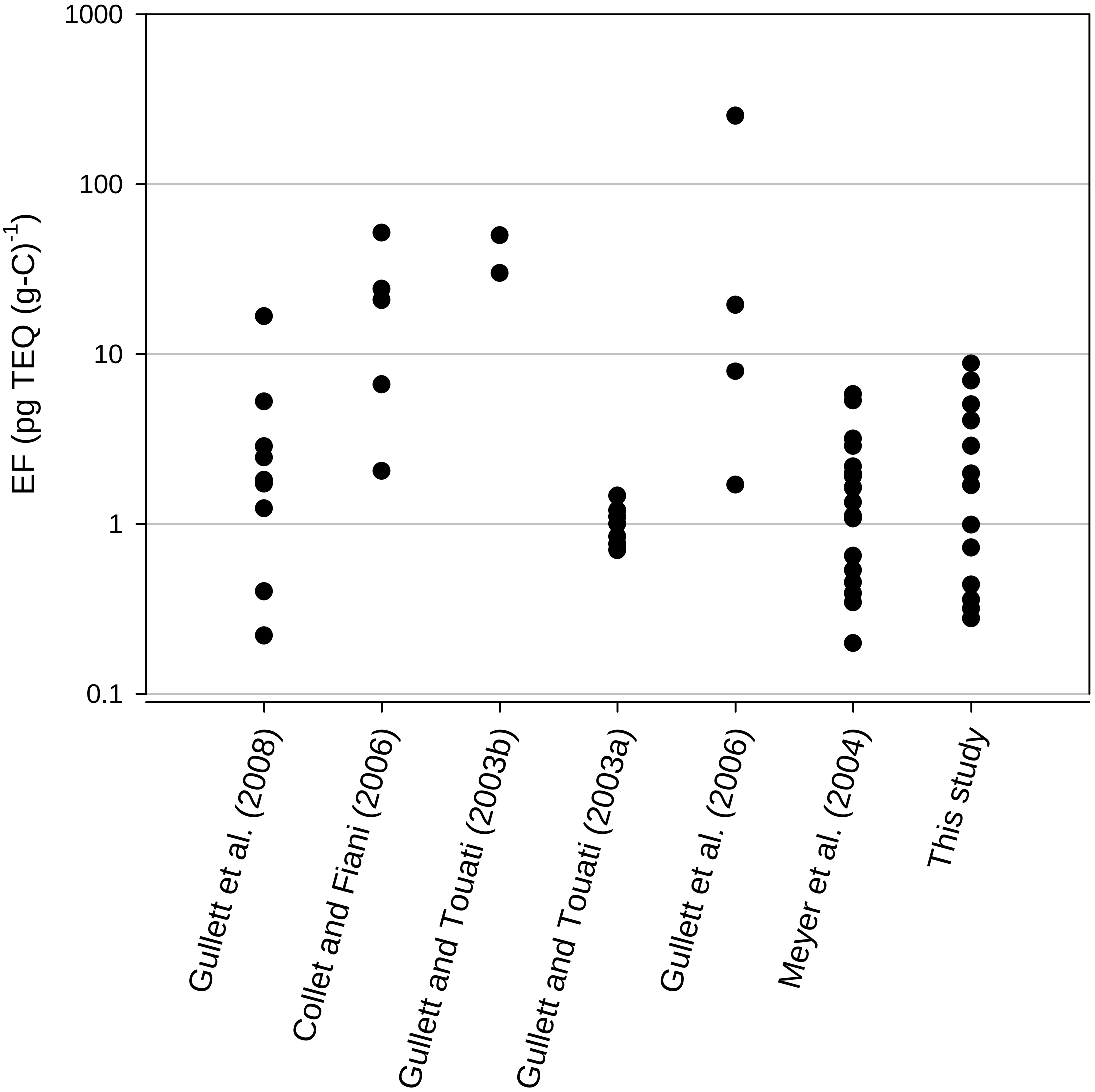

Figure 5-2 Comparison of emission factors from the two Australian studies with a review o data published in the international literature.

A common finding through much of this work, particularly in Australia, is a congener pattern in which PCDD predominates and in which the higher chlorinated groups are more abundant than the less chlorinated groups. This pattern appears in heated soils (e.g. Prange et al., 2003 and Section 3), in fuels and in emissions to the atmosphere (Prange et al., 2002b, Meyer et al., 2004, this study). The pattern is observed in studies with such different and independent experimental methodologies that the possibility of it being an artefact seems very unlikely. A major consequence of this congener pattern is relatively small TEF-weighted mass compared to emissions from other combustion sources.

Overall, the evidence indicates that the emissions factors measured in the field in both studies are valid. The laboratory tests showed unequivocally that substantial emission of PCDD/PCDF and dl-PCB results when soil is heated to temperatures that are routinely observed in surface soils during bushfires. The more volatile congeners were emitted at higher rates, but much of this material could be newly-formed. Recent work reviewed by Gonzalez-Perez et al. (2004) and Certini (2004) shows that major transformations of soil carbon occur when soil is heated. Above 150 ^{o}C pyrolysis commences, rapidly increasing in rate between 200 °C and 250 °C. By 450 °C carbon consumption is almost complete. Among the transformations occurring at temperatures above 200 °C is an enrichment of the organic matter with aromatic compounds. Voss et al. (1987) report similar findings for PCDD/PCDF formation where maximum formation occurred at 350 °C; above this destruction pathways became more active and little emission was observed at 450 °C. Therefore it is not surprising that our laboratory tests indicated substantial PCDD/PCDF and dl-PCB formation.

The laboratory tests are used in Experiment III to define the fraction of the soil PCDD/PCDF and dl-PCB that is labile and therefore a key question is how applicable are these results to the field. Many authors report that surface heating rarely penetrates more than a few centimetres into the soil. Tomkins et al. (1991) clearly showed that the temperature profile is shallow in prescribed burning and wildfires; only in stationary fires, such as the firing of windrows is the heat penetration substantial. Raison et al. (1986) investigated the issue comprehensively and reported that while soil surface temperatures reached 450 °C at 2 cm depth, temperatures never exceeded 100 °C. There are many similar observations reported for forest fires (e. g. Bradstock et al., 1992, Meyer et al., 1997, Molina and Llinares, 2001). In grasslands, there is even less subsurface heating (Morgan, 1999); temperatures at 10 mm depth increase less than 10 °C (Morgan, 1999). The duration of the heat pulse is also variable from forests to grasslands. In grasslands surface heating duration is typically 2 to 5 minutes (e. g. Totthill and Shaw, 1968, Scotter, 1970, Morgan, 1999); in forests, the duration of surface temperatures above 100 °C ranges from 10 to 20 minutes at fuel loads of 15 to 20 t ha^{-1} (Raison et al., 1986, Molina and Llinares, 2001) to 35 minutes at 40 t ha^{-1} (Molina and Llinares, 2001). Overall these data are consistent with our observations and confirm that only the soil surface layer is likely to be subjected to temperatures that are sufficiently high to cause combustion of soil organic matter.

The duration of the laboratory tests (30 minutes) is relatively long compared with the field tests in which soil surface temperatures remained above 200 °C for between 2 and 26 minutes, following arrival of the fire front. Bryant et al. (2005) report a very similar laboratory test to this study in which both soil and furnace temperatures were monitored. In their study soil temperature increased linearly from ambient to 400 °C over the course of 10 minutes, while the duration of smoke emission ranged from 11 to 18 minutes. Chemical transformations and emissions are most likely to occur during this period and therefore it may not be the total duration of the test that is relevant, but the duration of the initial heating phase. Given that the latter is comparable to the duration of surface heating in forest fires, it seems reasonable to apply our laboratory data to field scenarios.

It appears that both the soil and the fuel combustion can be sources of PCDD/PCDF and dl-PCBs; the issue, therefore, is the relative contribution from each source to the smoke emissions. From the previous discussion, heating is confined to the very shallow surface layer, at most 5 mm. The mass balance for these conditions suggest that potentially up to 80% of the total emitted mass of PCDD/PCDF homologue groups is derived from the pre-combustion pool. When the TEF weightings are applied, because much of the mass is in the higher chlorinated and less toxic congeners, on average between 25% and 50% of the TEF-weighted PCDD/PCDF and dl-PCB mass in the smoke could be due to remobilisation of congeners already present in fuel and soil. However we need to apply some caveats to this conclusion. First, it assumes that the pre-combustion PCDD/PCDF and dl-PCB is sufficiently stable to escape transformation within the combustion zone. Remobilisation and emission will also be determined by factors affecting transport, such as the depth of fuel bed, its porosity and the rate of gaseous exchange between the soil and the atmosphere. These mass balance results therefore are, at best, upper limits of the potential redistribution fraction. Reality probably lies between these and the lower limit of zero contribution from pre-combustion sources. As indicated at the start, to determine precisely how much of the PCDD/PCDF and dl-PCB derived from the soil and preburn fuel is released by physical processes, will require a far more complex programme than was possible in this study.

The difference in duration of the heat pulse between forests and grasslands is also important. The impact of soil composition on emission probably only applies to forest and woodland fires where surface heating is significant, but not to fast-moving grassland fires where surface heating is of very short duration.

Because soil composition appears to be a factor in determining emissions from bushfires, it is appropriate to reconsider the best way to classify emission factors. In the 2004 NDP study (Meyer et al., 2004) the fires were classified by fire class into wildfires, prescribed fires, savanna fires and agricultural waste fires, following the conventions used in the National Greenhouse Gas Inventory (NGGIC, 2006; Meyer, 2004). However, as indicated earlier, this might not be the best classification. A cluster analysis of the combined PCDD/PCDF homologue and 2,3,7,8-Cl congener emission factor data from the current study and 2004 NDP study shows that measurements made in the tropical coastal region including the NT cluster into one group, while the data from Vic, WA, inland NT and inland Qld (Mt Barker) sites form a second group (Figure 5-3). The only exception to this pattern was the test in which Griffith University litter was burned at Mt Barker (A-Eb-GU-S). This suggests that the natural clustering is determined by fire location rather than fire class. In spatial terms, this grouping has strong similarities to the distribution of PCDD/PCDF and dl-PCB concentration reported for Australian soils. Müller et al. (1999), Gauss et al. (2001) and Prange et al. (2002) found that coastal soils in Qld have unusually high OCDD concentrations in contrast to most other soils in the world or elsewhere in Australia. Sampling over a wider domain, the 2004 NDP soils study (Müller et al., 2004) also found that PCDD/PCDF and dl-PCB concentrations in soils in remote areas and inland agricultural areas were substantially lower than tropical coastal regions. The cluster analysis does not prove causality, however it is consistent with the conclusion of the previous section that soil PCDD/PCDF and dl-PCB is a component of bushfire emissions.

