National Dioxins Program

Technical Report No. 1
Dioxins Emissions from Bushfires in Australia

A consultancy funded by the Australian Government
Department of the Environment and Heritage

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This technical report is No. 1 of 12 under the National Dioxins Program:

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2. Dioxins emissions from Motor Vehicles in Australia
3. Australian Inventory of Dioxins emissions 2004
4. Dioxins in Ambient Air in Australia
5. Dioxins in Soils in Australia
6. Dioxins in Aquatic Environments in Australia
7. Dioxins in Fauna in Australia
8. Dioxins in Agricultural Commodities in Australia
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Foreword

When the Australian Government established the four year National Dioxins Program in 2001, our knowledge about the incidence of dioxins in Australia was very limited.

The aim of the program was to improve this knowledge base so that governments were in a better position to consider appropriate management actions. Starting in mid 2001, a range of studies were undertaken which involved measuring emissions from sources such as bushfires, as well as dioxin levels in the environment, food and population. The findings of these studies were used to shed light on the risk dioxins pose to our health and the environment.

This work has been completed and the findings are now presented in a series of twelve technical reports.

Having good information is essential if there is to be timely and effective action by governments; these studies are a start. Our next step is to foster informed debate on how we should tackle dioxins in Australia, as this is an obligation under the Stockholm Convention on Persistent Organic Pollutants. The Department of the Environment and Heritage will be working closely with other Australian Government, State and Territory agencies to take this step.

Ultimately, the effective management of dioxins will be the shared responsibility of all government jurisdictions with the support of the community and industry.

David Borthwick

David Borthwick

Secretary

Department of the Environment and Heritage

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- the Department of Agriculture, Fisheries and Forestry, who assessed the levels of dioxins in agricultural commodities
- Food Standards Australia New Zealand and the Department of Health and Ageing and who assessed the levels of dioxins in foods and assessed the health effects of dioxins
- officers of the Chemical Assessment Section in DEH who assessed the ecological effects of dioxins
- members of the National Dioxins Project Team which included representatives from the State and Territory environment protection agencies, the Australian Health Ministers Conference and the Primary Industries Ministers Council
- members of the National Dioxins Consultative Group which included representatives from industry and agricultural sectors, environment and public health groups and research institutions.

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Project Team

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Our special thanks also extend to the staff of AGAL Sydney, for excellent service, attention and interest in the analysis of the project's samples.

Executive Summary

The review, Sources of Dioxins and Furans in Australia: Air Emissions 1998, previously estimated the total emission of dioxins and furans to air from prescribed burns and bushfires to be 72 to 1,700 g TEQ per year. Using the measured field emission rates from the current study the total emission of dioxins, furans and dioxin-like PCBs to air is estimated to be 31-495 g TEQ per year, 70% lower than the previous estimate.

Based on overseas literature, biomass burning from bushfires, prescribed fires, and agricultural stubble fires was thought to be the major source of toxic dioxin, furan and coplanar PCB emissions in Australia. However, because there were no direct measurements of emissions from Australian fuels the uncertainty was very large, with a twenty-fold range from the minimum to the maximum. The bushfire project was commissioned to reduce this uncertainty by directly measuring the emissions of dioxins, furans, and coplanar PCBs from fires in the field, or in laboratory environments that adequately reproduce field combustion characteristics. These data were then used to reassess the emissions from field burning of biomass in Australia during the last decade.

The project found that dioxin and furan emissions in Australia may have been previously overestimated by at least a factor of three. Measured emission rates from fires in the field were at the minimum of the previous estimates, because these previous estimates were largely based on laboratory measurements. The discrepancy arises due to differences in combustion characteristics between field fires and laboratory simulations.

The project was designed to measure dioxin emissions from 21 field burns and 19 laboratory tests so as to replicate closely the combustion processes of open fires in the field. Field sampling requires the ability to sample very large volumes of smoke within the short duration of many field fires, typically from 15 minutes to 3 hours. A set of high volume samplers were designed and constructed that could be operated from the tray of a 4WD vehicle. These units could be quickly relocated to stay within the smoke plume as the fire front progressed. The samplers also measured total suspended particulate matter (TSP) and carbon dioxide (CO_2) concentration in order to relate the dioxin concentrations measured in the smoke plume to the combusted fuel mass, and thus, to derive emission factors. The field burns comprised 13 prescribed fuel reduction fires in SE Queensland, Central Victoria, and SW Western Australia, 2 cane burns, 4 fires in tropical savanna woodlands, and 2 samples from wildfires in NE Victoria.

Total emission factors observed in the field burns ranged from 0.1 to 2.9 pg TEQ (g fuel)$^{-1}$ for total polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF) and polychlorinated biphenyls (PCBs) with means of 0.9, 1.2, 0.5 and 1.1 pg TEQ (g fuel)$^{-1}$ for total PCDD/PCDF for prescribed fire, savanna fires, wildfires, and sugar cane fires, respectively. These are comparable to the minimum of the previous estimates of 0.5 to 30 pg TEQ (g fuel)$^{-1}$. Dioxin was the major component (70%) with furans and PCB contributing a further 20 and 10%, respectively. The congener patterns were not uniform across all states. Emissions from cane fires and prescribed forest fires in Queensland were dominated by OCDD; in Victoria, WA and, to some extent NT, the lower chlorinated homologue groups were equally important. The main furan

homologue group was TCDF and the main toxic congeners were 2,3,7,8-TCDF and 1,2,3,7,8-PeCDF. The number of observations was too small to demonstrate significant differences between classes of field burns; however, one significant and unexpected outcome was that when individual wildfires and prescribed burns were compared then prescribed burns were the stronger dioxin emitters.

Laboratory tests do not adequately simulate the combustion processes occurring in the field. The dioxin and furan emissions from the laboratory tests were substantially different to the field measurements. The laboratory burns were conducted on cereal straw, native sorghum, sugar cane trash and forest leaf litter in the test corridor at the CSIRO fire-testing laboratory. Fuel of known provenance was laid on the floor of the corridor to a loading of either 20 or 30 t ha^{-1}. Emission rates for the grass fuels of straw, sorghum and sugar cane, were high, averaging 17, 35 and 5 pg TEQ (g fuel)$^{-1}$, respectively, and ranged from 1.5 to 59 TEQ (g fuel)$^{-1}$. These rates are 10-times higher than the field measurements but comparable with previously reported estimates from laboratory tests. In contrast to the field burns, the PCDD homologue groups contributed less than 30% of total mass emissions and 35 to 40% of the TEQ emissions. The most abundant homologue groups were TCDF and TCDD. Emission rates from leaf litter combustion in the laboratory ranged from 0.1 to 0.9 pg TEQ (g fuel)$^{-1}$ and averaged less than a third of the field observations. Congener profiles for leaf litter burns in the laboratory were weighted toward furans.

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

Using the measured field emission rates, the total emission of PCDD/PCDF and PCBs from agricultural, forest and savanna fires in Australia were calculated and compared with the previous estimates, which were reported for the base year of 1994. The revised emission estimate for 1994 is 142 g TEQ with 95% confidence range of 31 to 494 g. This is 70% lower than the previous estimate of 72 to 1,708 g, which was based on emission factors sourced from overseas studies. Savanna fires accounted for 83% of these emissions. Wildfires, prescribed fires, and agricultural fires emit 12 g TEQ (range 6 to 23 g TEQ at 95% confidence limit) which is 95% less than previous estimate (10 to 470 g TEQ. Total emissions increased from 140 g TEQ in 1990 to 229 g TEQ in 2001, entirely due to increased savanna fire activity. This increase may be an artifact arising from a change in the methods used to estimate fire scar areas, and is currently under investigation. Emissions from wildfires, prescribed fires and agricultural fires were unchanged over this period.

Glossary/Abbreviations

Congeners: Closely related chemicals, derived from the same parent compound.

Dioxins: "Dioxins" refer to the group of persistent chlorinated chemical compounds, polychlorinated dibenzodioxins (PCDDs), which share similar chemical structures, properties and biological characteristics, including toxicity. For the purpose of the National Dioxins Program the term "dioxins" is used in a broader sense, encompassing the PCDDs, the closely related polychlorinated dibenzofurans (PCDFs or furans) and co-planar polychlorinated biphenyls (PCBs). Overall, these three families of related chemicals include several hundred congeners. The World Health Organization (WHO) considers that 29 of these congeners have significant toxicity.

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 WHO98-TEQ World Health Organization toxic equivalents, based on WHO98-TEF World Health Organization toxic equivalency factors. This system updates and expands the widely adopted system of International Toxic Equivalents Factors (I-TEFs and TEQs) proposed by the North Atlantic Treaty Organization, and includes factors for humans and other mammals.

AGAL	Australian Government Analytical Laboratory
CALM	Department of Conservation and Land Management (Western Australia)
CAR	CSIRO Atmospheric Research
CDD	Chlorinated dibenzo-*p*-dioxin
CDF	Chlorinated dibenzofuran
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_2-C	Mass of carbon in CO_2
CSIRO	Commonwealth Scientific Industrial Research Organisation
EA	Environment Australia
LOD	Limit of detection
NRCET	National Research Centre for Environmental Toxicology
PCB	Co-planar polychlorinated biphenyls
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans

TEF	World Health Organization toxic equivalency factor
TEQ	World Health Organization toxic equivalent
TSP	Total suspended particulate matter
WHO	World Health Organization
VOC	Volatile organic carbon

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1 Introduction

1.1 Background

This project, "Determination of ambient environmental levels of dioxins in Australia - Assessment of the levels of dioxins in bushfires in Australia", or the bushfire project, is an integral part of a comprehensive Australian National Dioxins Program being conducted by Environment Australia. Announced in the 2001-02 Budget, the National Dioxins Program is a four-year activity set up to assess, and manage, dioxins and dioxins-like substances in Australia.

The aims of the National Dioxins Program are to:

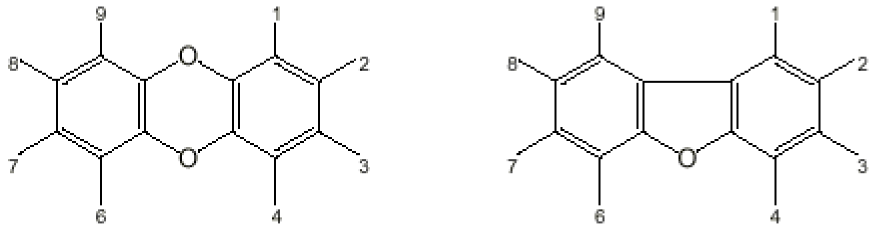
- ensure protection of the health of the Australian population and environment from exposure to dioxins
- ensure that international obligations concerning dioxins are met
- complement work of other government agencies in protecting the integrity of Australia's food.

Activities of the National Dioxins Program comprise three phases:

Phase 1 – determination of levels of dioxins in Australia
Phase 2 – assessment of the impact of dioxins on human health and the environment
Phase 3 – in light of the assessed impacts: reduction, and where feasible elimination, of releases of dioxins in Australia.

Dioxins are predominantly generated as unintended by-products of combustion processes and are usually discharged into the atmosphere. Consequently, atmospheric transport represents the primary route for transport of dioxins into the environment.

Dioxins and furans are both considered to be persistent organic pollutants (POP). A dioxin is any compound containing the dibenzo-p-dioxin nucleus, whereas a furan is any compound containing the dibenzofuran nucleus. The general chemical formulae for each of these compounds are presented in Figure 1.1.