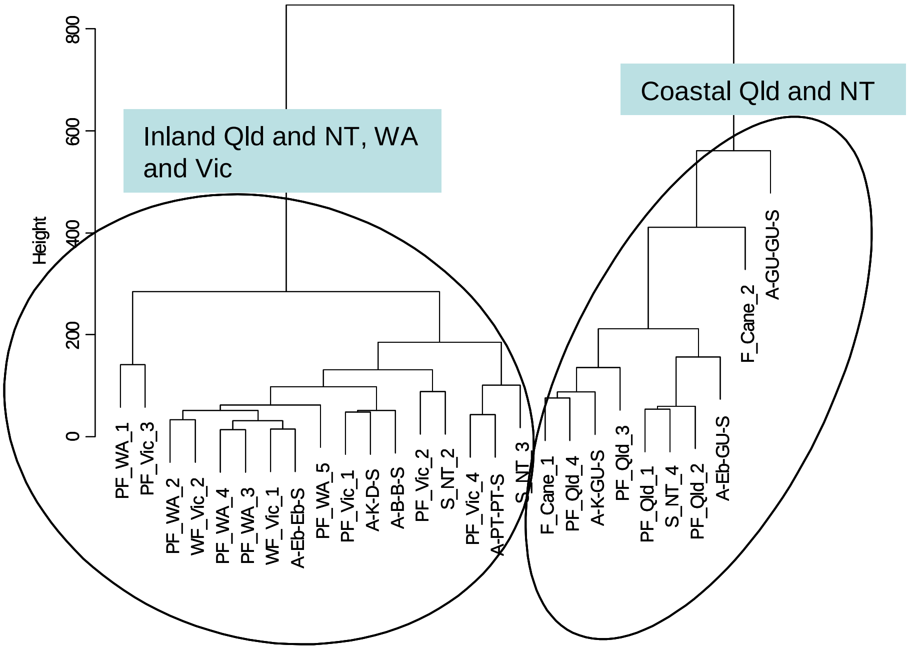

Figure 5-3 Cluster analysis of the 2,3,7,8-Cl PCDD/PCDF congener and homologue group EFs from current study and the 2004 NDP study (Meyer et al., 2004 field data)

In summary:

1. This study is consistent with the conclusions of the 2004 NDP bushfires project (Meyer et al., 2004) that 2,3,7,8-Cl PCDD/PCDF and dl-PCB emission factors in Australia were relatively small.
2. There is good evidence that PCDD and PCDF formation can occur during the combustion of organic soil carbon in the shallow surface layer heated by burning forest fuels.
3. It was also found that PCDD/PCDF and dl-PCB emissions occur from the combustion of fuel in the absence of soil.
4. A proportion of total PCDD and PCDF mass detected in smoke in the field might be derived from the pre combustion soil pool. Our current best estimate is that the upper limit upper is between 25% and 50% of the TEF-weighted PCDD/PCDF and dl-PCB mass and between 30% and 80% of the total mass. The lower limit remains at zero.
5. It appears that emission rates of PCDD and PCDF from bushfires in Australia are determined not by fire class or intensity but by the geographic location of the fire.

6 National emissions inventory

6.1 Emissions to air

The 2004 NDP study (Meyer et al., 2004) concluded that Australia's PCDD, PCDF and dl-PCB emission from bushfires and agricultural waste burning ranged from 44.6 in 1990 to 77.2 kg in 2001, or using WHO_{97} TEFs, from 139 g TEQ in 1990 to 228 g TEQ. Using the 2004 inventory methodology for the current inventory year, 2005, the emissions are 28 to 177 kg PCDD/PCDF and dl-PCBs and 50 to 795 g TEQ.

There have been some changes since 2004. The National Greenhouse Gas Inventory (NGGI) methodology was revised in 2006, reducing the interannual averaging period from 10 years to 3 years in line with Intergovernmental Panel on Climate Change (IPCC) inventory conventions (IPCC, 2000). Also, the savanna regions were separated into grassland and woodland areas with improved parameterisations of fuel loads and burning efficiencies. In this section we use as the reference case the current NGGI methodology (AGO, 2006) with the modifications described in Meyer et al. (2004) for the 2005 inventory year. In effect this is the average of emissions for the financial years 2003/4, 2004/5 and 2005/6. The extent of large fires in Australia for 2004 to 2006 is shown in Figure 6-1. Average annual fire area from 1982 to the present is 38.2 Mha (Meyer, 2004). In comparison, the areas burned in 2004 and 2006 (26 Mha and 15 Mha respectively) are significantly below average while 2005 (62 Mha) was significantly higher. Most fire activity occurs in the arid grasslands and savanna woodlands of the NT, WA and, to a smaller degree, in Qld. New EFs for prescribed fires and savanna fires were estimated as the means of the combined data from the 2004 NDP bushfire study and the current work (Table 6-1). To retain consistency with the 2004 NDP bushfire study, non-detects were assigned the concentration of 0.5 MDL. Changes in average emission factor due to inclusion of the new measurements were small despite some minor differences in methodology. For total homologue mass there was almost no change in the emission factor for prescribed fires, but there was a reduction of approximately 30% in the savanna fire emission factor. For TEF-weighted mass there was no change in the savanna fire emission factor but an increase of approximately 30% in the prescribed burning emission factor. The 95% uncertainty bounds of the estimates are calculated using the

Monte Carlo analysis described in detail by Meyer et al. (2004). A minor consequence of using a Monte Carlo analysis for calculating national emissions is that the mean of the probability density function for the total emission does not always equal the sum of the component emissions.

Using these data in the methodology described above, the estimated emissions for Australia in 2005 are 40 kg PCDD, PCDF and PCB homologue mass with a 95% confidence range of 13 to 110 kg which is equivalent to 168 g TEQ with a 95% confidence range of 49 g to 500 g (Table 6-2). This is consistent with emissions reported in the 2004 NDP study.

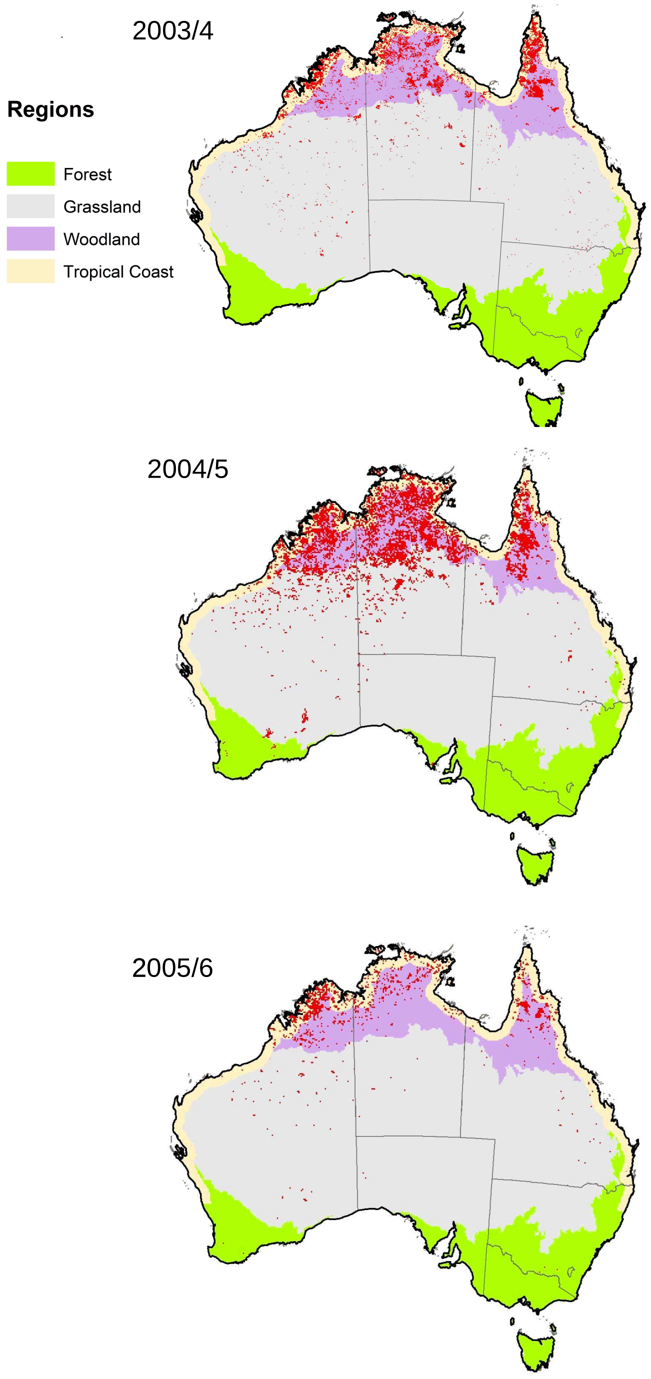

Figure 6-1 The distribution of fires in Australia in the financial years 2003/4, 2004/5 and 2005/6

Table 6-1 Revised emission factors

Mass EF (pg (g CO_2-C)$^{-1}$)					
		Cane	Prescribed	Savanna	Wildfire
Meyer et al., 2004	PCDD	610	293	274	70
	PCDF	44	65	96	16
	PCBs	497	521	285	671
	Total	***1151***	***879***	***654***	***757***
This study	PCDD		550	74	
	PCDF		101	46	
	PCBs		223	27	
	Total		***874***	***147***	
Combined data	PCDD	610	364	194	70
	PCDF	44	75	76	16
	PCBs	497	438	182	671
	Total	***1151***	***878***	***451***	***757***
TEF-weighted EF (pg TEQ (g CO_2-C)$^{-1}$)					
Meyer et al., 2004	PCDD	1.77	1.23	2.03	0.65
	PCDF	0.14	0.36	0.16	0.13
	PCBs	0.07	0.18	0.07	0.13
	Total	***1.98***	***1.77***	***2.26***	***0.91***
This study	PCDD		2.85	1.80	
	PCDF		0.84	0.39	
	PCBs		0.23	0.01	
	Total		***3.92***	***2.20***	
Combined data	PCDD	1.77	1.68	1.94	0.65
	PCDF	0.14	0.50	0.25	0.13
	PCBs	0.07	0.19	0.05	0.13
	Total	***1.98***	***2.37***	***2.23***	***0.91***

Table 6-2 Estimated emissions of PCDD/PCDF and dl-PCB from biomass combustion from Australia in 2005 using the current NGGI methodology

Mass of PCDD/PCDF homologue groups and dl-PCB (kg)						
	Savanna	Wildfire	Prescribed	Crop	Total and 95% confidence range	
PCDD	13.1	0.5	0.6	1.5	15.7	6.2 – 37.5
PCDF	5.1	0.1	0.1	0.1	5.4	1.5 – 16.3
PCB	12.2	4.5	0.7	1.2	18.7	6.5 – 48.2
Total	30.4	5.1	1.5	2.7	39.7	13.1 – 110.1
TEF-weighted mass PCDD/PCDF and dl-PCB (g TEQ)						
PCDD	131.1	4.3	2.9	4.2	142.6	40.6 – 436
PCDF	17.1	0.9	0.9	0.3	19.2	5.8 – 57.8
PCB	3.2	0.9	0.3	0.2	4.5	1.9 – 11.0
Total	152.8	6.2	4.1	4.7	167.8	49.2 – 499.7

However, the results of the current study suggest that the inventory methodology can be improved by:

1. Grouping emission factors by regions based on the PCDD/PCDF content of rural and remote area soils in coastal and inland Australia.

2. Distinguishing between total emission and the component that is newly-formed by the fire; that is, estimating the fraction of the total emission that is due to redistribution of existing material.

In order to implement these improvements the following changes to the methodology are required:

1. The savanna fire regional classes are extended to:
    a. coastal, which is the coastal strip 75 km wide north of 30^{o} S (see Figure 6-1)
    b. grassland
    c. woodland.
2. Prescribed fires and wildfires in Qld are assumed to occur in the coastal belt. In all other states these fires are classed as inland forest. This is because the spatial fire statistics for more accurate stratification are not currently available.
3. Emission factors for prescribed fires, are grouped into tropical coastal (coastal) and inland (forest).
4. The agricultural components of the methodology remain unchanged.

To assess the significance of pre-combustion sources of PCDD/PCDF and dl-PCB we refer to Experiments II and III. To recapitulate, Experiment II indicates how much of the observed emissions can be explained by fuel combustion alone while Experiment III assesses how the fraction of the observed emission that might be contributed by pre-combustion sources, assuming the congeners pass through the combustion zone unchanged. Both experiments are limited in accuracy by their small sample sizes. Experiment III is most likely to give an upper limit of the fraction derived from pre-combustion sources, i.e. a lower limit of the fraction likely to be formed by combustion. Experiment II is more likely to give a result closer to the fraction achieved in practice. The two experiments yielded similar results for TEF-weighted emissions, but Experiment II suggested that a much larger fraction of the total mass of PCDD/PCDF homologues might be derived from pre-combustion sources. The average results of these tests are summarised in Table 6-3. For the inventory calculations we assume a scenario where 26% of homologue mass with a standard deviation of 40% and 70% of TEF-weighted mass with a standard deviation of 25% in the smoke emission is formed by combustion. This can only apply to fires that burn surface fuels. In crop residue fires the fuel is elevated therefore we assume that all the PCDD/PCDF and dl-PCB emitted forms during combustion.

Table 6-3 Summary of results from Experiments II and II. The percentage of PCDD/PCDF emission solely explained by formation during combustion.

Congener	Percentage of PCDD/PCDF emission explained solely by new formation		
	Experiment II[a] (all tests)	Experiment II tropical coastal soils[a]	Experiment III[b]
Homologue groups	72 (30-100)	64 (49-71)	26 ± 40
TEF weighted 2,3,7,8 - PCDD/PCDF and PCBs	84 (48-100)	61 (49-72)	71 ± 25

[a] range across all tests
[b] standard deviation of all tests

The revised average emission factors and their standard deviations are presented in Table 6-4. One result of applying a more appropriate classification is a substantial reduction in the variance of the EFs. The coefficients of variance (CV) for the classifications of prescribed fires and savanna fires were 100% and 112% respectively. In comparison the CVs of the reclassified categories of “coastal” and “inland” are 51% and 66% respectively.

Table 6-4 Revised emission factors and standard deviations using the regionalisation of tropical-coastal, inland forest woodland and grassland, and forest wildfire

Mass Emission Factor (pg (g CO_2-C)$^{-1}$)				
	Sugar Cane	**Coast**	**Forest**	**Wildfire**
PCDD	610 (262)	620 (356)	139 (133)	70 (71)
PCDF	44 (36)	72 (54)	77 (58)	16 (18)
PCB	497 (376)	256 (169)	464 (397)	671 (330)
Total	1151 (674)	947 (470)	681 (450)	757 (419)
TEF_{WHO97}-weighted mass Emission Factor (pg TEQ (g CO_2-C)$^{-1}$)				
PCDD	1.77 (1.10)	3.49 (1.65)	0.61 (0.43)	0.65 (0.76)
PCDF	0.14 (0.13)	0.85 (1.04)	0.18 (0.17)	0.13 (0.15)
PCB	0.07 (0.04)	0.23 (0.17)	0.12 (0.09)	0.13 (0.10)
Total	1.98 (1.26)	4.56 (2.33)	0.91 (0.60)	0.91 (1.01)

The national emission estimates for the 2005 inventory year and their 95% confidence bounds are presented in Table 6-5. This table allows two comparisons; (1) the impact of the revised classification on total emissions to air and (2) the fraction of this total emissions that might be redistribution of pre-existing PCDD/PCDF and dl-PCB. Only the first is consistent with current international accounting guidelines for PCDD/PCDF and dl-PCB. Compared to the 2004 methodology, the first revision led to:

- a reduction of 14% in total emissions from 168 g TEQ to 147 g TEQ
- a narrowing of the 95% uncertainty limits from a range of 49 g TEQ to 500 g TEQ to a range of 60 g TEQ to 323 g TEQ, a 51% improvement.

Most of the emission, 66%, occurs in the coastal regions of the Kimberly in WA, NT and Cape York (Table 6-7). A further 25% occurs in the savanna woodlands of the Kimberly, the NT and Cape York, and the arid grasslands of inland Australia. Prescribed burning and wildfires in temperate forests and southern Qld contribute 5.7% and the remaining 3.2% is due to agricultural waste burning (i.e. cereal stubble and to a lesser extent sugar cane). This conclusion is well based.

A proportion of the total emission is likely to be redistribution of existing material. Our current knowledge of this fraction is less certain, however our best estimate at this stage is that 19 kg of total homologue mass (7 kg to 44 kg, 95% confidence range) or 104 g TEQ (36 g TEQ to 234 g TEQ, 95% confidence range) of new material was released to the atmosphere by bushfires and agricultural burning in Australia in 2005. This is 38% less than the estimate from the revised 2004 methodology. Because grass fires are unlikely to heat the soil significantly, redistribution of PCDD/PCDFs is likely to occur predominantly in forest fires. This shifts the proportions of new emissions towards grassland emissions and agricultural burning, which increase to 5% and 4.7% respectively. This conclusion, our ‘best estimate’ is less certain because although the regionalisation and the resultant mean emission factors are robust, the fraction of new material released is less well defined.

In summary, this study has confirmed the findings of the 2004 NDP study (Meyer et al., 2004) but has suggested that the inventory should be revised by:

- grouping emission factors by regions based on the PCDD/PCDF content of rural and remote area soils in coastal and inland Australia.
- distinguishing between total emission and the component which is newly-formed by the fire, that is, estimating the fraction of the total emission that is due to redistribution of existing material.

These revisions reduce the estimate of the total TEF-weighted emissions in 2005 by 15% from 168 g TEQ to 147 g TEQ. Some of this is almost certainly redistribution of existing PCDD/PCDF and dl-PCB. Our best estimate is that at least 104 g TEQ is new material.

Table 6-5 Estimated emissions of PCDD/PCDF and dl-PCB from open burning in Australia in 2005. 95% confidence limits are shown in brackets.

Total emissions	Mass of PCDD/PCDF homologues and dl-PCBs						
	Tropical coast	Woodland	Grassland	Forest	Total fire	Agricultural burning	Total
	Kg						
PCDF	1.5	2.7	0.4	0.3	4.9	0.1	5.0
PCDD	13.0	4.8	0.8	1.0	19.7	1.4	21.1
PCB	5.4	16.1	2.6	4.8	28.8	1.2	30.0
Total	**19.9** (5.6 – 51.4)	**23.5** (5.2 – 58.6)	**3.7** (0.8 – 11.1)	**6.1** (2.6 – 13.4)	***53.2*** (22.2 – 114.1)	***2.7*** (0.9 – 7.4)	***56.0*** (25 – 117)
	TEF-weighted mass (g TEQ)						
PCDF	17.8	6.2	1.0	1.6	26.6	0.3	26.9
PCDD	73.6	21.1	3.4	7.0	105.2	4.2	109.4
PCB	4.8	4.1	0.6	1.1	10.6	0.2	10.7
Total	**96.3** (27 – 248)	**31.6** (7 – 92)	**5.0** (1 – 15)	**9.7** (3 – 27)	**142.6** (55 – 73)	**4.7** (3 – 8)	**147.3** (60 – 323)

Table 6-6 Estimated emissions of newly-formed PCDD, PCDF and dl-PCB from open burning in Australia in 2005. 95% confidence limits are shown in brackets.

	Mass of PCDD/PCDF homologues and dl-PCBs						
	Tropical coast	Woodland	Grassland	Forest	Total fire	Agricultural burning	Total
	Kg						
NSW&ACT	0.00	0.00	0.09	0.25	0.34	0.78	1.13
Tas	0.00	0.00	0.02	0.03	0.05	0.00	0.06
WA	2.43	1.51	1.66	0.89	6.50	0.87	7.36
SA	0.00	0.00	0.03	0.00	0.03	0.36	0.39
Vic	0.00	0.00	0.04	0.26	0.30	0.31	0.61
Qld	0.58	0.70	0.29	0.16	1.73	0.42	2.15
NT	2.19	3.93	1.60	0.00	7.74	0.00	7.72
Total	5.19 (0.8 – 15.1)	6.14 (0.8 – 19.8)	3.73 (0.8 – 11.0)	1.60 (0.3 – 4.2)	16.66 (4.6 – 40.0)	2.75 (0.9 – 7.4)	19.41 (6.9 – 43.8)
	TEF-weighted mass (g TEQ)						
NSW&ACT	0.0	0.0	0.1	0.8	0.9	1.3	2.3
Tas	0.0	0.0	0.0	0.1	0.1	0.0	0.1
WA	30.8	5.3	2.2	2.8	41.1	1.5	42.6
SA	0.0	0.0	0.0	0.0	0.0	0.6	0.7
Vic	0.0	0.0	0.1	0.8	0.9	0.5	1.4
Qld	7.3	2.4	0.4	2.1	12.2	0.7	12.9
NT	27.7	13.8	2.2	0.0	43.7	0.0	43.7
Total	65.8 (15 – 177)	21.6 (4 – 64)	5.0 (1 – 14)	6.6 (2 – 18)	99.0 (31 – 45)	4.7 (2 – 8)	103.7 (36 – 234)

Table 6-7 The distribution of the total and newly formed emission of TEF-weighted PCDD/PCDF and dl-PCB mass in Australia in 2005

	Total emission						
	Tropical coast	Woodland	Grassland	Forest	Total fire	Agricultural burning	Total
NSW&ACT	0%	0%	0%	1%	1%	1%	2%
Tas	0%	0%	0%	0%	0%	0%	0%
WA	31%	5%	2%	3%	40%	1%	41%
SA	0%	0%	0%	0%	0%	0%	0%
Vic	0%	0%	0%	1%	1%	0%	1%
Qld	7%	2%	0%	2%	12%	0%	12%
NT	27%	14%	1%	0%	43%	0%	43%
Total	65%	21%	3%	7%	97%	3%	100%
Formed during combustion							
All States	63.4%	20.8%	4.8%	6.4%	95.5%	4.5%	100.0%

6.2 Emissions estimated using the UNEP toolkit

The national reporting of PCDD/PCDF and dl-PCB emissions is guided by the UNEP toolkit (UNEP, 2005) categories, methodologies and factors. The emphasis is to use reliable country-specific information where possible so long as the accuracy and relevance of the data are demonstrated by independent review. Emissions from bushfires, prescribed fires and crop residue burning are addressed in Section 6.1: open burning processes, subcategory A, biomass burning. The toolkit identifies two release routes, emissions to air and emissions to land and four source categories; (1) forest fires, (2) grassland and moorland fires, (3) agricultural residue burning in the field, impacted poor conditions and (4) agricultural residue burning in the field, not impacted. The toolkit provides some default emission factors for each of the sources and release routes, recognising the small number of experiments providing relevant guidance. At the date of preparation there were no field data available and the default factors were based on the range studies, the most reliable of which are those by Gullett and Touati at the USEPA, who measured emission in a test facility specifically designed for open burning studies. Other groups relied on combustion chambers and furnaces operated in a manner intended to replicate the combustion properties of open fires. The emission factors published in these reports vary by a factor of 100, leading to major uncertainties in the recommended default emission factors. The UNEP toolkit recommends in the absence of country-specific data a default emission factor of 5 pg TEQ (g fuel burned)$^{-1}$ applied to forest and grassland fires and 0.5 pg TEQ (g fuel burned)$^{-1}$ applied to crop residue, unimpacted by poor combustion practices and PCDD precursors in the form of pesticide residues. For emissions to land as ash residue the UNEP toolkit recommends EFs of 4 pg TEQ (g fuel burned)$^{-1}$ for forest and grassland fires and 10 pg TEQ (g fuel burned)$^{-1}$ for agricultural residues. Combining these EFs with the mass of fuel burned in Australia in 2005 in forest, grassland and crop residue fires, the UNEP methodology estimates Australian emissions to be respectively 771 g TEQ to air and 674 g TEQ to land (Table 6-8). The former is 420% larger than our current best estimate (Table 6-5), principally due to the very large difference between the default EFs and the EFs measured in Australia. Allowing for the conversion from a fuel carbon base to a fuel mass base, the default forest emission factor is more than twice the emission factor for tropical coastal fires measured in Australia and approximately 10 times the emission factor for woodland and forest fires (Table 6-4). The default emission factor for crop residue is comparable to the Australian estimate.