Dibenzo-p-dioxin

Dibenzofuran

Figure 1.1. General Formulae of Dioxins and Furans.

Each of the positions numbered 1 through 4 and 6 through 9 can be substituted with a chlorine or other halogen atom, an organic radical or a hydrogen atom.

Because the principal environmental concern lies with chlorinated species, the usual abbreviation for dioxins is CDD (chlorinated dibenzo-p-dioxins) and that for furans is CDF (chlorinated dibenzofurans). In all, there are 210 different chlorinated dioxin and furan isomers, which arise when a chlorine atom occupies one or more of the eight positions shown in Figure 1.1

In this report, the following abbreviations will be used to denote different numbers of chlorine atoms present on dioxins and furans:

T – tetra (four chlorine atoms attached)

Pe – penta (five chlorine atoms attached)

Hx – hexa (six chlorine atoms attached)

Hp – hepta (seven chlorine atoms attached)

O – octa (eight chlorine atoms attached).

Physical properties of the various CDD/CDF compounds indicate decreasing volatility with increasing number of chlorine atoms. The most toxic of the dioxins is 2,3,7,8-tetrachlorodibenzo-p-dioxin, which we abbreviate as 2,3,7,8-TCDD. Other dioxins tend to be quantified in terms of an ‘equivalency factor’ (discussed further in Table 3.1). Total emissions from a particular source are then discussed in terms of total equivalent (TEQ) TCDD emitted.

A review of sources of dioxins and furans in Australia (Environment Australia, 2002) has shown that, from the limited data available, emissions of dioxins are expected to be low. A range of possible sources of dioxins in Australia was identified; these include bushfires and prescribed burning, residential wood combustion and industrial processes. Potentially, these sources could be expected to contribute up to 95% of the total dioxin emissions, with up to 75% from fossil fuel and biomass combustion alone.

The high frequency of fires in natural forest and grassland makes Australia unique among developed nations. Agricultural, forest and grassland fires are the dominant emissions of many pollutants. For example, these fires account for approximately 80% of national carbon monoxide (CO) and 42% of nitrogen oxides (NOx) and 58% of VOCs of emission (EA, 2003). In most other western countries these sources are relatively minor contributors, and, therefore, there has been relatively little international incentive to characterize this air toxic components of this source in detail. This was notably the case when the review of dioxin sources was conducted (EA, 2002), which found that there were no direct measurements of emissions from bushfires or agricultural fires in the field, or from laboratory simulations designed to simulate the class of open combustion that occurs in fires in the field. Instead, emission factors derived from wood and agricultural fuel combustion from small-scale laboratory simulations or from tests of wood combustion in domestic and commercial wood heaters and furnaces were used as surrogates. These emission factors ranged from 1 to 28 pg TEQ kg fuel-1 (EA, 2002), with little indication of where the mean might lie, or of the factors that might control the emission rates. The result of this was that the emissions from natural fires, the source that was potentially the largest in the country, was known to lie with a range (70 to 1,400 g TEQ per year) that varied more than twenty fold from minimum to maximum.

That emissions occur was inferred from wood combustion measurements in these and other categories (Gras et al., 2002), and from indirect measures, including the increases in dioxin concentrations in soil and atmospheric deposition rates near fires (Gabos et al., 2002; Kim et al., 2003; Prange et al., 2002). However, the process of dioxin production during combustion is extremely complex and even in extensively studied sources such as municipal waste incinerators, considerable debate surrounds the details of the mechanisms (Stanmore, 2004). At this stage it is not possible to extrapolate from current knowledge to combustion classes that are relatively uncharacterised. Key issues such as the extent of *de novo* synthesis compared with synthesis from precursors deposited on soil or absorbed by vegetation, and the importance of revolatilisation and redistribution of dioxins in surface soil are only recently being addressed (Stanmore 2004; Prange et al., 2003). Given this degree of uncertainty the prime task for characterizing dioxin emission from fires in agricultural or native forest and grassland in Australia must be to measure them.

This project was commissioned with one key objective- to measure the emissions from fires in the field and/or in laboratory environments that adequately reproduce field combustion characteristics. Only from a reliable set of directly measured emission factors can the uncertainties in Australia's dioxin emissions from biomass fires in the field be assessed and reduced.

1.2 Objectives

The overall objective of the bushfire project was to characterize dioxin emissions from bushfires in Australia under various scenarios including wildfires, prescribed burns and laboratory controlled fires.

This project aimed to:

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

1.3 Project scope

The bushfire project was implemented in four stages:

Stage 1: site establishment and sample collection

Stage 2: analysis

Stage 3: collation and processing of data

Stage 4: reporting of results and conclusions.

The project implementation plan was developed at project inception (see Appendix 1). This plan aimed to determine the dioxin emission factors and congener profiles from classes of fires likely to impact on populated and agricultural areas. This plan concentrated principally on field sampling of prescribed fires in forest and topical savanna woodland, pine plantations, slash burns for forest regeneration following logging, wildfires and sugar cane and cereal crop residue burns. The aim was to collect 40 samples from 20 fires. This was to be supported by a series of laboratory tests in which crop and forest fuels were burned in a test corridor/dilution tunnel in which a fire progressed across a bed of fuel simulating the fire characteristics of fuel reduction burns in forests or stubble burning in crops. Three issues required modifications to the design.

- It was not possible to collect more than one sample of adequate volume and carbon mass from a single fire in the field.
- The 2002/3 fire season in southern Australia was exceptional with the prescribed burning program in spring 2002 reduced due to extreme fire risk and in autumn 2003 reduced due to early rains.
- Safe access to wildfire fronts was not possible and was not allowed by fire control officers.

Additionally, as new information emerged in the literature during the course of the project, which questioned whether laboratory tests produced comparable emissions to field tests, and whether the source of dioxins was *de novo* synthesis during combustion or re-emission of dioxins already in the fuel. Given these practical considerations and the emerging scientific questions the focus of the study was shifted slightly. Originally, the main objective was to determine the emission characteristics from a sufficiently broad sample of fires for use in an inventory disaggregated to fire class and fire region. The modified focus addressed in this report aimed to:

- determine the distribution of emission factors observed in low-temperature prescribed fires in forests, savanna woodlands, and sugar cane production
- determine whether laboratory tests accurately simulate combustion in the field and, therefore, whether emission factors derived from laboratory tests can be used to estimate emissions in the field
- determine the extent to which dioxins present in smoke plumes are produced by volatilisation of dioxins present in the fuel, compared to synthesis from pyrolysis products.

The revised program shown in Table 1.1 consisted of:

1. Field sampling from prescribed fuel reduction burning in forests, savanna woodland and sugar cane production
2. Laboratory measurements of cereal stubble, sugar cane trash, savanna grasses and forest fuels burned under controlled conditions similar to field conditions
3. Dioxin content of samples of fuels and ash residues from both field and laboratory tests.

Table 1.1. Sampling program. a. Field samples, b. Laboratory tests, and c. fuel analyses.

a. Field Samples

Vegetation class	Location	Intensity class	Number
Tropical savanna woodland	Darwin and Kakadu	Permitted and non-permitted	4
Forest – mixed Eucalypt	Victoria	Wildfire	2
Forest – mixed Eucalypt	Victoria	Hazard reduction – low intensity	4
Coastal forest or open woodland	Southeast Queensland	Hazard reduction – low intensity	4
Southwest Western Australia – Jarrah forest	Western Australia	Hazard reduction – low intensity	5
Crop residues – cereal sugar	Queensland, Western Australia, New South Wales		2
Total			**21**

b. Laboratory tests

Fuel	Source	Fuel load (kg m^{-3})	Ventilation	Number
Wheat straw	Local Melbourne supplier of produce	2		4
Sugar can trash	Southeast Queensland	2		3
Sorghum		2		3
Eucalyptus obliqua forest – fine fuel	Wombat State Forest, Victoria	2		3
Wheat straw	Local Melbourne supplier produce	3.5	Assisted	3
Box/Ironbark forest	Loddon State Forest, Victoria	3.5	Assisted	1
Sugar cane trash	Southeast Queensland	3.5	Assisted	1
Coastal forest	Southeast Queensland	3	Assisted	1
Total				**20**

c. Fuel analyses

Fuel	Number
Savanna, forest litter, sorghum, sugar cane	7
Ash residue	3
Total	**11**

2 Project design

This section outlines the methodologies for Stages 1 and 2. Stage 1 consisted of two parts. Part A is a field measurement programme principally addressing forest and savannah woodland fires, and Part B is a laboratory programme addressing crop residue and forest litter combustion.

2.1 Field program

2.1.1 Field sampling requirements

The principal issue in the design of a field sampling system was to ensure that sufficient smoke was sampled to trap sufficient dioxin mass for analysis. At the experimental design stage there were no published Australian data available to indicate directly the quantities of smoke required to trap measurable quantities of PCDD/PCDF. However, a target sample size was estimated from some unpublished field measurements, and some indirect measures of smoke quantity, and some relevant laboratory-based measurements. The argument, presented in detail in Appendix 1, indicated that:

- The relevant measurement of sample size is the quantity of CO_2-C derived from the combustion, which passed through the dioxin trap. Typically more than 90% of fuel carbon emitted during combustion is in the form of CO_2. Therefore, the mass of CO_2-C additional to the ambient background concentration present in the smoke is directly proportional to the mass of fuel carbon emitted during combustion
- From the comprehensive study of emission characteristics from Australian fuels burned in domestic wood heaters (Gras et al., 2002), and from the field measurements of Prange and Mueller (pers.comm.) it was concluded that the gaseous emissions from about 20 g of fuel would probably trap 10 g of emitted carbon, which yields sufficient PCDD/PCDF for precise analysis
- In a typical smoke plume, a gas sample of between 50 and 250 m^3 would contain the emissions from 10 g of emitted carbon. At an air flow rate of 1 m^3 min^{-1}, which is at the upper operating range of standard dioxin traps and portable pumps, this would require 1 to 4 hours of sampling.

By design, most prescribed fires are completed within a few hours (typically less than 4). Agricultural residue fires such as sugar cane and cereals are of even shorter duration, 15 to 30 minutes. This experimental program, therefore, required a field sampler that could directly measure the amount of fuel carbon sampled. It was also likely that more than one fire might need to be sampled to collect sufficient sample for analysis. In summary, the target was to sample 5 to 10 g of CO_2-C within 2 to 4 hours of sampling at 1 m^3 min^{-1} from one or more fires for each dioxin analysis.

The design requirements, therefore, were:

1. easy mobility, so that the sampler could be kept in the main smoke plume as the fire progressed
2. high flow capacity with a design flow of 1 m^3 min^{-1} for maximum sample collection within the limited duration of most prescribed fires

3. easy and rapid filter changing in the event that high particle loads blocked the filter and restricted air sample flow
4. real-time CO_2 monitoring to determine the sample size (volatilised fuel C) prior to analysis
5. integrated data acquisition
6. a capacity for sampling of TSP (total suspended particles), CO (carbon monoxide), CH_4 (methane) and VOC (volatile organic carbon) in parallel with the dioxin sampling to determine related combustion and emission properties.

Sample system

The sampling system designed and constructed at CSIRO Atmospheric Research (AR) comprised a high capacity air pump, a 50 mm diameter anodised aluminium inlet assembled in sections with a total height of 4.7 m above the base of the rig, a large area (254 × 203 mm) particle filter and a sampler head that could be quickly disassembled should it prove necessary to change filters during sampling. It is shown schematically in Figure 2.1.

The units were operated with either a centrifugal air blower (Regenair SR4, GAST, Benton Harbour, MI, USA) powered by 9 HP petrol motor (Honda), or by a rotary vane air pump powered from a 3-kVA generator. Flow rate through the dioxin trap is measured with an Annubar type flow meter (Model AWR71, Dietrich Standard, Boulder, Co, USA). The absolute and differential air pressures from the Annubar flow meter were measured and logged. In addition, samplers operated in Queensland used a calibrated gasmeter where the gas values were corrected for the pressure difference using a pressure gauge.

A small airflow was drawn from the base of 4 m snorkel for determination of total suspended particles (TSP) mass and CO_2 concentration. This air stream first passed through a Teflon filter for TSP determination and then via a 12 V diaphragm pump (KNMP50KNDC, Neuberger, New Jersey, USA), a buffer volume of approximately 1 litre to dissipate the pressure pulses and a mass flow meter to a CO_2 analyser (Gascard II, Edinburgh Instruments, Edinburgh, UK). Air from the CO_2 analyser was exhausted through a gas meter (ML2500, Toyo, Japan) from which the integrated sample flow was determined. The pump speed was regulated via feedback from the mass flow meter to maintain a constant airflow of approximately 1,000 cm^3 min^{-1}.

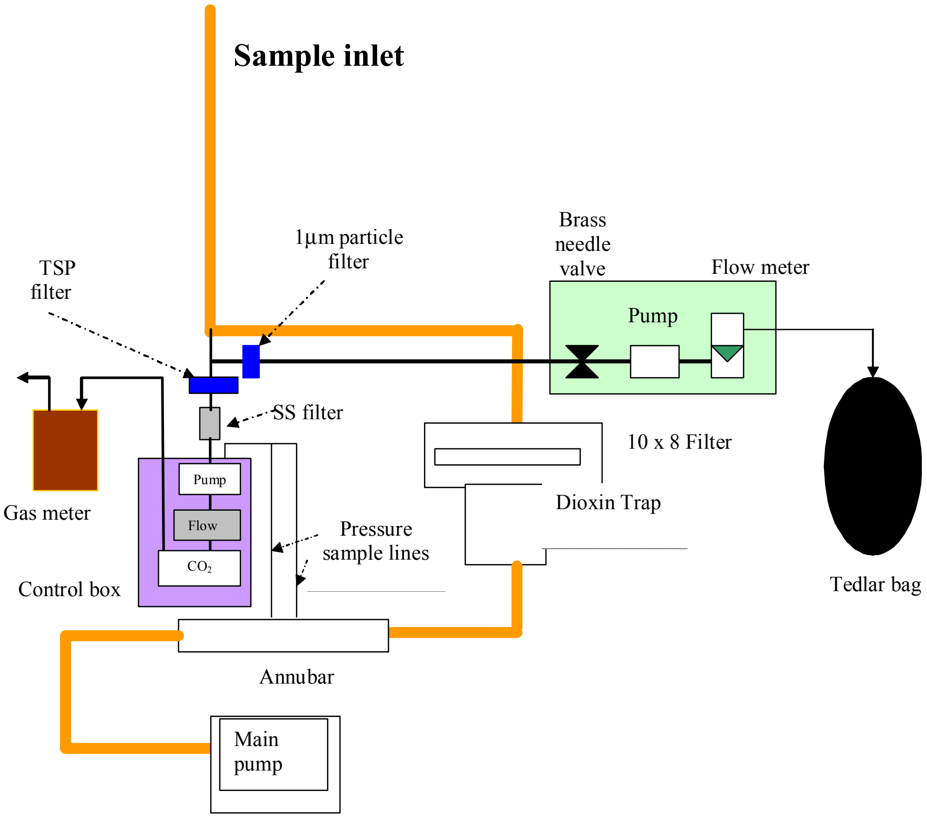


Figure 2.1. Schematic diagram of the dioxin sampling system.

A second gas sample was collected for determination of the average CO_2, CO, CH_4, and VOC concentration during the sampling period. This sample was drawn either from the TSP/CO_2 sample port, or from a port in the sampler head below the main filter. This sample was pumped by a Teflon diaphragm pump (Model MPU487-NO5, Neuberger, NJ, USA), needle valve and flow meter into an 80 litre Tedlar bag, which was either returned directly to the laboratory for analysis, or was sub-sampled into dual-valve SUMMA canisters (Scientific Instrument Services, USA). The sample flow rate was set at the beginning of each test to ensure that a sample of 40 litres to 80 litres was collected within the expected duration of the fire and maintained constant by manual adjustment.

The main sample line and the sample head were constructed from anodised aluminium. The TSP filter was connected to the inlet port with ¼” stainless steel. The criterion gas sample line was constructed of PFA-Teflon.

The sampling unit is shown in detail in Figures 2.2 to 2.10.

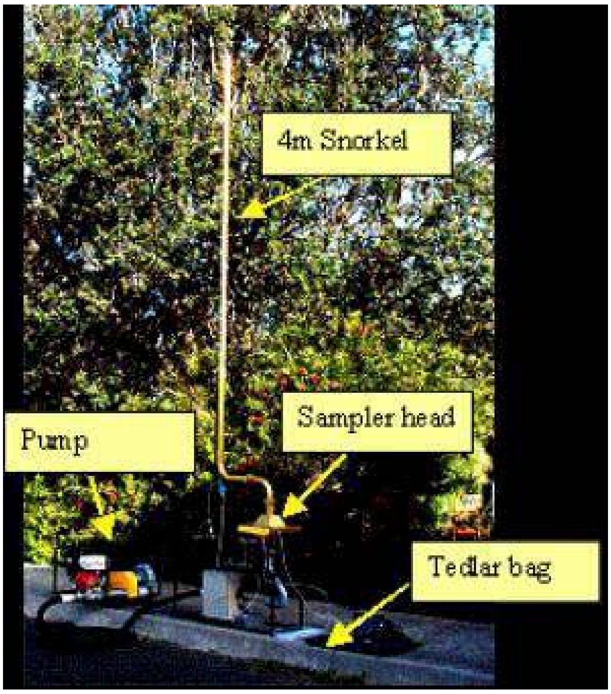


Figure 2.2. **The dioxin sampler fully assembled.**

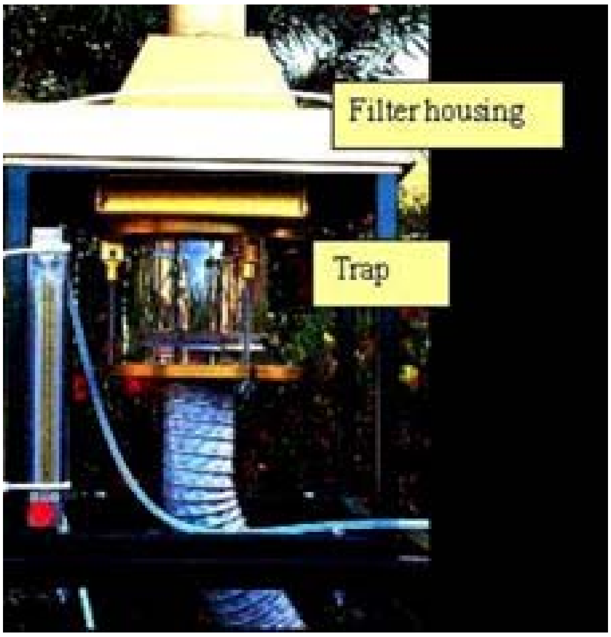


Figure 2.3. **Dioxin trap (130 mm glass) and housing.**

The trap is clamped in position against two plates and sealed against silicon gaskets. The exhaust line is 60 mm diameter silicon-coated glass fibre fabric enclosed in a polyethylene sleeve.

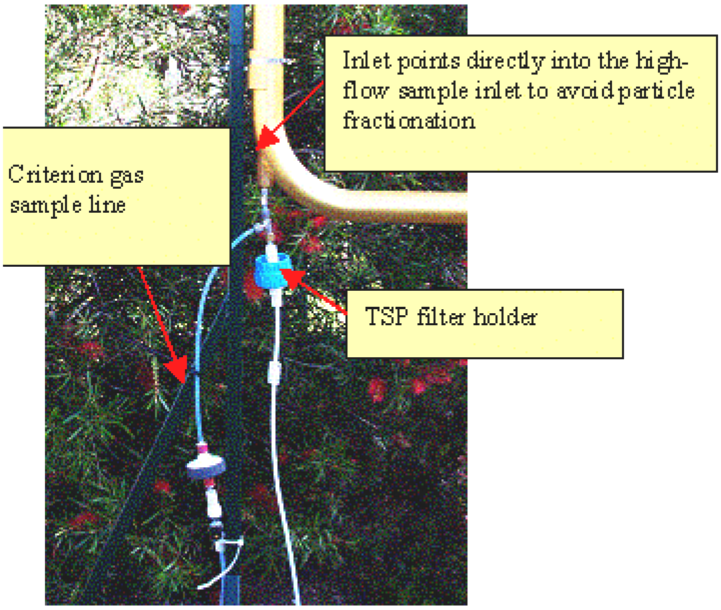


Figure 2.4. **The location of the CO_2/TSP sample and the criterion pollutant sample lines.**

Figure 2.5. **Sample head design.**

The sample head was connected to the inlet line by a quick-release clamp. The upper part of the head can then be opened by removing four screws to access the filter assembly.

Figure 2.6. The sample head opened to show the filter holder.

A stainless steel mesh (not shown) supports the filter that is sealed against a closed-cell foam gasket.

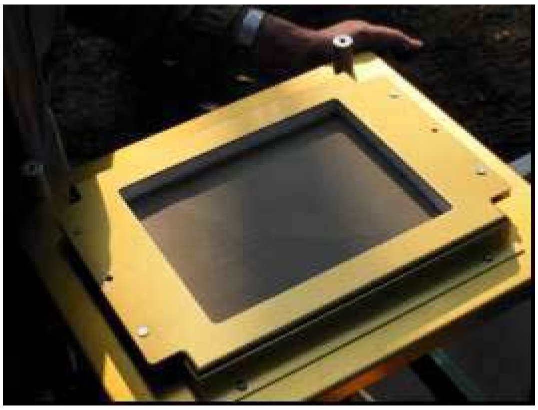


Figure 2.7. An exposed filter.

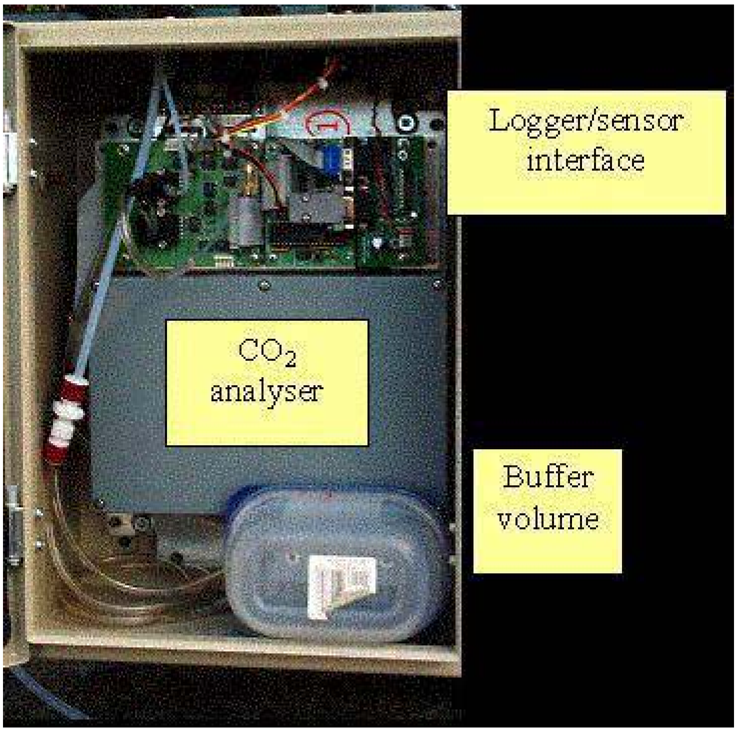


Figure 2.8. The data logger and sensor interface unit.