Table 6-8 Emission of PCDD/PCDF and dl-PCB estimated for Australia in 2005 using the UNEP default methodology and Australian activity data

	Mass burned (Kt)	EF to air (µg TEQ t^{-1})	Emission to air (g TEQ)	EF to land (µg TEQ t^{-1})	Emission to land (g TEQ)
Forest	141,398	5	707	4	566
Grassland	12,172	5	61	4	49
Agricultural	5,937	0.5	3	10	59
Total			**771**		**674**

6.2.1 Emissions to land as residual ash

The 2004 NDP bushfires study (Meyer et al., 2004) and the current study provide emission factors for Australian conditions for release of PCDD/PCDF and dl-PCB to air. To date we have not addressed the releases to land, however the measurements of PCDD/PCDF and dl-PCB content in ash from the laboratory tests of the 2004 study and the field measurements in this study provide enough data to make a preliminary assessment or the emissions from open burning remaining in the ash residues. Following the terminology from Section 4.5, emissions to land (E_{land}) are calculated as

$$E_{land}= A*FL* BEF*F_{ash}*D_{ash}$$

Where F_{ash} is the fraction of burned biomass that remains as ash. For small patches where burning is complete F_{ash} approximates (1-BEF), however for large fires, which are patchy, BEF is the combination of the patchiness of the burn and the fraction of fuel exposed to fire that is consumed in combustion. BEF for the Blakeville, Potter's Tk and Guildford burns were respectively 0.85, 0.82 and 0.88 The BEF for the laboratory tests from the 2004 study averaged 0.84, 0.93.93 and 0.8 respectively for cane residue, wheat straw, sorghum straw and forest litter. The value used in the NGGI for cereal and cane residues is 0.96. Heavy fuels leave approximately 10% of the total burned mass as ash (Russell-Smith et al., 2009). Combining these, we set F_{ash} to 0.15 for prescribed fires, 0.10 for wildfires and 0.06 for crop residues.

Table 6-9 Ash content of field and laboratory samples (D_{ash})

Congener	Field								Laboratory				Average (Standard deviation)
	This study							NDP (2004)					
	PT-PT	B-B	G-G	GU-Eb	Eb-Eb	D-K	GU-GU	NT4	straw1	Straw2	cane	Litter	
	Homologue mass (pg (g ash)$^{-1}$)												
PCDD	111	40	172	21	768	104	288	556	46	148	14	39	192 (237)
PCDF	68	14	45	2	10	46	10	13	44	100	51	5	34 (30)
PCB	445	137	164	18	47	10	59	126	124	78	258	56	1027 (122)
Total	**623**	**191**	**381**	**41**	**825**	**160**	**356**	**694**	**214**	**327**	**324**	**101**	**353 (245)**
	TEF-weighted mass (pg (g ash)$^{-1}$)												
PCDD	1.2	0.7	1.0	0.3	3.4	0.6	0.5	2.2	1.5	1.5	0.6	0.6	1.2 (0.9)
PCDF	0.7	0.3	0.4	0.0	0.1	0.7	0.2	0.4	0.4	2.2	0.5	0.1	0.5 (0.6)
PCB	3.2	0.9	1.3	0.0	0.2	0.0	0.0	0.5	0.4	0.2	0.2	0.1	0.6 (0.9)
Total	**5.1**	**2.0**	**2.6**	**0.4**	**3.7**	**1.3**	**0.7**	**3.1**	**2.3**	**3.8**	**1.3**	**0.7**	**2.2 (1.4)**

The concentration of PCDD/PCDF and dl-PCB in ash (D_{ash}) from both field and laboratory studies range from 0.4 to 5 pg TEQ (g ash)$^{-1}$ averaging 2.2. This is two orders of magnitude less than the value of 200 pg (g ash)$^{-1}$ presented as typical in the UNEP toolkit. Total homologue mass averages 408 pg (g ash)$^{-1}$ and 241 pg (g ash)$^{-1}$ for the field and laboratory samples respectively (Table 6-9). Applying these values to the 2005 activity data, we estimate that emissions to land from open burning in Australia to be 49 g TEQ (Table 6-10), 93% less than estimated using the default methodology. This is a major discrepancy which clearly calls for further clarification.

Finally, all calculations in this study have used the WHO$_{97}$-TEF weightings. In 2005, WHO revised some of the values in the light of new data. The impact of this change on the emission estimates for open burning in Australia is small. Applying the revised regional stratification and the WHO$_{2005}$-TEF reduces the estimated emissions by 4% from 148 g TEQ using WHO$_{97}$-TEF to 141 g TEQ (Table 6-10).

Table 6-10 Summary of emissions to air and to land in Australia in 2005 of PCDD/PCDF and dl-PCB mass and TEF weighted mass using alternative methodologies.

Study	Methodology		Mass (Kg)		TEF-weighted (g TEQ)	
			Mean	Range	Mean	Range
NDP 2004			75	29 – 177.	233	50 – 795
This study	Fire classes & 2004 EF		56.3	25 – 129	170	25 – 564
	Fire classes & 2007 EF		39.7	13 – 110	168	50 – 500
	Regionalisation & 2007 EF	Total	56.0	25 – 117	147	60 – 323
		New formation	19.4	7 – 44	104	36 – 234
		Ash	7.6	2.5 – 18.3	48.5	17 – 114
	Regionalisation , 2007 EF, WHO-2005 TEF	Total	56.0	25 – 117	141	59 – 300
UNEP toolkit		to air			771	
		to land			674	

6.3 Areas for future improvement

The new emissions estimates are substantially different from the 2004 NDP estimates. The new regionalisation is a useful improvement over the 2004 inventory stratification; however it would be valuable to confirm by further soil analysis that the boundaries of the regions are appropriate. It would also be valuable to confirm by further measurements in a wider range of coastal forest, inland forest and woodland ecosystems, that the emission factors are unbiased.

Our investigation of volatilisation of soil PCDD and PCDF is at best a preliminary study. At this stage we have only shown that soil is a potential source of PCDD and PCDF in bushfire smoke. None of our tests quantify the volatilised fraction with accuracy. The PCDD/PCDF chemistry occurring during the combustion of soil carbon, the PCDD/PCDF chemistry occurring during fuel combustion and the transport of PCDD/PCDF from soil through the fuel bed to the atmosphere all require further study.

The emission to land from open burning needs to be investigated in detail. Estimates based on PCDD/PCDF and dl-PCB content of ash from both the 2004 NDP study and this work are substantially lower than the current Australian estimates based on the UNEP toolkit methodology and default emission factors. This calls for further clarification.

Redistribution and dispersion of PCDD/PCDF dl-PCBs and precursor compounds is an area of investigation that needs closer attention. PCDD/PCDf and precursers are deposited onto vegetation, via both stomatal uptake and surface absorption into lipophilic waxes and leaf cuticules. The deposition velocity for these processes, particularly for gas-phase compounds is high, (Horstman and McLachlan,1998; Trapp et al., 2001). This will result in higher rates of deposition around the emission sources and could lead to significant regional differences in the precombustion pools in the fuels and the upper layer of the soil which is rich in organic matter formed from decay of leaf litter. A likely consequence will be regional differences in emission rates from bushfires. Such as we have found in this study.

Finally, studies currently in progress are suggesting that very long distance transport of particulate matter occurs with many fires, particularly the savanna fires in northern Australia (Meyer et al., 2008; Luhar et al., 2008) with the consequence that the spatial pattern of smoke and PCDD/PCDF and dl-PCB impacts on the Australian population may be very different from the spatial patterns of the emissions themselves. It is possible that the 75% of national emissions that occur in the WA and NT savanna woodlands and coastal strip are dispersed and deposited in the Indian Ocean and become part of the natural background. The emissions relevant to the Australian population may be the remaining 25%, which is comprised of prescribed fires, wildfires and agricultural fires in the southern states and southern Qld. It is possible that these emissions might impact directly on population centres, or deposit on agricultural land where they might then enter the food chain. This requires further investigation.

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8 Appendix 1

8.1 Dioxin analysis

This section describes the method used for determination of tetra through octachlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) and dioxin-like polychlorinated biphenyl congeners (dl-PCB) in environmental matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method provides data on all 2,3,7,8-chlorinated PCDD (seven) and PCDF (ten) congeners, plus the 12 dl-PCB congeners that are assigned a TEF by WHO. The PCDD/PCDF and dl-PCBs are determined by the isotope dilution quantitation technique. This technique allows determination of the toxic equivalent (TEQ) as well as the dl-PCB toxic equivalent for the dl-PCBs in a sample using WHO_{97} toxicity equivalency factors (TEFs) listed in Table 8-1. The total toxic equivalents (WHO_{97}-TEQ) are calculated as the sum of TEQ of PCDD/PCDF plus TEQ of dl-PCBs

The detection limits and quantification levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The method is ‘performance based’. The analytical methodology for the determination of PCDD/PCDF and dl-PCBs are based on USEPA methods 1613B and 1668A, respectively.

Samples are analysed on an as-received basis. Clean-up is affected by partitioning with sulfuric acid then distilled water. Further purification is performed using column chromatography on acid and base modified silica gels, basic alumina and carbon dispersed on celite. After cleanup, the extract is concentrated to near dryness. Immediately prior to injection, internal standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph (GC). The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup and GC/MS systems.

8.1.1 PCDD/PCDF and dl-PCB analyses

The following standards were all purchased from Wellington Laboratories (Guelph, Canada) and were used for calibration, quantification and determination of recovery of PCDD/PCDF and dl-PCBs.