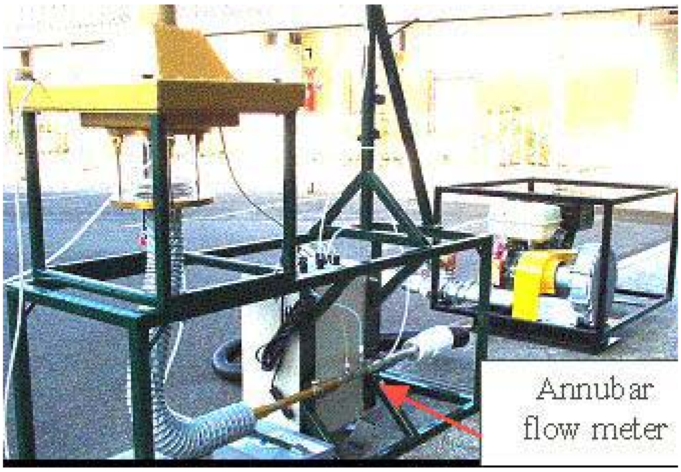


Figure 2.9. Rear view of the sample unit rack.

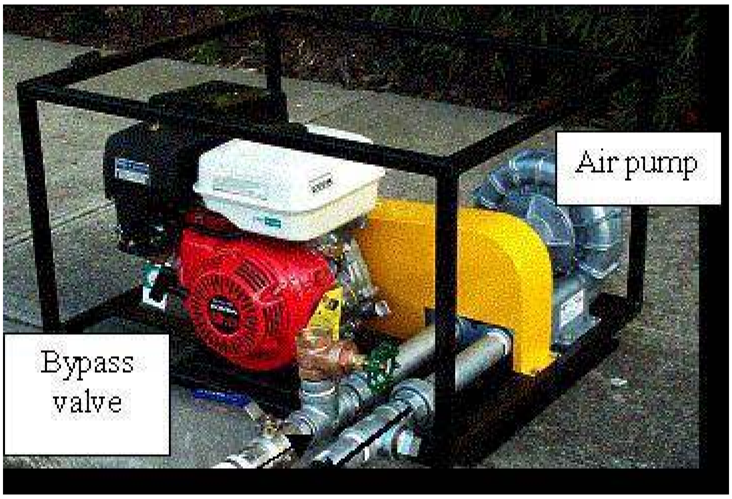


Figure 2.10. A petrol-driven air pump.

The sample units were monitored by a microprocessor-based data acquisition and control system designed and constructed by CSIRO. The units recorded battery voltage, air temperature, trap temperature, absolute pressure in the annubar sensor, differential pressure across the annubar sensor ports, CO_2/TSP sample flow rate, CO_2 concentration, and temperature of the CO_2 sample cell. Additionally, they controlled the CO_2/TSP sample pump speed via a feedback loop from the mass flow sensor to maintain a constant flow rate despite increasing resistance to airflow due to loading of the TSP filter. The logger was powered from the vehicle cigarette lighter and communicated via RS232. Each unit could be monitored and controlled from a laptop PC if required but was designed to operate automatically when powered.

2.1.2 Field sampler design and protocols

All gas trap components were prepared for sampling at AGAL Sydney. This comprised clean-up, a batch blank verification analysis, XAD-2 packing, spiking and trap assembly. Cleaned traps were wrapped in pre-cleaned aluminium foil, labelled for shipping and sent to CAR Aspendale. Filters were baked at 400 ºC for 24 hours. They were loaded into cleaned filter-holders wrapped in pre-cleaned aluminium foil. Weighed 47 mm stretched Teflon filters (Pall *Teflo* 2 µm pore size PTFE with polymethylpentene support ring, R2PJ047) were conditioned for 24 hours, weighed and loaded into cleaned polyethylene filter holders, sealed with pre-cleaned aluminium foil and sealed in polythene bags. Summa canisters were cleaned, filled with zero air to one atmosphere overpressure and analysed before shipping.

Dioxin traps were shipped out using clean air-tight metal canisters, with the wrapped traps packed in clean polyurethane foam. Filters were shipped in cleaned aluminium foil in polythene bags; either by air freight with the traps. Returning samples and log-sheets were sent to CSIRO. Samples were forwarded as a batch to AGAL. All of the filters were stored and traps were stored in a freezer until shipped to AGAL for analysis.

Each field unit was deployed with a dioxin trap (PUF/XAD-2 cartridge spiked with ^{13}C-labelled congeners), and preloaded 254 mm × 203 mm and 47 mm TSP filter cartridges, ready and three 3-litre stainless steel canisters cleaned and filled with zero air.

Readings of ambient (i.e. background) and CO_2-free air were taken either prior to ignition or upwind of the smoke plume. CO_2 free-air was produced by scrubbing ambient air with Carbosorb. Sampling of dioxins, TSP and criteria gas pollutants were commenced and stopped simultaneously to ensure that the samples were comparable. Where feasible, CO_2 zero readings were also checked briefly every two hours during sampling. After completion of the smoke sampling, the dioxin trap, and filter cartridges were removed from the sample unit, wrapped in baked aluminium foil and sealed in zip-lock plastic bags. A background sample of ambient air upwind or remote from the smoke plume was then collected in a Tedlar bag, and the ambient and zero CO_2 signals were again recorded by the data logger.

On return to the laboratory, the Tedlar bags were either analysed directly at CSIRO for the criterion gas pollutants, or sub-sampled into 3-litre Summa canisters. In the latter case the smoke sample was pumped though a pair of 3-litre flasks connected in series, taking care to flush both flasks with a minimum of 12 litres before closing the exit valve and pressurising the canisters to approximately one atmosphere overpressure. The background air sample was sub-sampled into a single canister.

2.1.3 Field sampling locations

Twenty one field burns were sampled for PCDD/PCDF in this project. Their locations are shown in Figure 2.11.

Figure 2.11. Locations of the field burns sampled for PCDD/PCDF.

The time and locations of these samples are given in Table 2.1

Table 2.1. Field samples: Location, date and class of burn

Fire	Sample	Date	Location	State	Lat, Long	Class	Fire type[1]
1	PF_WA_1	10-Dec-02	Andrew Block	WA	115.8806E, 34.1167S	Forest	FRB
2	PF_WA_2	14-Feb-03	Northumberland	WA	116.8833E, 34.1600S	Forest	FRB
3	PF_WA_3	3-Nov-03	Andrew Block	WA	115.8607E, 34.1128S	Forest	Post-harvest
4	PF_WA_4	5-Nov-03	Mack Block	WA	115.9063E, 34.1106S	Forest	FRB
5	PF_WA_5	6-Nov-03	Yardup Block	WA	116.2359E, 34.1911S	Forest	FRB
6	PF_Vic_1	18-Nov-02	Barkstead	Vic	144.107E, 37.477S	Forest	FRB
7	PF_Vic_2	1-Apr-03	Cobaw	Vic	144.639E, 37.251S	Forest	Wildfire
8	WF_Vic_1	23-Jan-03	Ovens Staging Area	Vic	146.7618E, 36.5913S	Wildfire	Wildfire
9	WF_Vic_2	22-Jan-03	Mt Beauty football ground	Vic	147.1704E, 36.7405S	Wildfire	
10	PF_Vic_3	10-Nov-03	Beaufort	Vic	144.121E, 37.376S	Forest	FRB
11	PF_Vic_4	11-Nov-03	Daylesford	Vic	143.389E, 37.419S	Forest	FRB
12	F_Cane_1	26-Nov-02	Sunshine Coast	Qld		Sugar cane	
13	F_Cane_2	2-Dec-02 & 12-Dec-02	Sunshine Coast	Qld		Sugar cane	
14	PF_Qld_1	17-Dec-02 & 19-Dec-02	Griffith Uni	Qld		Forest	
15	PF_Qld_2	5-Aug-03	Bunyaville	Qld	152.9367E, 27.3742S	Woodland	FRB
16	PF_Qld_3	14-Aug-03	Seaview Range	Qld	152.2878E, 25.4569S	Woodland	FRB
17	PF_Qld_4	6-Aug-03	Samford State Forest & Mt Nebo	Qld	152.9077E, 27.3758S	Woodland	FRB
17	PF_Qld_4	4-Sep-03	Samford State Forest & Mt Nebo	Qld	152.7653E, 27.4259E	Woodland	FRB
18	S_NT_1	22-May-03	Wilman Reserve	NT		Savanna	
19	S_NT_2	22-Jul-03	Namambu Ck -Run 2	NT	132.669E, 12.668S	Savanna	
20	S_NT_3	22-Jul-03	Namambu Ck -Run 3	NT	132.674E, 12.637S	Savanna	
21	S_NT_4	9-Oct-03	Berrimah- sample	NT	136.932E, 12.418S	Savanna	

[1] FRB: Fuel reduction burn

2.1.4 Field sampler operational performance

The sampling system was successfully deployed at all field locations with target mass of volatilised fuel carbon achieved on 18 out of 21 samples and the remaining 3 samples sufficiently concentrated to yield interpretable results. A typical example of field sample collection is shown below.

The prescribed burn at Barkstead in central Victoria was conducted on 18-Nov-02.An area of 4 ha of messmate/stringy bark forest in the Wombat forest 20 km south of Daylesford was burned with the sampling unit deployed initially downwind of the backing fire, but later relocated as the fire front receded. Figure 2.12 shows two stages of the fires progression.

Figure 2.12. Progress of the Barkstead prescribed fire.

The sampling unit in operation on the tray of a Hilux twin-cab 4WD at the Barkstead fire is shown in Figure 2.13. One extension piece was fitted to the inlet giving a total inlet height of approximately 3.5 m above the ground. In this configuration it was possible to move the unit safely around the perimeter of the fire without dismantling. An air-flow of 0.9 m^3 min^{-1} was maintained throughout the three hour sampling period with no significant increase in vacuum or resistance to flow and consequently no filter change was required. Air temperature at the sample head was indistinguishable from ambient temperature.

Figure 2.13. Smoke sampling in progress.

The pump and sample rack were mounted on the tray of the twin-cab utility and could be moved around the boundary of the fire to optimise sample collection. Total elevation of the inlet was approx 3 m.

The time-series of CO_2 concentration is shown in Figure 2.14. Ambient CO_2 concentration within the canopy was approximately 345 ppm of CO_2. The increase in CO_2 concentration in the smoke plume due to carbon emission from the fire varied between 0 and 650 ppm of CO_2, averaging 92 ppm of CO_2 through the duration of the burn. The total amount of CO_2-C passing through the trap was 7.7 g, which was within the required range of 5-10 g specified in the project implementation plan. The time-series of this fire was very similar to the scenario estimated from Hurst et al. (1996) for the Kapalga, NT experiments and confirmed that the proposed sampling strategy was feasible.

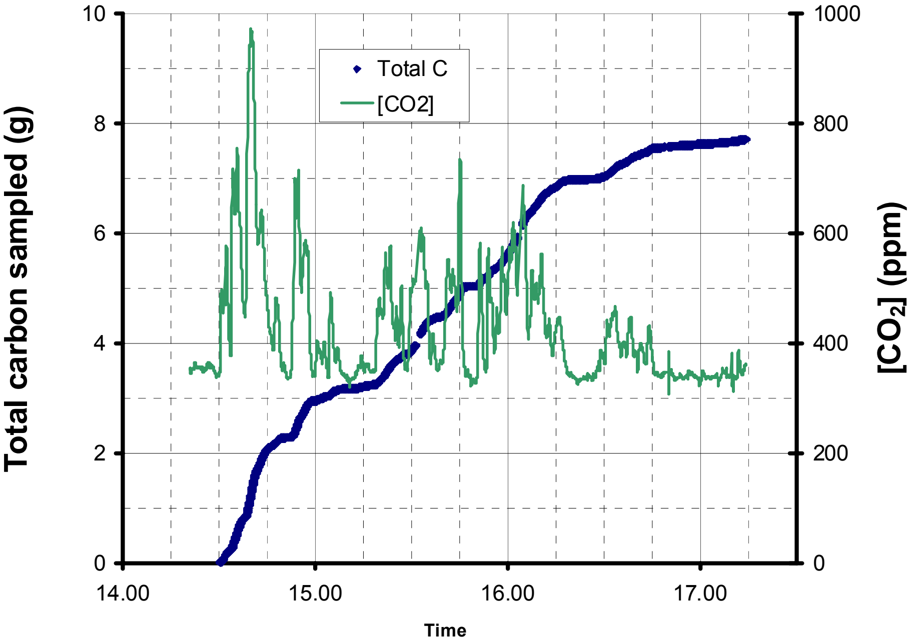


Figure 2.14. Prescribed fire in Messmate/Stringy bark forest at Barkstead 18th Nov 2002.

Time-course of CO_2 concentration and the total CO_2-C from the smoke plume passing through the dioxin trap.

Experimental fires in south-west Western Australia

Field samples were collected from five fires in dry sclerophyll eucalypt forest in the south-west of Western Australia. This forest had an over storey of Jarrah (*Eucalyptus marginata*) and Marri (*Corymbia calophylla*) up to 30 m tall, an understorey shrub layer 1 to 2 m tall, and a layer of surface fuel comprised of eucalypt and shrub leaf litter. Three of the samples (samples 26 [WA_1], 28 [WA_4] and 29 [WA_5]) were collected from fires of low intensity (< 500 kW m^{-1}) that were spreading slowly with average flame heights of less than 0.5 m in leaf litter fuel. For these fires it was possible to locate the vehicle-mounted sampler unit within about 20 m of the flaming zone and the origin of the smoke was readily apparent (Figures 2.15a and 2.15b). A further sample was collected from a post-harvest silvicultural burn in Andrew forest block (sample 30 [WA_3]) where dense smoke from the combustion of woody debris and logging slash persisted for several hours after the fine fuel had been consumed (Figures 2.15c and 2.15d). In this case the sampler was more than 100 m away from the main source of the smoke emissions. These four fires were conducted in spring (November to December) with surface litter moisture contents of 12 to 16% (ODW), and some residual moisture in the deeper parts of the litter profile. The fifth sample [WA_2] was collected during a burning-out operation undertaken to contain a wildfire in Northumberland forest block during dry conditions in February 2003. The moisture content of the surface litter was 8%. For the first hour the sampler was located in well-mixed drift smoke originating from a low intensity fire about 100 m upwind of the vehicle. The fire then increased in intensity and the sampler was moved to within 30 m of an active fire front burning in the shrub layer with flames up to 4 m tall. Smoke was dense, black to brown in colour, and contained a noticeable quantity of ash. This intense fire behaviour persisted for 10 minutes to 15 minutes.

Figure 2.15. Dioxin sampling in Jarrah/Marri Forest in south-west Western Australia.

A. Low intensity fuel reduction burn in Jarrah forest at Yardup block on 6-Nov-2003
B. Sampling unit on vehicle at Yardup experiencing moderately dense smoke from both sides of the track. Flames were within 20 m of the vehicle.
C. Smoke from combustion of woody debris during the post-harvest burn at Andrew block on 3-Nov-2003.
D. The burn was conducted during moist fuel conditions in spring and was not intended to consume larger logs.

Experimental fires in South East Queensland

In Queensland, prescribed fires were sampled in Eucalypt woodland in the Brisbane airshed, and near Maryborough/Gympie. The latter were typically large covering more than 1,000 ha and persisting for more than six hours during which approximately 10 g of CO_2-C was sampled in 60 m^3 of air (Figure 2.16c). Sugar cane fires were sampled on sugarcane farms on the Sunshine Coast south of Brisbane. These fires were completed in less than one hour permiting sampling times of only approximately 15-30 minutes. This was marginal and, therefore, the second field sample (sample 13) was taken from two successive cane fires.

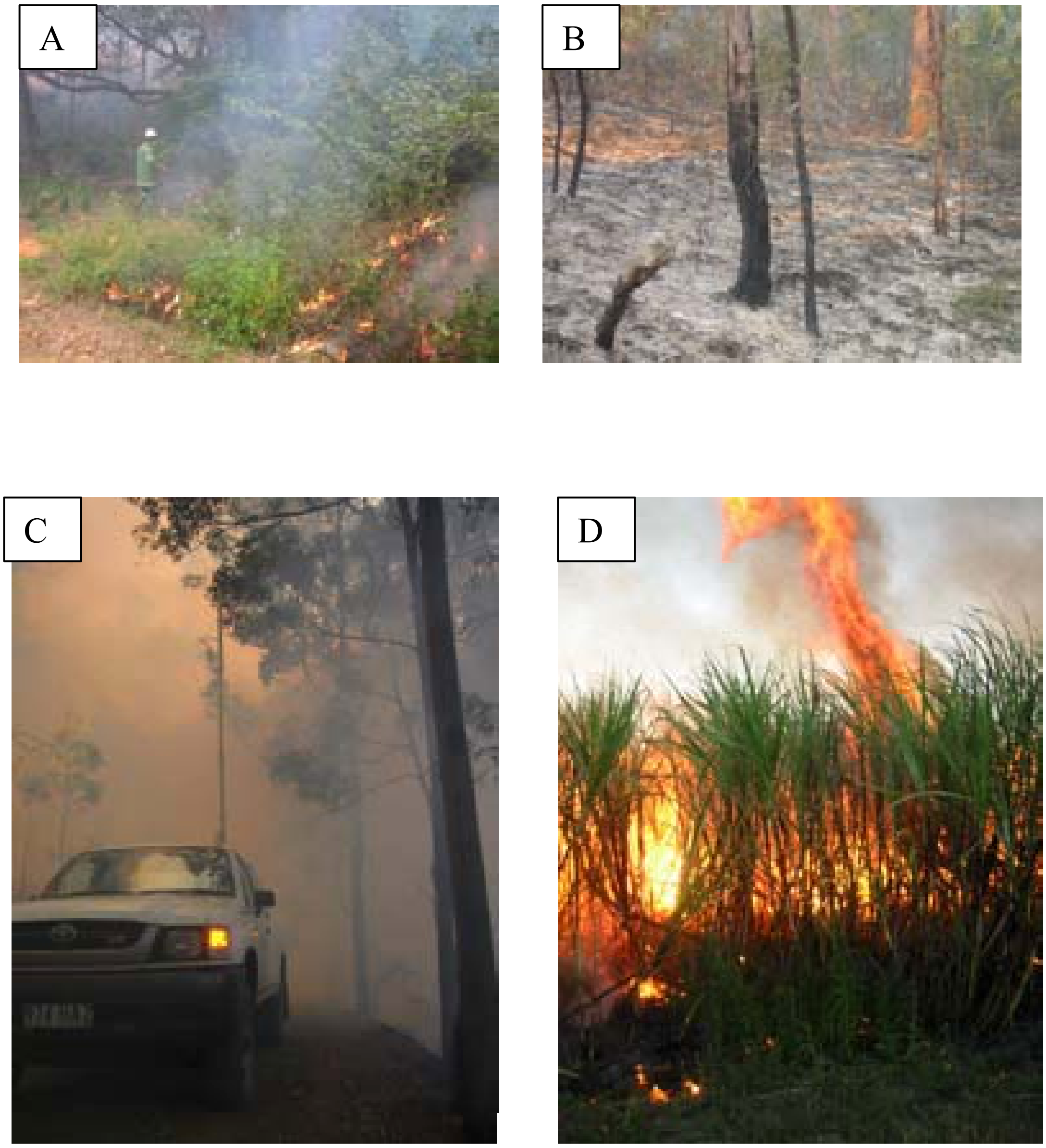


Figure 2.16. Dioxin sampling in Queensland.

A. Light-up
B. ash residue
C. smoke sampling at Mt Nebo
D. Sampling a cane fire on the Sunshine Coast.

2.2 Laboratory experiments

The aims of the laboratory studies were twofold. The first was to test the hypothesis that it is possible to simulate the combustion characteristics of fires in the field within the laboratory. It was clear from the study of wood heater combustion (Gras et al., 2002) that the characteristics of fires in field burns, in which the fire progresses across the unburnt fuel, is significantly different from that in a fixed combustion chamber. In the latter case a charge of fuel is added to the chamber and combustion proceeds through pyrolysis to char combustion. Therefore, it could not be assumed that the combustion chemistry and, therefore, the emission characteristics of fires conducted in laboratory test conditions are applicable to the field. In the event that they are applicable, laboratory tests offer substantial benefits, particularly the opportunity to sample large quantities of smoke.

Assuming that the laboratory tests yield sufficient information to permit extrapolation of the results to the field, the second aim was to explore the influence of fuel type on combustion properties including combustion temperature, combustion efficiency and fire intensity on dioxin emission rates. The laboratory tests offered the best opportunity to collect replicate samples for quality assurance of the dioxin analyses, and also provided the opportunity to test the combustion of agricultural residues, which are extremely difficult to sample in the field. Stubble burns are usually conducted in stable e atmospheric conditions in which the smoke plume rises rapidly from the surface.

The laboratory tests included four fuel types:

1. wheat straw
2. sorghum
3. sugar cane trash
4. leaf litter from three forest classes (messmate, box ironbark and tropical coastal woodland).

2.2.1 Test facility

The test facility was a corridor, 10 m long, 2.1 m high and 1 m wide. The adjacent burn room dimensions are 3.6 m by 2.4 m by 2.4 m high. The layout of the fire test room and corridor is shown in Fig.2.17. The corridor consists of eight modules, each 1.2 m long, framed in galvanised steel and lined with 44 mm of ceramic fibreboard. The far end of the corridor terminates beneath a 3 m by 3 m square smoke collection hood connected to an exhaust fan and gas-fired after-burner, which removes harmful and visible emissions from the exhaust gases.