PCDD/PCDF

- EPA-1613-CVS calibration and verification solutions (CS-1 to CS-5)
- EPA-1613-LCS labelled compound surrogate solution
- EPA-1613-ISS-ST internal standard solution
- EPA-23SSS surrogate standard solution field spike for ambient air and bushfire burn samples only
- EPA-23ISS internal standard solution – laboratory spike for ambient air and bushfire burn samples only

Dl-PCBs

- WP-CVS calibration and verification solutions (CS-1 to CS-7)
- WP-LCS labelled surrogate spiking solution

- WP-ISS internal standard solution
- WP-FS surrogate standard field spike for ambient air and bushfire burn samples

Acetone, dichloromethane, hexane, and toluene were all OmniSolv® grade sourced from Merck KgaA (Darmstadt, Germany). Ethyl acetate and anhydrous sodium sulfate (granular) were both AR grade sourced from Mallinckrodt (Kentucky, USA). AnalaR® sulfuric acid S.G. was sourced from Merck (Vic, Australia).

All chromatographic columns were purchased from Fluid Management Systems (Waltham, MA, USA) and were used without any further treatment. They comprised multi-layer (basic/neutral/acidic) silica, basic alumina and PX-21 carbon dispersed on celite, which are packed in individual Teflon columns and vacuum sealed in aluminium foil packages.

8.1.2 Sample preparation

8.1.2.1 Soil samples

Approximately 20 g of lyophilised samples were accurately weighed and spiked with a known amount of the respective PCDD/PCDF and dl-PCB isotopically labelled $^{13}C_{12}$ surrogate spiking solutions. Pressurized Fluid Extraction (PFE) was performed on the lyophilised samples using an Accelerated Solvent Extractor, ASE 100 (Dionex, Utah, USA) with toluene as the extracting solvent and a temperature and pressure of 150 ℃ and 1500 psi, respectively. The extracts were solvent exchanged in hexane and subsequently cleaned up using multiple extractions with concentrated sulfuric acid until the acid layer remained colourless. The hexane extracts were washed several times with water and dried with cleaned anhydrous sodium sulfate. The extracts were then concentrated prior to clean-up on the Power-Prep™ system.

8.1.2.2 Ash samples

Approximately 20 g of the ash samples were accurately weighed and spiked with a known amount of the respective PCDD/PCDF and dl-PCB isotopically labelled $^{13}C_{12}$ surrogate spiking solutions. All samples were then treated with sufficient concentrated HCl to cover the ash, placed in an ultrasonic bath for a minimum of two hours and then tumbled end-over end for two hours. The resultant sludges were filtered under vacuum through a GF/C filter and both the filtrate and the solid recovered for separate extractions as detailed below.

The solid residues were extracted using a Büchi Extraction System B-811 operated in the Hot Extraction mode with a solvent mixture of ethanol:toluene (68:32) for a minimum of four hours followed by toluene for an additional four hours. The acidic filtrate was extracted at least three times with dichloromethane. All solvent extracts were then combined and concentrated and then the solvent exchanged into hexane which was then subjected to multiple extractions with concentrated sulfuric acid until the acid layer remained colourless. The hexane extracts were washed several times with water and dried with cleaned anhydrous sodium sulfate. The extracts were then concentrated prior to clean-up on the Power-Prep™ system.

8.1.2.3 Vegetation samples

Approximately 20 g of lyophilised samples were accurately weighed and spiked with a known amount of the respective PCDD/PCDF and dl-PCB isotopically labelled $^{13}C_{12}$ surrogate spiking solutions. Pressurized fluid extraction (PFE) was performed on the lyophilised samples using ASE 100 system (Dionex, Utah, USA) with toluene as the extracting solvent and a temperature and pressure of 150 ℃ and 1500 psi, respectively. The extracts were solvent exchanged in hexane and subsequently cleaned up using multiple extractions with concentrated sulfuric acid until the acid layer remained colourless. The hexane extracts were washed several times with water and dried with cleaned anhydrous sodium sulfate. The extracts were then concentrated prior to clean-up on the Power-Prep™ system.

8.1.2.4 Ambient air and bushfire samples

Pre-cleaned XAD-2® resin 40 g were placed between 130 mm by 25 mm and 130 mm by 50 mm polyurethane foam plugs and spiked with a known amount of the respective PCDD/PCDF and dl-PCB isotopically labelled $^{13}C_{12}$ field surrogate spiking solutions. After spiking the cartridges were wrapped in aluminium foil and placed into individual paint tins for shipping to their destination. The cartridges are shown in Figure 8-1.

After sampling, the cartridges and associated filters were returned to the laboratory where they were placed into large glass soxhlet extractors (Figure 8-2) and spiked with a known amount of the respective PCDD/PCDF and dl-PCB isotopically labelled $^{13}C_{12}$ surrogate spiking solutions extracted for approximately 10 hours per day for 5 days. Cycle times were approximately once every 40 minutes. The extracts were solvent exchanged in hexane and subsequently cleaned up using multiple extractions with concentrated sulfuric acid until the acid layer remained colourless. The hexane extracts were washed several times with water and dried with cleaned anhydrous sodium sulfate. The extracts were then concentrated prior to clean-up on the Power-Prep™ system.

Figure 8-1 Ambient air and Bushfire cartridges

Figure 8-2 PUF/XAD Extraction system

8.1.2.5 Pressurized fluid system clean-up and purification

All sample extracts were then subjected to automated clean-up and purification through a Fluid Management Systems Inc. Power-Prep™ System. Elution through the different columns is computer controlled and requires applying the hexane extract first onto the multi-layer silica (acid/neutral/basic) and using hexane at a flow rate of 10 mL min^{-1} onto the alumina column. Dichloromethane:hexane (2:98) at 10 mL min^{-1} is used initially and then the solvent strength is modified to dichloromethane:hexane (50:50) and transferred to the carbon column which is eluted with ethyl acetate:toluene (50:50) in the forward direction at 10 mL min^{-1}. The flow is then reversed and the carbon column is eluted with toluene at 5 mL min^{-1}.

Two fractions are collected. The first fraction is collected from the alumina column during elution using dichloromethane:hexane (50:50) and contains the mono-ortho and di-ortho PCB. The second fraction containing PCDD/PCDF and non-ortho PCBs are eluted from the carbon column during the reverse elution with toluene. The two fractions are concentrated separately under vacuum and the respective recovery standards (EPA-1613-ISS-ST and WP-ISS) are added and then further concentrated using clean dry nitrogen to a final volume of 10 µL prior to HRGC/HRMS analysis.

8.1.3 High-resolution gas chromatography – high-resolution mass spectrometric (HRGC-HRMS) analysis

All experiments were conducted on a MAT95XL HRMS (ThermoFinnigan MAT GmbH, Bremen, Germany) coupled to an Agilent 6890 GC (Palo Alto, CA, USA) equipped with a CTC A200S autosampler. A DB-5 (J & W Scientific, Folsom, CA, USA) capillary column (60 m by 0.25 mm i.d., film thickness 0.25 µm) was used as the primary analytical column with ultra-high purity helium as the carrier gas. A flow rate of 1.0 mL min^{-1} was maintained throughout the chromatographic run. The temperature programme was from 100 ℃ (isothermal for 1 minute) then ramp 1 to 200 ℃ at 40 ^{o}C min^{-1}, ramp 2 to 235 ℃ (isothermal for 10 minutes) at 3 ℃ min $^{-1}$ and then ramp 3 to 310 ℃ (isothermal 9 minute) at 5 ℃ min $^{-1}$. A 1 µL splitless injection with an injector temperature of 290 ℃ was employed for all standards and sample extracts. The mass spectrometer operating conditions were: ion source and transfer line temperatures, 240 ℃ and 2 80 ℃, respectively; ionisation energy 45 eV, filament current 0.7 mA and electron multiplier voltage set to produce a gain of 10^{6}. Resolution was maintained at 10,000 (10% valley definition) throughout the sample sequence. Multiple ion detection (MID) experiments were performed in the electron impact mode with monitoring of the exact masses of either M^{+}, [M+2]$^{+}$, [M+4]$^{+}$ or ions [M+6]$^{+}$ for native and labelled compounds. Individual congeners are identified using the GC retention time and ion abundance ratios (Table 8-8) with reference to internal standards. A DB-dioxin (J & W Scientific, Folsom, CA, USA) capillary column (60 m by 0.25 mm i.d., film thickness 0.15 µm) was used for confirmation analysis when necessary.

Table 8-1 List of Analytes

Congener	**$^*WHO_{97}$-TEF**
PCDD	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0001
PCDF	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0001

Congener	**IUPAC No.**	**$^*WHO_{97}$-TEF**
Non-ortho PCBs		
3,3',4,4'-TeCB	PCB#77	0.0001
3,4,4',5-TeCB	PCB#81	0.0001
3,3',4,4',5-PeCB	PCB#126	0.1
3,3',4,4',5,5'-HxCBl	PCB#169	0.01
Mono-ortho PCBs		
2,3,3',4,4'-PeCB	PCB#105	0.0001
2,3,4,4',5-PeCB	PCB#114	0.0005
2,3',4,4',5-PeCB	PCB#118	0.0001
2',3,4,4',5-PeCB	PCB#123	0.0001
2,3,3',4,4',5-HxCB	PCB#156	0.0005
2,3,3',4,4',5'-HxCB	PCB#157	0.0005
2,3',4,4',5,5'-HxCB	PCB#167	0.00001
2,3,3',4,4',5,5'-HpCB	PCB#189	0.0001

$^*WHO_{97}$TEFs from Van den Berg et al. (1998).

TCDD – tetrachlorodibenzo-*p*-dioxin
PeCDD - pentachlorodibenzo-*p*-dioxin
HxCDD - hexachlorodibenzo-*p*-dioxin
HpCDD - heptachlorodibenzo-*p*-dioxin
OCDD - octachlorodibenzo-*p*-dioxin

TeCB – tetrachlorobiphenyl
HxCB – hexachlorobiphenyl

TCDF – tetrachlorodibenzofuran
PeCDF – pentachlorodibenzofuran
HxCDF – hexachlorodibenzofuran
HpCDF – heptachlorodibenzofuran
OCDF – octachlorodibenzofuran

PeCB – pentachlorobiphenyl
HpCB – heptachlorobiphenyl

Table 8-2 The MID Windows for PCDD/PCDF

MID Window	Accurate Mass	Ion Id	*Ion Type	Analyte (I= internal standard)
1	303.9016	M	R	TCDF
	305.8987	M+2	T	TCDF
	315.9419	M	R	TCDF (I)
	317.9389	M+2	T	TCDF (I)
	319.8965	M	R	TCDD
	321.8936	M+2	T	TCDD
	331.9368	M	R	TCDD (I)
	333.9338	M+2	T	TCDD (I)
2	339.8598	M+2	T	PeCDF
	341.8567	M+4	R	PeCDF
	351.9000	M+2	T	PeCDF (I)
	353.8980	M+4	R	PeCDF (I)
	355.8546	M+2	T	PeCDD
	357.8516	M+4	R	PeCDD
	367.8949	M+2	T	PeCDD (I)
	369.8919	M+4	R	PeCDD (I)
3	373.8208	M+2	T	HxCDF
	375.8178	M+4	R	HxCDF
	383.8639	M	R	HxCDF (I)
	385.8610	M+2	T	HxCDF (I)
	389.8156	M+2	T	HxCDD
	391.8127	M+4	R	HxCDD
	401.8559	M+2	T	HxCDD (I)
	403.8529	M+4	R	HxCDD (I)
4	407.7818	M+2	T	HpCDF
	409.7788	M+4	R	HpCDF
	417.8250	M	R	HpCDF (I)
	419.8220	M+2	T	HpCDF (I)
	423.7767	M+2	T	HpCDD
	425.7737	M+4	R	HpCDD
	435.8169	M+2	T	HpCDD (I)
	437.8140	M+4	R	HpCDD (I)
5	441.7428	M+2	T	OCDF
	443.7399	M+4	R	OCDF
	457.7377	M+2	T	OCDD
	459.7348	M+4	R	OCDD
	469.7780	M+2	T	OCDD (I)
	471.7750	M+4	R	OCDD (I)

*T=Target Ion=Quantitation Ion; R=Ratio Ion=Qualifier Ion.

8.1.4 Quality assurance/quality control criteria

The quality control and quality assurance criteria for data validation are presented in Table 8-9, Table 8-10 and Table 8-11.

Table 8-3 Theoretical Ion abundance ratios and quality control limits

No. of Chlorine Atoms	*m/z's forming the ratio	Theoretical Ratio	QC limits[1]	
			Lower	Upper
4[2]	M/(M+2)	0.77	0.65	0.89
5	(M+4)/(M+2)	0.65	0.56	0.76
6	(M+4)/(M+2)	0.81	0.70	0.95
6[3]	M/(M+2)	0.51	0.43	0.59
7	(M+4)/(M+2)	0.95	0.83	1.14
7[4]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

[1] QC limits represent ±15% windows around the theoretical ion abundance ratios.

[2] Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (clean-up standard).

[3] Used for $^{13}C_{12}$-HxCDF only.

[4] Used for $^{13}C_{12}$-HpCDF only.

* The ratio is defined as the Qualifier ion area (R) divided by the Quantitation ion area (T).

Table 8-4 The MID windows for non-ortho and mono-ortho PCBs

MID Window	Accurate Mass	Ion Id	Analyte (I= internal standard)
1	289.9224	M	TeCB
	291.9194	M+2	TeCB
	293.9165	M+4	TeCB
	301.9626	M	TeCB (I)
	303.9598	M+2	TeCB (I)
	323.8834	M	PeCB
	325.8804	M+2	PeCB
	327.8775	M+4	PeCB
	337.9207	M+2	PeCB (I)
	339.9178	M+4	PeCB (I)
2	359.8415	M+2	HxCB
	361.8365	M+4	HxCB
	363.8356	M+6	HxCB
	371.8817	M+2	HxCB (I)
	373.8788	M+4	HxCB (I)
	393.8025	M+2	HpCB
	395.7995	M+4	HpCB
	398.7966	M+6	HpCB
	405.8428	M+2	HpCB (I)
	407.8398	M+4	HpCB (I)

TeCB – tetrachlorobiphenyl

PeCB – pentachlorobiphenyl

HxCB – hexachlorobiphenyl

HpCB – heptachlorobiphenyl

Table 8-5 Theoretical Ion Abundance Ratios and QC Limits

No. of Chlorine Atoms	*m/z's forming the ratio	Theoretical Ratio	QC limits[1]	
			Lower	Upper
4	M/(M+2)	0.77	0.65	0.89
5	(M+4)/(M+2)	0.66	0.56	0.76
6	(M+4)/(M+2)	0.82	0.70	0.94
7	(M+4)/(M+2)	0.98	0.83	1.13

[1] QC limits represent ±15% windows around the theoretical ion abundance ratios

*The ratio is defined as the Qualifier ion area (R) divided by the Quantitation ion area (T)

8.1.5 Analyte identification and quantification criteria

PCDD/PCDF and dl-PCBs

For positive identification and quantification, the following criteria must be met:

- The retention time of the analyte must be within 1 second of the retention time of the corresponding $^{13}C_{12}$ surrogate standard
- The ion ratio obtained for the analyte must be ±15% of the theoretical ion ratio.
- The signal to noise ratio must be greater than 3:1.
- Levels of PCDD and PCDF congeners in a sample must be greater than 3 times any level found in the corresponding laboratory blank analysed.
- Surrogate standard recoveries must be in the range 25 to 150%.

For Ambient Air and Bushfire Samples

- Laboratory surrogate recovery must be in the range 50 to 120% for tetra/penta/hexa PCDD/PCDF congeners and 40-120% for hepta/octa PCDD/PCDF congeners.
- Field surrogate recovery must be in the range 50 to 120%.
- The analysis shall show the absence of polychlorinated diphenyl ethers (PCDPEs). Any PCDPEs that co-elute (± 2 seconds) with peaks in the PCDF channels indicates a positive interference, especially if the intensity of the PCDPE peak is 10% or more of the PCDF.

8.1.6 Quantification using the isotope dilution technique

The naturally occurring (native) compound is determined by reference to the same compound in which one or more atoms has been isotopically enriched. In this method, all carbon atoms for selected PCDD/PCDF and dl-PCB molecules have been substituted with carbon-13 to produce $^{13}C_{12}$-labeled analogs of the chlorinated dibenzo-*p*-dioxins, dibenzofurans and biphenyls, respectively. The $^{13}C_{12}$-labelled PCDD/PCDF and dl-PCBs are spiked into each sample and allow identification and correction of the concentration of the native compounds in the analytical process. Homologue totals for the tetra to octachloro dibenzo-*p*-dioxins and dibenzofurans are calculated by summing the total areas for each positively identified congener within each group and quantifying these totals using the mean relative response factor (RRF) of the determined RRFs for a homologue series.

The proprietary chromatographic integration package supplied with the Thermo Finnigan instrument, (Xcalibur®), was used to target all monitored compounds and create a text file that was further manipulated in Excel to produce the final certificate of analysis.

8.1.7 Quality assurance

PCDD/PCDF and dl-PCBs

- Batch sizes are typically 6 to 8 samples.
- A laboratory blank is analysed with each batch of samples.
- The HRMS resolution (≥10,000), performance and sensitivity are established for each MS run.
- The recoveries of all isotopically labelled surrogate standards are calculated and reported.

8.1.8 Data reporting

The bases of reporting for primary and quality control samples are given in Table 8-12.

- PCDD/PCDF and dl-PCBs data are corrected for recovery of $^{13}C_{12}$ surrogate standards.
- For all samples, data for quantified analytes are reported to 2 or 3 significant figures.
- Limit of detection data for non-quantified analytes are reported to 1 significant figure.
- Total toxic equivalents are calculated both excluding limit of detection values and at medium bound concentrations using half limit of detection values.

Table 8-6 Reporting Basis for Contaminant Concentrations

Contaminant class	Reporting basis
Soils, Vegetation and Ash Matrices	
PCDD and PCDF	**pg/g on a dry weight basis**. Total toxic equivalents for PCDD/PCDF (WHO_{97}-TEQ_{DF}) are calculated using the WHO Toxic Equivalency Factors (WHO_{97}-TEFs).
dl-PCBs	**pg/g on a dry weight basis.** Total toxic equivalents for dl-PCBs (WHO_{97}-TEQ_{P}) are calculated using the WHO Toxic Equivalency Factors (WHO_{97}-TEFs). Total toxic equivalents for PCDD/PCDF and dl-PCBs (WHO_{97}-TEQ_{DFP}) are calculated from the addition of the respective WHO_{97}-TEQ_{DF} and WHO_{97}-TEQ_{P} values.
Bushfire/Ambient Air matrices	
PCDD and PCDF	**pg on as received basis.** Total toxic equivalents for PCDD/PCDF (WHO_{97}-TEQ_{DF}) are calculated using the WHO Toxic Equivalency Factors (WHO_{97}-TEFs).
dl-PCBs	**pg on as received basis**. Total toxic equivalents for dl-PCBs (WHO_{97}-TEQ_{P}) are calculated using the WHO Toxic Equivalency Factors (WHO_{97}-TEFs). Total toxic equivalents for PCDD/PCDF and dl-PCBs (WHO_{97}-TEQ_{DFP}) are calculated from the addition of the respective WHO_{97}-TEQ_{DF} and WHO_{97}-TEQ_{P} values.

8.1.9 Analytical difficulties

Ambient Air and Bushfire Samples

- The PUF/XAD-2 sampling cartridges used were a scaled up version of the cartridges specified in the USEPA Method TO-9a and entailed an oversized soxhlet extractor to be employed. This required larger volumes (up to 1 litre) of toluene to be used for each sample and a total extraction time of five working days (8 to 10 hours per day) to achieve an equivalent cycle rate of a minimum of three cycles per hour demanded in the conventional PUF extraction. The larger volumes of solvent used for the extraction resulted in lengthy evaporation times.
- The bushfire samples in particular contained large amounts of organic material as evidenced by the dark yellow colour of the extract at the completion of the extraction and in some instances took on the appearance of a popular cola drink. Exchanging the concentrated toluene extract into hexane prior to the acid clean-up step also provided additional challenges with more polar material difficult to completely solubilise in the less polar hexane.
- Typically, up to five concentrated sulfuric acid washes are required but the bushfire samples, in particular, required up to 10 washes to be employed.
- Chromatographic clean-up and purification through the FMS leads to two fractions viz. mono-ortho PCBs from the alumina column and non-ortho PCBs and PCDD/PCDF after the carbon column. Both fractions were comparatively “dirty” leading to retention time shifts and then greater time expended during integration and processing. Several injections at different dilution levels were required with some samples on both polar and non-polar columns to resolve interferences.

Ash Samples

- To achieve similar detection levels to the soil samples a comparable mass was required to be tested. The ash samples were acid-treated prior to extraction as in the normal practice for bottom ash samples. Extra time was required for dealing with the additional acid fraction and also the high level of organic co-extractives as per the bushfire samples leading to similar problems being experienced.

Vegetation Samples

- To achieve similar detection levels to the soil samples a comparable mass was required to be tested. The vegetation samples also contained high levels of organic co-extractives as per the bushfire samples leading to similar problems being experienced.

8.2 Analysis data

The analysis data for all samples collected during the study are presented in Table 8-7 to Table 8-16.