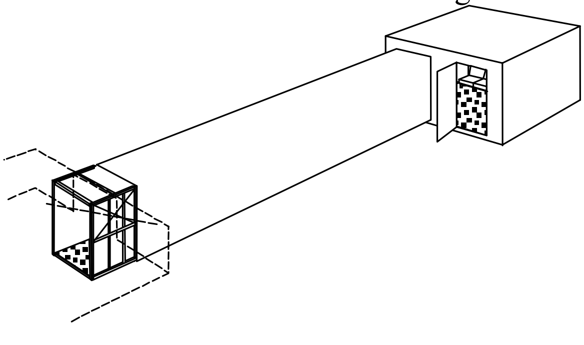


Figure 2.17. Schematic diagram of the laboratory fire-test room.

The concentrations of oxygen (O_2), carbon dioxide (CO_2) and carbon monoxide (CO) were continuously monitored in the exhaust duct together with air temperature and rate of airflow. These were used to derive the power output, and total energy yield. Thermocouples installed at 1m intervals within the fuel, recorded the rate of fire progression and flame temperature.

The fire was aerated by air drawn down the corridor by the progressing fire front and, therefore, the facility is best suited to investigate backing fires where the unburned fuel is preheated principally by radiation rather than by convection.

Two steps were taken to reduce the risk of contamination during the burns:

1. the corridor, floor and wall cladding were replaced with new materials for these tests
2. three high-temperature burns were conducted to precondition the unit.

The exhaust hood was routinely cleaned between test runs with a 50 kW propane burner operated for 20 minutes. Nevertheless it was considered essential to sample smoke as it emerged directly from the corridor and before it was exposed to the surfaces of the exhaust hood.

2.2.2 Sampling requirements

The primary sampling requirement was to trap a minimum of 10 g of carbon. The fire duration for laboratory burns can be very short, often less than 10 min duration, and therefore, it was necessary to trap high concentrations of smoke. The collection of undiluted combustion gases required modification of the dioxin sampler due to the extreme heat output during the laboratory burns. Exhaust gas temperature in the exhaust duct frequently exceed 200 to 300 ºC with high humidity. To allow for this, the dioxin sampler was modified by the addition of a 3 m long copper tube of 25 mm diameter and a side arm and gate valve to permit controlled dilution with ambient air. By adjusting the dilution ratio during sampling, it was possible to achieve concentrations of 1,000 to 8,000 ppm of CO_2 in the sample gas while limiting the dioxin sample trap temperature to less than 45 ºC. A CO_2 analyser (Model 6251, Licor, Lincoln, Nebraska, USA) was connected in series to the GasCard. The Licor signal voltage, and cell temperature, and the dioxin trap temperature were logged (Datataker, Model 800, Data Electronics, Melbourne, Victoria). Figure 2.18 shows the sampler installed at the test corridor facility at CSIRO Manufacturing and Infrastructure, Highett. The field sampler was located beside the test corridor with the inlet directly under the dilution hood. A flexible stainless steel tube extended the inlet tube on the sampler to the inlet port on the dilution hood.

Figure 2.18. Dioxin sampling system at the fires testing facility.

2.2.3 Protocols and experimental design

The conducted laboratory tests are shown in Table 2.2, comprising one ambient air blank and19 test burns in which the variables were fuel-type (four fuels plus a blank), fuel load (2 or 3 kg m^{-2}) and ventilation (natural or assisted).

Straw was sourced form a local produce supplier in Braeside, Victoria. Sugar cane was sourced from produce suppliers in Queensland where green cane trash is baled for use as mulch in horticulture. Native sorghum hay was sourced from a grower in Darwin, Northern Territory who supplies the Darwin market. The forest litter was collected in Messmate/Stringbark forest near Dayleford, Victoria.

The first set of tests followed the standard operational protocols for the test facility. Fibro sheeting screwed to the floor of the corridor was inspected and if brittle or cracked, the floor was replaced. This was required on average every second test. However, for the last six tests (samples 15 to 20), a 1 mm-thick mild steel plate was screwed on top of the fibro sheet, substantially increasing the life of the flooring.

Fuel was preconditioned at 22 ºC and 50% RH in a conditioning room for several days before the test. Because of the large quantities of fuel required for these tests it was not possible to break and spread the bales for rapid uniform conditioning. However, several days conditioning tended to bring the material to uniform air-dryness. A weighed mass of fuel, typically 35 or 56 kg, was then laid on the floor of the corridor to a depth of approximately 100 mm. Thermocouples were suspended in the centre of the corridor at 1 m-intervals along its length and inserted into the top of the fuel layer.

Prior to ignition, the exhaust fan was started, the afterburner ignited, and the logging commenced for all instruments to establish ambient baseline conditions. The fuel was then ignited in the anteroom with a propane torch, and once the fire was established the access door and observation port were closed. The dioxin sampler pumps were started at ignition time. Sampling ceased when most of the fuel was consumed and heat output was less than 50 kW. The unburned residue and ash was then dragged from the corridor into a steel tray located under the exhaust hood, allowed to cool and weighed to determine the burning efficiency.

Samples of fuel and ash were retained for dioxin analysis.

For the first series of tests, ventilation of the fire was maintained by convection generated by the combustion, with air draw along the floor of the corridor by the convection cell. This creates, in effect, a backing burn where unburned fuel is reheated solely by radiation. However, in the last seven tests (samples 14 to 20) ventilation was assisted by a high-capacity air-blower fitted to the observation port of the antechamber. This increased the preheating of unburned fuel at the flame front and dramatically increased the rate of spread. A typical straw burn with natural ventilation progressed at approximately 1 m min^{-1}, reaching the end of the corridor in 12 to 15 minutes. With forced ventilation, the rate of spread increased by a factor of four.

Figures 2.19 to 2.21 show the test corridor before and during test.

Table 2.2. Laboratory test schedule.

Test	Date	Sample	Fuel	Source	Fuel load (kg m^{-2})
1	22-May-03	L-straw-1	Straw	Producer in Braeside, Vic	1.93
2	23-May-03	L-straw-2			2.00
3	28-May-03	L-straw-3			1.85
4	29-May-03	L-litter-Vic1-1	Leaf litter	Wombat State Forest, Vic	1.98
5	13-Jun-03	L-litter-Vic1-2			2.03
6	16-Jun-03	L-litter-Vic1-3			1.97
7	17-Jun-03	L-cane-1	Sugar cane	Produce supplier, Qld	2.08
8	19-Jun-03	L-cane-2			1.95
9	25-Jun-03	L-cane-3			2.05
10	26-Jun-03	L-sorghum-1	Sorghum	Grower in Darwin, NT	2.00
11	27-Jun-03	L-sorghum-2			2.00
12	30-Jun-03	L-sorghum-3			1.99
13	30-Jun-03	L-straw-4	Straw	Producer in Braeside, Vic	1.96
14	3-Jul-03	L-blank	Blank	N/A	N/A
15	6-Oct-03	L-straw-5*	Straw	Producer in Braeside, Vic	2.81
16	7-Oct-03	L-cane-4*	Sugar cane	Produce supplier, Qld	1.39
17	8-Oct-03	L-litter-Vic2*	Leaf litter	Upper Loddon State Forest	3.03
18	9-Oct-03	L-straw-6*	Straw	Produce supplier, Qld	2.72
19	9-Oct-03	L-straw-7*	Straw	Producer in Braeside, Vic	2.93
20	10-Oct-03	L-litter-Qld	Leaf litter	Stanthorpe	2.24

* fan – a high-capacity air-blower fitted to observation port of the antechamber was used.

Figure 2.19. Laboratory burn L-litter-Vic1-1 prior to ignition.

Figure 2.20. Laboratory burn L-litter-Vic1-1, leaf litter from Wombat State Forest.

Figure 2.21. Laboratory burn L-straw-3, straw, unassisted ventilation.

The time-series of combustion for three contrasting tests is shown below. Test 3 was a straw burn with natural ventilation. Ignition was 3 minutes after commencement of the test. Combustion rapidly increased reaching a maximum 7 minutes (indicated by a line in Figure 2.22) after commencement when the fire front emerged from the ante-room into the corridor. At this point CO_2 concentration and oxygen draw down measured in the exhaust dust were approximately 29,000 ppm, smoke temperature was 180 ºC and CO concentration was 680 ppm (Fig.2.22). Once in the corridor, the fire front progressed at stable pace, CO_2 concentration and oxygen draw down stabilized at approximately 9,000 ppm and smoke temperature cooled to 100 ºC. Carbon monoxide concentration lagged behind CO_2 emission as smouldering continued in partly burned fuel behind the fire front. The fire-front reached the end of the corridor at 18 minutes following which CO_2 emission declined and CO emission increased as burned fuel continued to smoulder, and the combustion- driven convection declined.

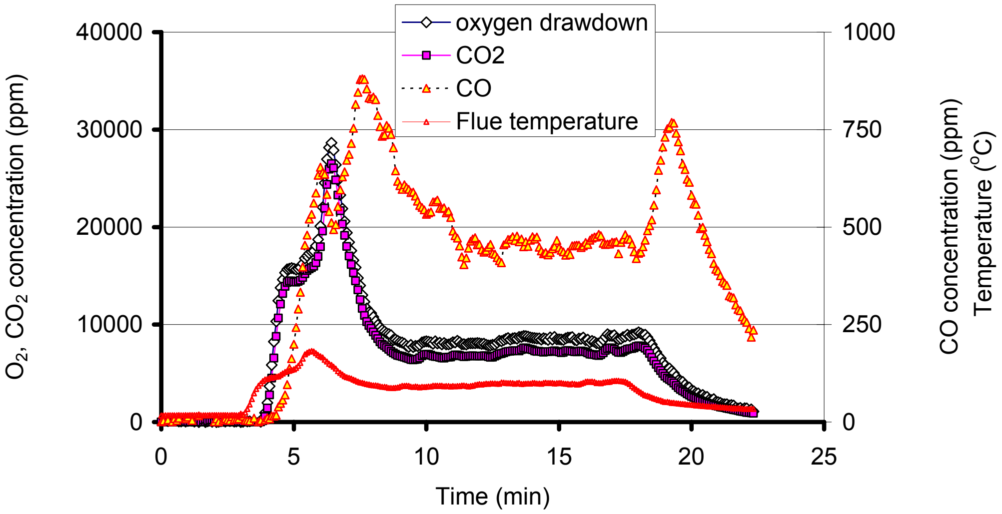


Figure 2.22. Time-series of O_2 consumption, CO_2 & CO emission from laboratory test L-straw-3.

The progression of the fire front is clearly illustrated by the time-series of the temperature readings (Figure 2.23) with temperature rising rapidly from near ambient to 700 ºC as the front passes, and then slowly declining as the fuel smoulders and cools. The temperature traces in this figure indicate that some of the straw continued to burn or smoulder for an extended time.

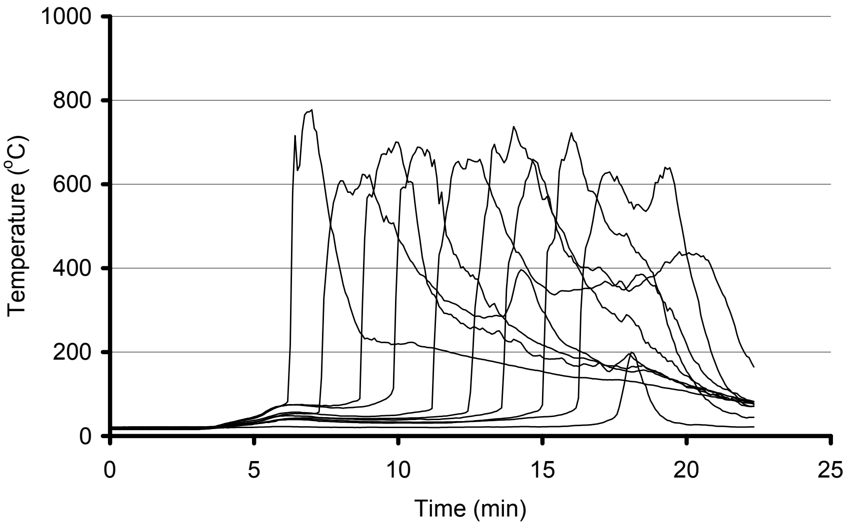


Figure 2.23. Time-series of combustion temp. within the fuel bed, laboratory test, L-straw-3.