Table 8-7 PCDD and PCDF mass (pg) measured in smoke samples collected in field burns

Type	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke
ID	A-Eb-GU-S	A-GU-GU-S	A-K-GU-S	A-K-GU-B	A-Eb-D-S	A-K-D-S	A-K-D-B	A-K-Eb-B	A-Eb-Eb-S	A-PT-PT-S
CO_2-C (g)	112.2	102.4	45.0	51.4	57.2	71.1	62.0	29.0	42.7	25.8
Volume (m^3)	28.9	45.6	22.2	32.3	15.6	31.5	31.8	17.4	17.9	55.5
2,3,7,8-TCDD	44	<20	6.1	<9	390	76	15	<2	<3	<5
Total TCDD isomers	4750	10500	450	1560	4760	1460	190	52	92	1440
1,2,3,7,8-PeCDD	340	360	60	130	480	120	5.8	<5	<10	<10
Total PeCDD isomers	3870	15000	680	1850	2970	1260	52	41	32	120
1,2,3,4,7,8-HxCDD	360	630	77	240	230	74	1.7	4.8	<1	9.9
1,2,3,6,7,8-HxCDD	410	480	98	200	250	150	3.6	7.4	16	12
1,2,3,7,8,9-HxCDD	580	620	130	280	250	120	<3	8.6	17	13
Total HxCDD isomers	9820	23300	1900	5550	2900	2170	50	99	95	380
1,2,3,4,6,7,8-HpCDD	4680	7540	1240	2790	990	790	19	68	38	100
Total HpCDD isomers	11500	23100	3600	6840	1960	1910	41	170	89	280
OCDD	45600	78000	13400	28700	1800	2910	220	980	<300	820
2,3,7,8-TCDF	1170	120	16	27	3870	260	490	37	14	31
Total TCDF isomers	14600	8260	570	1300	53400	4730	7730	520	630	2440
1,2,3,7,8-PeCDF	290	15	<3	<7	1460	56	120	<6	<4	<9
2,3,4,7,8-PeCDF	320	48	13	<7	2130	35	76	<7	<9	<7
Total PeCDF isomers	3790	570	860	100	15400	380	840	40	130	41
1,2,3,4,7,8-HxCDF	310	37	<6	<7	1480	9.6	20	<3	<2	<5
1,2,3,6,7,8-HxCDF	160	13	6.2	4.1	1040	9.2	20	2.8	<3	<2
2,3,4,6,7,8-HxCDF	180	12	11	<3	1070	4.1	8.2	<2	<2	<3
1,2,3,7,8,9-HxCDF	5.5	<10	<3	<6	130	1.3	4.1	<1	<3	<3
Total HxCDF isomers	2030	610	530	50	9300	57	130	16	43	31
1,2,3,4,6,7,8-HpCDF	730	44	25	8.8	2320	4.2	10	<2	<4	5.1
1,2,3,4,7,8,9-HpCDF	73	4.9	<5	<6	350	<1	2.8	<2	<2	<4
Total HpCDF isomers	900	59	52	11	3680	6.7	17	<4	<6	5.1
OCDF	650	110	<50	110	860	<6	<90	<7	<7	<50

Table 8-8 PCDD and PCDF mass (pg) measured in smoke samples collected in field burns, and concentration in ambient air at or near the sampling locations

Type	Smoke	Smoke	Smoke	Smoke	Smoke	Bkd	Bkd	Bkd	Bkd
ID	A-B-B-S	A-G-G-S	A-As-PT-B	A-As-B-B	A-As-G-B	A-Bkd-B	A-Bkd-K	A-Bkd-Asp	A-Bkd-Eb
CO$_2$-C (g)	50.9	75.9	65.6	126.4	91.6				
Volume (m^3)	32.4	22.4	26.6	50.3	40.5	10227	5168	8624	3907
2,3,7,8-TCDD	<4	110	46	<10	<10	14	9.5	95	6.9
Total TCDD isomers	1570	9840	560	6600	2550	220	170	2050	55
1,2,3,7,8-PeCDD	3.5	320	<20	58	9.3	11	<1	73	<3
Total PeCDD isomers	150	7310	350	3740	1130	160	84	1230	28
1,2,3,4,7,8-HxCDD	4.3	290	<10	160	24	4.1	5.3	25	4.6
1,2,3,6,7,8-HxCDD	7	360	47	90	22	8.4	17	93	21
1,2,3,7,8,9-HxCDD	10	440	40	180	26	6.5	13	59	18
Total HxCDD isomers	170	8940	470	3130	1220	110	150	1060	140
1,2,3,4,6,7,8-HpCDD	67	2650	200	1290	340	50	82	350	160
Total HpCDD isomers	170	6590	410	3350	1020	98	150	700	240
OCDD	600	10300	790	6680	2170	200	440	1590	440
2,3,7,8-TCDF	14	1000	61	<6	<9	72	41	170	18
Total TCDF isomers	3750	22500	1230	3440	3090	2020	790	9170	370
1,2,3,7,8-PeCDF	<5	630	96	<10	<5	33	54	150	35
2,3,4,7,8-PeCDF	<6	770	37	<9	<5	43	22	130	15
Total PeCDF isomers	24	11800	260	67	<40	570	330	2650	180
1,2,3,4,7,8-HxCDF	<2	660	67	<7	<3	28	47	140	48
1,2,3,6,7,8-HxCDF	1.9	700	46	4	3	23	32	130	34
2,3,4,6,7,8-HxCDF	<2	980	<9	<2	4	23	4.9	67	6.8
1,2,3,7,8,9-HxCDF	<2	290	<8	3.8	<2	2.8	3.3	11	4.2
Total HxCDF isomers	12	6490	280	76	26	230	180	1220	190
1,2,3,4,6,7,8-HpCDF	5.5	1230	64	19	<7	43	48	200	81
1,2,3,4,7,8,9-HpCDF	<3	220	30	3.7	<2	6.5	14	26	34
Total HpCDF isomers	5.5	1660	140	23	<9	69	80	320	150
OCDF	<20	470	67	<40	<30	<100	<50	78	130

Table 8-9 PCDD and PCDF concentrations (pg g^{-1}) measured in litter, soil and ash (part 1)

Type	Litter	Litter	Soil	Soil	Ash	Litter	Soil	Soil	Ash	Soil	Litter
ID	L-GU-F	L-GU-C	S-GU	S-GU	Ash-GU-GU	L-Eb	S-Eb	S-Eb	Ash-Eb-Eb	S-K	L-D
2,3,7,8-TCDD	<0.1	<0.1	1.5	0.35	<0.3	<0.2	<0.1	<0.1	0.55	0.54	<0.2
Total TCDD isomers	0.44	1.7	22	3.6	12	<1	4.5	2.3	9.4	3.4	<1
1,2,3,7,8-PeCDD	<0.2	<0.2	4.1	<0.3	<0.2	<0.2	0.23	<0.2	1.6	<0.7	<0.1
Total PeCDD isomers	<1	1.4	36	3.9	<1	<1	0.49	<1	20	3.3	<0.6
1,2,3,4,7,8-HxCDD	<0.09	<0.2	6.3	0.53	<0.3	<0.1	0.11	<0.08	1.4	1.2	<0.1
1,2,3,6,7,8-HxCDD	<0.08	<0.2	8.6	0.84	<0.4	<0.1	1.7	0.95	2.8	1.4	<0.1
1,2,3,7,8,9-HxCDD	<0.07	<0.2	11	1.2	<2	<0.2	2.4	1.4	3.7	2.2	<0.08
Total HxCDD isomers	0.59	4.5	150	16	13	<0.5	6.7	3.8	49	37	<0.4
1,2,3,4,6,7,8-HpCDD	0.62	5.1	310	50	7.1	<0.3	4	1.8	39	100	<0.1
Total HpCDD isomers	1.4	12	810	120	22	0.51	9	4.4	100	280	<0.1
OCDD	35	240	42100	9080	240	7.4	50	42	590	28700	5.9
2,3,7,8-TCDF	<0.2	<0.3	0.66	<0.2	<0.5	<0.2	0.2	<0.06	0.77	<0.08	<0.3
Total TCDF isomers	1.6	2.8	11	5.8	5	<2	15	8.9	7.1	4.9	<2
1,2,3,7,8-PeCDF	<0.04	<0.09	0.23	<0.1	0.37	<0.1	0.34	0.22	0.14	<0.08	<0.05
2,3,4,7,8-PeCDF	<0.1	<0.1	0.32	<0.09	<0.3	<0.06	0.12	<0.04	<0.1	0.1	<0.03
Total PeCDF isomers	<0.5	<0.7	2.1	<0.7	2.8	<0.6	1.2	0.22	0.93	0.38	<0.3
1,2,3,4,7,8-HxCDF	<0.04	<0.1	<0.2	<0.1	<0.2	<0.1	0.11	<0.04	<0.1	<0.1	<0.04
1,2,3,6,7,8-HxCDF	<0.05	<0.1	0.15	<0.1	0.28	<0.1	0.35	0.25	0.076	<0.09	<0.04
2,3,4,6,7,8-HxCDF	<0.05	<0.09	0.13	<0.09	<0.2	<0.2	0.099	<0.07	0.061	<0.1	<0.05
1,2,3,7,8,9-HxCDF	<0.04	<0.06	0.27	<0.1	<0.1	<0.1	1.3	1.2	<0.04	<0.2	<0.05
Total HxCDF isomers	0.23	0.77	2.3	<1	1.5	<0.8	1.9	1.5	1	1.5	<0.3
1,2,3,4,6,7,8-HpCDF	0.12	0.37	1.6	0.36	0.39	<0.2	0.44	0.14	0.23	0.94	<0.08
1,2,3,4,7,8,9-HpCDF	<0.08	<0.2	0.24	<0.06	<0.08	<0.2	<0.05	0.077	<0.09	<0.08	<0.08
Total HpCDF isomers	0.12	0.37	4.1	0.65	0.39	<0.4	0.55	0.22	0.57	2.8	<0.2
OCDF	<1	<0.9	<10	0.55	<0.2	<0.2	<0.9	<0.2	<1	4.4	<0.1

Table 8-10 PCDD and PCDF concentrations (pg g^{-1}) measured in litter, soil and ash (part 2)

Type	Ash	Ash	Litter	Soil	Ash	Litter	Soil	Ash	Litter	Soil	Ash
ID	Ash-D-K	Ash-GU-Eb	L-PT	S-PT	Ash-PT-PT	L-B	S-B	Ash-B-B	L-G	S-G	Ash-G
2,3,7,8-TCDD	0.34	<0.3	<0.09	<0.3	<1	<0.1	<0.3	<0.5	<0.07	<0.4	<0.5
Total TCDD isomers	1.2	2.4	0.92	8.9	21	0.84	2.7	3.5	4.3	17	54
1,2,3,7,8-PeCDD	<0.2	<0.2	<0.2	<0.4	<1	<0.2	<0.3	<0.7	<0.1	<0.4	<1
Total PeCDD isomers	1.2	<1	<1	2.3	<5	<1	<2	<4	0.6	2.4	11
1,2,3,4,7,8-HxCDD	0.32	<0.1	<0.1	<0.4	<1	<0.09	<0.3	<0.4	<0.09	<0.3	<1
1,2,3,6,7,8-HxCDD	0.58	0.31	<0.1	<0.3	<0.8	<0.1	<0.4	<0.5	<0.1	<0.2	<0.7
1,2,3,7,8,9-HxCDD	<0.6	0.49	<0.1	<0.3	<0.7	<0.1	<0.3	<0.3	<0.09	<0.3	<1
Total HxCDD isomers	8.3	1.4	0.81	3.6	7.2	1.1	1.7	<2	1.6	3.7	27
1,2,3,4,6,7,8-HpCDD	4.5	0.75	0.61	2.7	4.1	1.1	2.3	2.6	0.57	3.2	8
Total HpCDD isomers	10	1.8	1.5	6.1	12	2.6	4.7	4.9	1.4	7.1	27
OCDD	83	15	12	41	68	27	81	29	13	53	53
2,3,7,8-TCDF	4.9	<0.2	<0.2	<0.3	<2	<0.07	<0.6	<0.8	<0.1	0.55	<1
Total TCDF isomers	42	1.5	1.1	18	57	2.6	11	9	0.97	17	39
1,2,3,7,8-PeCDF	<0.8	<0.06	<0.08	<0.5	<1	<0.05	<0.3	<0.9	<0.08	<0.5	<0.8
2,3,4,7,8-PeCDF	<0.5	<0.05	<0.06	<0.3	<2	<0.08	<0.2	<0.7	<0.06	<0.4	<0.8
Total PeCDF isomers	2.8	<0.4	<0.5	<3	<10	<0.5	<2	<6	<0.5	<3	<6
1,2,3,4,7,8-HxCDF	<0.2	<0.07	<0.06	<0.2	<0.6	<0.05	<0.2	<0.5	<0.04	<0.2	<0.6
1,2,3,6,7,8-HxCDF	<0.2	<0.1	<0.07	<0.2	<0.5	<0.06	<0.2	<0.5	<0.03	<0.2	<0.6
2,3,4,6,7,8-HxCDF	<0.1	<0.09	<0.06	<0.2	<0.5	<0.04	<0.2	<0.4	<0.04	<0.2	<0.5
1,2,3,7,8,9-HxCDF	<0.06	<0.09	<0.07	<0.1	<0.4	<0.04	<0.08	<0.3	<0.03	<0.1	<0.3
Total HxCDF isomers	0.6	<0.5	0.21	0.67	3.6	0.28	0.41	<2	0.37	1.1	<3
1,2,3,4,6,7,8-HpCDF	0.12	<0.1	<0.1	0.46	<0.9	0.18	0.33	<0.5	0.11	0.54	<0.6
1,2,3,4,7,8,9-HpCDF	<0.06	<0.08	<0.1	<0.1	<0.4	<0.1	<0.2	<0.3	<0.06	<0.1	<0.2
Total HpCDF isomers	0.12	<0.2	<0.2	0.46	<2	0.18	0.33	<1	0.11	0.54	<1
OCDF	<0.2	<0.1	<0.7	<2	<3	<0.3	<0.5	<0.7	<1	<2	<1

Table 8-11 PCDD and PCDF mass (pg) trapped from purge air in the dioxin volatilisation tests

Type ID	Laboratory Lab-air	Laboratory Lab-Eb	Laboratory Lab-GU	Laboratory Lab-G	Laboratory Lab-PT	Laboratory Lab-B
Volume (m^3)	91.1	81	79.6	71.8	78.5	79.7
2,3,7,8-TCDD	<2	<7	<4	<10	<0.7	<0.5
Total TCDD isomers	<10	180	1480	36400	2270	2060
1,2,3,7,8-PeCDD	<2	<6	<7	<20	<2	<4
Total PeCDD isomers	<10	<40	280	2210	260	230
1,2,3,4,7,8-HxCDD	<1	<2	11	31	4.0	<2
1,2,3,6,7,8-HxCDD	<1	6	16	63	9.2	5.9
1,2,3,7,8,9-HxCDD	<0.5	<4	<20	<50	3.9	4.9
Total HxCDD isomers	<4	15	350	1630	300	240
1,2,3,4,6,7,8-HpCDD	8.9	<4	540	400	70	58
Total HpCDD isomers	18	4.8	1340	1240	190	280
OCDD	210	64	31600	2430	650	760
2,3,7,8-TCDF	<4	<0.6	<6	<10	<3	<1
Total TCDF isomers	<30	91	630	15500	1690	1540
1,2,3,7,8-PeCDF	<1	<2	<3	<8	<1	<1
2,3,4,7,8-PeCDF	<0.5	<2	<2	<5	<2	<1
Total PeCDF isomers	<6	<10	<20	<40	27	<7
1,2,3,4,7,8-HxCDF	<2	<2	<4	<9	2.1	2.2
1,2,3,6,7,8-HxCDF	<0.7	<2	<2	<4	1.9	2.1
2,3,4,6,7,8-HxCDF	<0.9	<0.6	<1	<4	<0.3	0.47
1,2,3,7,8,9-HxCDF	<0.7	<2	<4	<6	<0.2	<2
Total HxCDF isomers	<7	<10	19	58	11	6.8
1,2,3,4,6,7,8-HpCDF	<2	<1	6.6	<20	<4	6.4
1,2,3,4,7,8,9-HpCDF	<0.9	<1	<2	<4	<1	2.0
Total HpCDF isomers	<4	<2	8.5	<30	<6	8.4
OCDF	<9	<6	<10	<10	<10	<6

Table 8-12 PCB mass (pg) measured in smoke samples collected in field burns

Type	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke	Smoke
ID	A-Eb-GU-S	A-GU-GU-S	A-K-GU-S	A-K-GU-B	A-Eb-D-S	A-K-D-S	A-K-D-B	A-K-Eb-B	A-Eb-Eb-S	A-PT-PT-S
CO_2-C (g)	112.2	102.4	45.0	51.4	57.1	71.1	62.0	29.0	42.7	25.8
Volume (m^3)	28.8	45.6	22.1	32.2	15.5	31.3	31.8	17.4	17.9	55.5
PCB 77	3640	3370	690	1330	3490	180	310	65	110	300
PCB 81	180	110	29	42	470	19	44	<10	5.4	<10
PCB 126	490	370	74	140	1070	<10	25	<5	7.1	<10
PCB 169	54	<6	<8	<9	170	<5	<2	<5	<2	<10
PCB 105	6250	7750	2280	4100	2150	260	610	300	470	1340
PCB 114	260	280	80	160	170	17	32	16	21	70
PCB 118	17100	18400	4520	7520	4020	<600	1350	<600	1030	3320
PCB 123	250	1510	350	670	160	<5	<20	44	84	<50
PCB 156	1510	1580	360	710	620	<70	120	<50	160	220
PCB 157	440	450	91	210	300	<20	29	<40	36	<60
PCB 167	770	710	220	480	260	<20	45	<20	<70	<50
PCB 189	190	100	32	61	440	<6	<5	<20	<20	<30

Table 8-13 PCB mass (pg) measured in smoke samples collected in field burns, and concentration in ambient air at or near the sampling locations

Type	Smoke	Smoke	Smoke	Smoke	Smoke	Bkd	Bkd	Bkd	Bkd
ID	A-B-B-S	A-G-G-S	A-As-PT-B	A-As-B-B	A-As-G-B	A-Bkd-B	A-Bkd-K	A-Bkd-Asp	A-Bkd-Eb
CO_2-C (g)	50.97	75.93	65.56	126.42	91.62				
Volume (m^3)	32.39	22.41	26.62	50.29	40.53	10227.00	5168.80	8624.71	3907.99
PCB 77	290	1720	110	190	270	680	4700	3350	5990
PCB 81	<10	240	<8	<50	<30	49	210	280	210
PCB 126	17	570	<20	<40	<40	33	190	150	150
PCB 169	<6	<200	<5	<100	<20	<3	<5	16	<2
PCB 105	1280	1710	540	950	1410	4660	3200	22800	2240
PCB 114	70	140	<200	<40	84	300	150	1560	160
PCB 118	3250	3910	1640	2080	3280	12800	8120	52300	5730
PCB 123	<30	<100	<50	<50	<50	220	160	970	130
PCB 156	240	510	110	<200	280	680	250	4950	190
PCB 157	69	210	68	<80	<60	140	93	1170	47
PCB 167	120	150	<60	<100	<200	290	160	2150	120
PCB 189	11	<300	<80	<100	<60	<20	<20	130	<6

Table 8-14 PCB concentrations (pg g^{-1}) measured in litter, soil and ash (part 1)

Type	Litter	Litter	Soil	Soil	Ash	Litter	Soil	Soil	Ash	Soil	Litter
ID	L-GU-F	L-GU-C	S-GU	S-GU	Ash-GU-GU	L-Eb	S-Eb	S-Eb	Ash-Eb-Eb	S-K	L-D
PCB 77	9.5	62	<30	14	6.3	2.1	<3	<2	<10	<2	1.2
PCB 81	0.28	1.7	11	<0.6	<0.3	<0.2	<0.2	<0.2	<2	<0.2	<0.2
PCB 126	0.85	6	11	2.4	<0.6	<0.2	0.48	<0.2	1.7	<0.3	<0.1
PCB 169	<0.07	<0.2	3.7	<0.1	<0.2	<0.06	<0.2	<0.03	0.71	<0.2	<0.09
PCB 105	27	110	<50	31	14	11	<20	6.5	<20	<4	19
PCB 114	1.3	4.3	<7	<0.8	<0.8	<1	<0.7	<0.4	<2	<0.2	<1
PCB 118	62	240	<100	64	29	27	<30	15	<40	<8	62
PCB 123	<0.8	4.1	<3	1.8	<0.6	<0.7	<0.8	<0.5	<2	<0.2	<1
PCB 156	6.7	26	<20	10	4.6	<3	<6	2.4	<8	<2	3.2
PCB 157	1.5	6.6	<8	3	1.2	<2	<1	<0.5	<2	<0.4	<0.6
PCB 167	<2	13	<9	5.2	2.4	<0.8	<3	1	<2	0.7	<0.6
PCB 189	<1	<3	3.3	1.2	<0.8	<9	<0.5	<0.7	<0.9	<0.7	<1

Table 8-15 PCB concentrations (pg g^{-1}) measured in litter, soil and ash (part 2)

Type	Ash	Ash	Litter	Soil	Ash	Litter	Soil	Ash	Litter	Soil	Ash
ID	Ash-D-K	Ash-GU-Eb	L-PT	S-PT	Ash-PT-PT	L-B	S-B	Ash-B-B	L-G	S-G	Ash-G
PCB 77	<2	<3	12	6.5	120	12	4.9	<30	5.7	8.1	<40
PCB 81	<0.1	<0.2	0.42	0.26	56	0.41	<0.1	<10	0.2	0.29	<20
PCB 126	<0.3	<0.2	0.79	0.77	30	0.83	<0.7	9	0.43	0.99	12
PCB 169	<0.07	<0.1	<0.09	<0.2	<20	<0.07	<0.2	<5	<0.1	<0.2	<6
PCB 105	<4	<4	23	18	<90	25	21	<40	16	31	<50
PCB 114	<0.4	<0.2	<1	1	<30	0.99	1.2	<9	0.91	1.7	<10
PCB 118	<10	11	62	42	<200	65	50	<100	44	77	<100
PCB 123	<0.6	<0.3	<0.7	<0.6	<20	<0.7	<0.9	<20	<0.5	1.2	<30
PCB 156	<1	<2	4.7	<5	<40	5.1	8.7	<20	<3	11	<20
PCB 157	<0.6	<0.8	1.6	1.2	15	<1	1.8	4.7	<0.5	2.7	6.2
PCB 167	<0.5	0.7	1.8	2.5	19	<3	3.6	<6	<0.8	3.9	<9
PCB 189	<0.8	<1	<4	<0.5	<9	<3	<0.7	<6	<2	1.1	<7

Table 8-16 PCB mass (pg) trapped from purge air in the PCDD/PCDF volatilisation tests

Type	Laboratory	Laboratory	Laboratory	Laboratory	Laboratory	Laboratory
ID	Lab-air	Lab-Eb	Lab-GU	Lab-G	Lab-PT	Lab-B
Volume (m^3)	91.1	81	79.6	71.8	78.5	79.7
PCB 77	<20	<20	490	310	170	68
PCB 81	<1	<3	25	<20	3.9	<2
PCB 126	<1	<3	29	43	<20	7.8
PCB 169	<1	<2	<2	<7	40	<0.2
PCB 105	2210	1490	7270	2460	270	330
PCB 114	180	120	590	210	15	17
PCB 118	6840	4480	26200	7310	770	890
PCB 123	89	71	420	99	19	20
PCB 156	<100	<90	1460	220	67	120
PCB 157	<10	<20	160	<40	19	24
PCB 167	<40	<50	520	130	32	63
PCB 189	<10	<20	57	<100	<6	15