Thermocouples were placed at 1 m intervals along the length of the tunnel at the top of the fuel bed.

Forest litter from Wombat State Forest packed more densely than straw, and consequently burned more slowly. Qualitatively, the time-series of emissions was very similar to the straw burn with peak emissions of CO_2 occurring as the fire emerged into the corridor, stabilising, and then increasing slightly in intensity as the front approached the end of the corridor and ventilation increased (Figure 2.24). This is also illustrated in the fuel combustion temperatures. The fire front progressed at approximately 0.2 m min^{-1}, and flame temperatures increased from 350 ºC at the entrance of the corridor to 600 ºC after 4 m (Figure 2.25). Smoke temperature was low, barely exceeding 60 ºC in the exhaust duct.

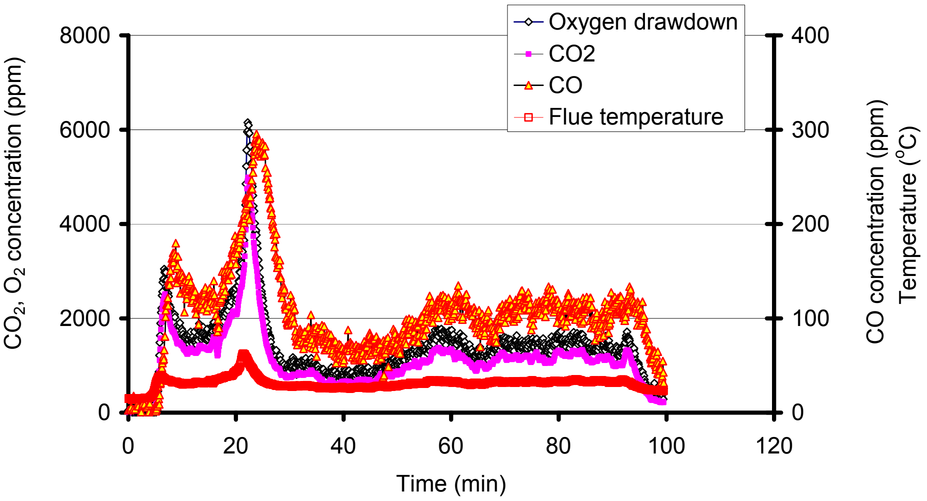


Figure 2.24. Time-series of O_2 consumption, CO_2 & CO emission from laboratory test L-litter-Vic1-1.

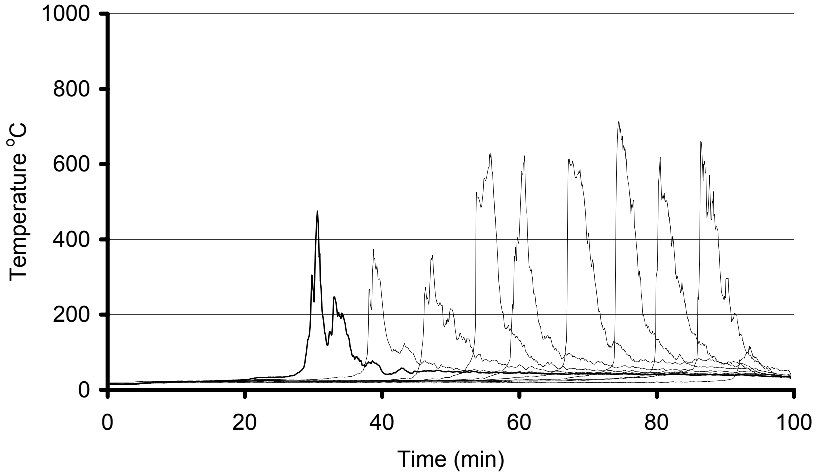


Figure 2.25. Time-course of combustion temp. within the fuel load for laboratory test L-litter-Vic1-1.

Thermocouples were placed at 1 m intervals along the length of the tunnel at the top of the fuel bed.

Forced ventilation produced a substantially different fire progression, as shown by the wheat straw burn (L-straw-5) in Figure 2.26. The fire flashed over as it emerged from the ante-room and raced down the corridor. The CO_2 concentration and O_2 draw down peaked at 72,000 ppm and the peak in CO emission at this point suggests combustion was O_2 limited. Temperature of smoke in the exhaust duct peaked at 350 ºC.

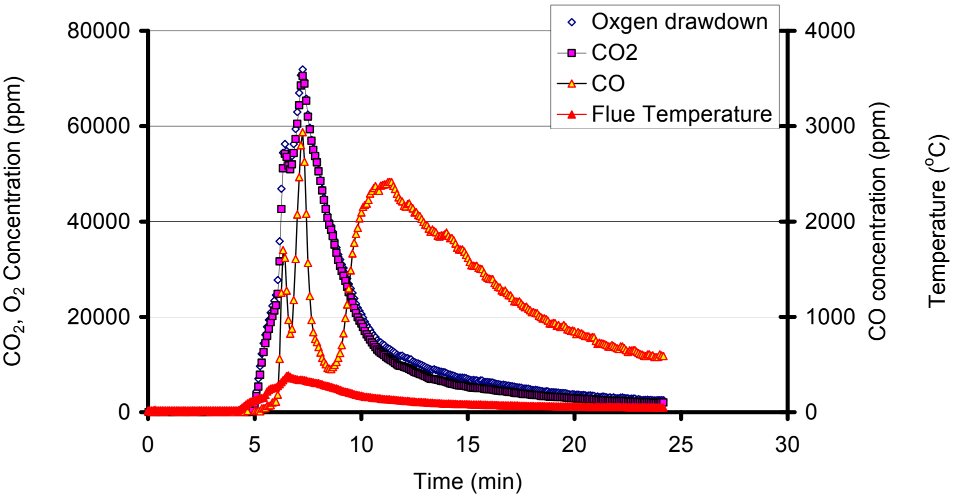


Figure 2.26. Time-series of O_2 consumption, CO_2 & CO emission from laboratory test L-straw-5.

Flaming combustion was completed within 5 to 6 minutes of ignition with the remaining fuel burning by smouldering combustion along the full length of the corridor. The intensity of this fire is clearly shown in the time-series of the thermocouple temperatures (Figure 2.27), which peaked at 700 to 800 ºC and remained above 400 ºC for most of the test.

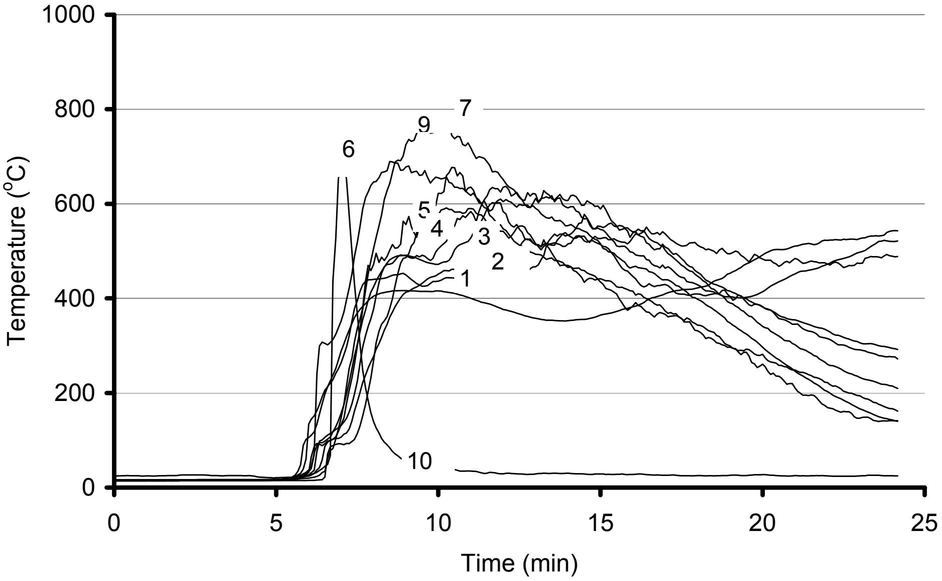


Figure 2.27. Laboratory Test L-straw-5, Wheat Straw, fan assisted.

Time-course of combustion temperature within the fuel bed. Thermocouples were placed at 1 m intervals along the length of the tunnel at the top of the fuel bed.

Tables 2.3 and 2.4 group the laboratory tests together in terms of the material being burned, and provide the physical and chemical properties of the tests. Key physical properties – the speed of the fire front, the maximum temperature, and the mean combustion temperature – are given in Table 2.3 whereas key chemical properties – the combustion efficiency, and the sensible heat release – are given in Table 2.4.

In summary, these 19 tests provided a wide range of fire intensities, rates of spread and combustion characteristics. There was little difference between the rates of propagation of the grass fuels (straw, sorghum, sugar cane) or of the duration of the tests with natural ventilation. In all cases the front propagated at approximately 1 m min^{-1}, the rate of spread of a very low intensity prescribed fire, and much more slowly than the grass fires in the field. Equally, there was little difference in mean maximum combustion temperature or average flame temperature, which averaged approximately 650 ºC. Smouldering combustion continued after passage of the flame front (Figure 2.23) resulting in the test corridor maintaining a significant temperature (200 to 300 ºC) along its length.

The forest litter fire tests propagated more slowly with a rate of spread of 15 cm min^{-1}, however, the mean combustion temperature of 520 ºC was only slightly lower than in the grasses (Figure 2.25 and Table 2.3). The slow rate of spread was sufficient to allow smouldering to cease behind the flame front resulting in significantly lower average temperatures in the corridor.

Forced ventilation and higher fuel loads increased the rate of spread in straw fires by an order of magnitude, but without significant increase in the mean combustion temperature. The corridor, however, remained hot during the remaining smouldering phase.

The proportion of the fuel combusted varied greatly between fuel types but seemed to be independent of combustion speed, with almost 28% of sugar cane fuel remaining as char and ash compared with 8% for wheat straw and 6% for sorghum. This was similar to the denser forest litter and may reflect the higher proportion of twigs and fibrous material in both cane trash and forest litter.

Table 2.3. Thermal properties of laboratory test burns.

Test Number	Sample ID	Material Burnt	Ventilation	Duration of burn (min)	Rate of spread (m.min^{-1})	Mean Max. Temp. (°C)	Mean temp. of burning fuel (°C)
1	L-straw_1	Straw	natural	22	0.83	588	312
2	L-straw_2	Straw	natural	22	1.06	708	337
3	L-straw_3	Straw	natural	22	0.79	661	271
13	L-straw_4	Straw	natural	29	0.85	630	236
15	L-straw_5	Straw	forced	24	10.3	671	381
18	L-straw_6	Straw	forced	27	8.8	645	334
19	L-straw_7	Straw	forced	25	7.1	671	289
7	L-cane_1	Sugar cane	natural	28	0.97	592	206
8	L-cane_2	Sugar cane	natural	29	0.80	601	237
9	L-cane_3	Sugar cane	natural	30	1.04	604	204
16	L-cane_4	Sugar cane	forced	20	1.13	620	271
10	L-sorghum_1	Sorghum	natural	25	1.27	661	234
11[*]	L-sorghum_2	Sorghum	natural	30	1.22	625	171
12	L-sorghum_3	Sorghum	natural	30	1.11	635	199
4	L-litter_Vic1_1	Leaf litter	natural	99	0.14	540	102
5	L-litter_Vic1_2	Leaf litter	natural	106	0.12	510	92
6	L-litter_Vic1_3	Leaf litter	natural	106	0.10	436	81
17	L-litter_Vic2	Leaf litter	forced	102	0.15	610	182
20[#]	L-litter_Qld	Leaf litter	forced	97	0.10	116	86
Straw mean (1 standard deviation)			natural	23.6 (3)	0.88 (0.12)	646 (51)	289 (45)
Straw mean (1 standard deviation)			forced	25.5 (1)	8.7 (1.6)	662 (15)	334 (46)
Sugar can mean (1 standard deviation)			natural	26.5 (4)	1.0 (0.14)	604 (12)	229 (32)
Sorghum mean (1 standard deviation)			natural	28.4 (3)	1.2 (0.08)	640 (19)	201 (32)
Leaf litter mean (1 standard deviation)			natural	103.7 (4)	0.13 (0.02)	523 (72)	114 (46)

[*] Sample lost during dioxin analysis,

[#] Burn failed to propagate and test was terminated prematurely

Combustion efficiency, i.e. the fraction of carbon in the smoke plume, which is fully oxidised ($[CO_2]/\sum[C]$), was calculated for the three main stages of combustion in the laboratory tests. These were the combustion in the anteroom until flashover (anteroom), the phase of steady progress down the corridor, and the smouldering stage following the extinction of the fire front on reaching the end of the corridor (post burn). In all cases the first two stages showed high combustion efficiencies above 0.9, and in many case above 0.95. The forest litter burned with the lowest average efficiency reflecting the large contribution of the smouldering combustion phase due to the slow rate of propagation of these fires.

Power output (or fire-line intensity), while substantial at up to 2 MW m^{-1} in the sorghum and forced straw burns, was mostly characteristic of low intensity prescribed fires, which are typically 1,000 kW m^{-1} fire-line intensity. The forest fuel tests were the lowest of the four fuel classes at 300 kW m^{-1} peak, which is about average for low-intensity prescribed burns (McArthur 1962).

Table 2.4. Combustion properties of laboratory test burns.

Sample	Venti-lation	% fuel burned	Combustion efficiency $[CO_2]/([CO]+[CO_2])$%			Max. sensible heat output	Average power (kW)	Total sensible heat release
			anteroom	corridor	post-burn	(MW)		(GJ)
L-straw_1	natural	93.7	92.3	91.2	84.5	1.1	338	0.441
L-straw_2	natural	94.3	95.6	95.8	83.3	0.9	378	0.476
L-straw_3	natural	90.9	97.6	93.5	83.3	1.1	326	0.427
L-straw_4	natural	87.5	97.7	95.5	83.2	1.0	274	0.460
L-straw_5	forced	92.1	99.4	97.5	81.5	1.9	420	0.595
L-straw_6	forced	93.2	96.2	98.2	82.4	2.0	387	0.613
L-straw_7	forced	93.4	99.6	98.1	78.0	1.7	428	0.636
L-cane_1	natural	84.0	96.5	92.2	74.8	1.0	231	0.387
L-cane_2	natural	84.3	96.9	92.5	75.2	0.7	223	0.377
L-cane_3	natural	83.3	98.0	93.0	75.8	0.8	223	0.382
L-cane_4	forced	82.6	96.3	93.1	77.4	0.4	177	0.207
L-sorghum_1	natural	93.0	100.2	97.7	83.0	1.6	337	0.491
L-sorghum_2	natural	94.0	86.7	97.4	82.3	1.6	276	0.490
L-sorghum_3	natural	95.1	93.9	98.1	83.0	1.5	277	0.493
L-litter_Vic1_1	natural	79.6	91.8	91.2	85.9	0.3	71	0.419
L-litter_Vic1_2	natural	77.0	91.9	90.5	87.2	0.3	71	0.453
L-litter_Vic1_3	natural	76.2	92.2	92.0	90.9	0.2	45	0.284
L-litter_Vic2	forced	86.7	93.1	91.6	84.0	0.2	112	0.684
L-litter_Qld	forced	NA	87.2	88.9	NA	0.3	29	0.171
Mean (1 Standard Deviation)								
Straw	natural	92.2 (3.1)	95.8 (2.5)	94.0 (2.1)	83.5 (0.6)	1.0 (0.1)	329 (43)	0.45 (0.02)
Straw	forced	92.9 (0.7)	98.4 (1.9)	98.0 (0.4)	80.7 (2.3)	1.9 (0.2)	412 (22)	0.61 (0.02)
Sugar cane	natural	83.5 (0.7)	96.9 (0.7)	92.7 (0.4)	75.8 (1.1)	0.7 (0.3)	213 (25)	0.34 (0.09)
Sorghum*	natural	94.0 (1.0)	93.6 (6.8)	97.8 (0.4)	82.8 (0.4)	1.5 (0.1)	297 (35)	0.49 (0.00)
Leaf litter#	natural	79.9 (4.8)	92.3 (0.6)	92.3 (0.6)	88.0 (2.9)	0.3 (0.1)	62 (15)	0.40 (0.09)

[*] L-sorghum_2 was lost during dioxin analysis.

[#] L-litter_Qld burn failed to propagate and test was terminated prematurely.

Total sensible heat production reflected the calorific value of the fuels and the fuel loads showing only minor differences between fuel classes.

The salient features of these tests, therefore, are:

- All tests burned at temperatures of 600 to 700 ºC, which while high is well short of the 800 to 1,000 ºC known to occur in wildfires and in high temperature biomass combustion in efficient furnaces.
- The test corridor remained sufficiently hot for the duration of the tests (20 minutes) to support active combustion chemistry – a condition atypical of open fires where atmospheric cooling occurs.
- The fire properties were broadly consistent with low intensity field fires.

2.3 Sample analysis

Analytical protocols and details are given in the project implementation plan (Appendix 1). They are presented here in summary to document minor variations from the project implementation plan.

2.3.1 Dioxins analysis

At AGAL Sydney, the concentrations of the 29 toxic dioxin and dioxin-like species were determined by analysis, at the ultra-trace level, in combined aerosol and gas phase samples. The dioxin, furan and PCB congeners analysed are listed in Table 2.5, together with their toxicity, as measured by the toxic equivalent factor (TEF) as determined by the World Health Organization (WHO). The TEF is explained in the glossary on page vii of this report. On return of the samples to AGAL, the sampling components were spiked with ^{13}C-labelled internal standards (filters, PUFs and XAD-2 resin) and extracted together using a hot soxhlet extraction in toluene. Clean-up involved partitioning with sulphuric acid then distilled water, followed by column chromatography on acid- and base-modified silica gels, neutral alumina and carbon dispersed on celite.

Analysis for dioxins, and dioxin-like compounds, was performed using a high resolution Gas Chromatograph – high resolution Mass Spectrometer HRGC-HRMS (ThermoQuest Finnigan MAT95XL) that has sensitivity for 2,3,7,8-TCDD of better than 10 fg with a signal to noise ratio of 10:1.

Individual congeners were identified using the GC retention time and ion abundance ratios, with reference to internal standards. Quantitative analysis was performed using selected ion current profiles following a variety of methodologies that are congener specific and requiring calibration as described, for example, in USEPA Methods 1613, TO-9A and 1668.

The reference laboratory used for analysing the duplicate quality control samples was the Ministry of the Environment, Laboratory Services Branch, Ontario, Canada.

The following objectives were adopted for the analysis and reporting of all samples and establishing limit of detection (LOD):

- retention time of the analyte within 1 second of the retention time of the corresponding ^{13}C surrogate standard
- ion ratio obtained for the analyte within ±10% (±20% for PCBs) of the theoretical ion ratio

- signal-to-noise ratio greater than 3:1
- levels of PCDD/PCDF and ‘dioxin-like’ PCB congeners in a sample greater than 5 times any level found in the corresponding laboratory blank analysed (3 times the level in the blank for OCDD)
- surrogate standard recoveries in the range of 10 to 120%.

Table 2.5. Dioxin, furan and PCB congeners to be analysed in the study.

Dioxins	**IUPAC No.**	**WHO-TEF**
2,3,7,8-TetraCDD		1
1,2,3,7,8-PentaCDD		1
1,2,3,4,7,8-HexaCDD		0.1
1,2,3,6,7,8-HexaCDD		0.1
1,2,3,7,8,9-HexaCDD		0.1
1,2,3,4,6,7,8-HeptaCDD		0.01
OctaCDD		0.0001
Furans		
2,3,7,8-TetraCDF		0.1
1,2,3,7,8-PentaCDF		0.05
2,3,4,7,8-PentaCDF		0.5
1,2,3,4,7,8-HexaCDF		0.1
1,2,3,6,7,8-HexaCDF		0.1
1,2,3,7,8,9-HexaCDF		0.1
2,3,4,6,7,8-HexaCDF		0.1
1,2,3,4,6,7,8-HeptaCDF		0.01
1,2,3,4,7,8,9-HeptaCDF		0.01
OctaCDF		0.0001
CDD – chlorinated dibenzo-*p*-dioxin		
CDF – chlorinated dibenzofuran		
Congener	**IUPAC No.**	**WHO-TEF**
Non-ortho PCBs		
3,3',4,4'-tetrachlorobiphenyl	PCB#77	0.0001
3,4,4',5-tetrachlorobiphenyl	PCB#81	0.0001
3,3',4,4',5-pentachlorobiphenyl	PCB#126	0.1
3,3',4,4',5,5'-hexachlorobiphenyl	PCB#169	0.01
Mono-ortho PCBs		
2,3,3',4,4'-pentachlorobiphenyl	PCB#105	0.0001
2,3,4,4',5pentachlorobiphenyl	PCB#114	0.0005
2,3',4,4',5-pentachlorobiphenyl	PCB#118	0.0001
2',3,4,4',5-pentachlorobiphenyl	PCB#123	0.0001
2,3,3',4,4',5-hexachlorobiphenyl	PCB#156	0.0005
2,3,3',4,4',5'-hexachlorobiphenyl	PCB#157	0.0005
2,3',4,4',5,5'-hexachlorobiphenyl	PCB#167	0.00001
2,3,3',4,4',5,5'-heptachlorobiphenyl	PCB#189	0.0001

2.3.2 Particle mass

Total suspended particle (TSP) concentrations were measured on most of the smoke samples as described in the project implementation plan by sub-sampling from the main sample flow onto 47 mm-diameter stretched Teflon filter, at known flow.

2.3.3 Ambient air

Two samples of ambient air were also collected, one on completion of the first series of laboratory tests following L-straw_4, and one at Berrimah, Darwin following burn S-NT4. Several of the rural sites in the ambient study that was run as a parallel study (see http://www.deh.gov.au/industry/chemicals/dioxins/updates.html) also provided a valuable and accurate guide to ambient PCDD/PCDF concentrations. The sites at Boroolite (Vic), Berrimah (NT), Mutdapilly (Qld) and Duncraig (WA), sampled air masses similar to the forest sites. Ambient concentrations in NSW may be found in Department of Environment and Conservation (2003).