

## Field and laboratory based emission factors for PCDD/PCDF/PCB from sugarcane fires

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### Introduction

Combustion processes such as waste incinerators or certain industrial processes are widely considered the primary source for the formation and release of dioxin-like chemicals into the atmosphere in industrialised countries. Results obtained over the last decade however identified elevated levels of dioxin-like chemicals, particularly higher chlorinated polychlorinated dibenzo-*p*-dioxins (PCDDs) along the Queensland coastline<sup>1,2</sup>. The concentrations of OCDD for example are consistently greater than 1000 pg g<sup>-1</sup> dm and the distribution is widespread along much of the coastline including aquatic sediments. Sugarcane cultivation is a key agricultural commodity of the region and traditionally sugarcane harvesting included the combustion of the cane prior to the harvesting. Notably in the last two decades the use of canefires as a management tool has been reduced substantially and now burning the cane before harvest is rather an exception than the norm in most regions of Queensland. In the light of elevated levels of PCDDs in soils used for sugar cultivation suggestions have been made that the burning of cane may contribute or even be associated with the unexpected high levels of PCDDs in Queensland coastal soils<sup>3</sup>.

The formation of chemicals during combustion processes can be evaluated either in field experiments or during laboratory burns. Measuring emission of trace pollutants such as polychlorinated dibenzo-*p*-dioxins and furans (PCDD/PCDFs) in field samples is difficult since fires are often short, difficult to access, the smoke escapes usually upwards due to convection and frequently local turbulence carries the smoke away from the sampling equipment. Hence to our knowledge, with the exception of the study by Prange et al.<sup>4</sup> no field data are available on the levels of dioxin-like chemicals in smoke from forest fires and to date no study has measured directly emissions of dioxin-like chemicals from a sugar cane fire under field conditions.

As a result of the difficulties associated with high volume field sampling of emissions of trace pollutants from `outdoor` fires most combustion experiments of trace semivolatiles have been carried out in laboratory experiments where a given amount of biomass was burned under controlled conditions. For dioxin-like chemicals the emission factors that are usually applied for biomass combustion have been derived in such studies, and the few published emission factors for dioxin-like chemicals from agricultural fires are all based on laboratory combustion experiments.

This study was part of Australia's National Dioxin Program's Bushfire Study. In this paper we report results of field and laboratory experiments on the emissions of dioxin-like chemicals from sugar cane fires with the aim to:

- determine emission factors for dioxin-like chemicals from cane fires;
- evaluate whether cane fires are an important source for dioxin-like chemicals; and to
- assess whether laboratory combustion chambers and field experiments provide similar emission factors and dioxin emission profiles (i.e. whether laboratory experiments can provide good data to evaluate the emission of dioxin-like chemicals in real field fires).

## Methods and Materials

### Field sampling

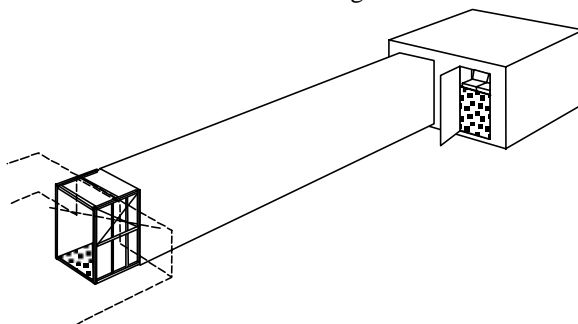
For the field measurements we sampled smoke from cane crops burned in normal agricultural practice near Moolooloba, about 100 km north of Brisbane. Canefires are rapid fires and are particularly hard to sample due to their short duration. Most of the smoke collected originated from the initial period where, for the protection of other fields, the down-wind side of fields were ignited resulting in a comparatively slow moving fires. When subsequently the upwind side were set alight the fire progressed rapidly and sampling duration was short. The dioxin-like chemicals were sampled in a mobile sampling system, specifically designed for high volume field sampling of smoke by CSIRO Atmospheric Research (AR). The sampler inlet consisted of a 4 m snorkel, through which air was drawn at a flow rate of 0.5 to 1.5 m<sup>3</sup> min<sup>-1</sup> through a 10" x 8" quartz filter and XAD-2 resin /PUF suitable for trapping PCDD/PCDFs and dioxin-like PCBs. In order to determine the efficiency of the smoke collection and to evaluate carbon based emission factors, air collected through the inlet was continuously monitored for CO<sub>2</sub> concentration and all data (both field and laboratory based data) are expressed as pg/g fuel carbon. (Note that on average one gram dry weight of fuel vegetations contains about 50 % carbon with > 90 % being emitted as CO<sub>2</sub>. Hence the fuel based emission factor can be assumed as 0.5 \* carbon based emission factor). Preliminary calculations suggest that an air sample consisting of an air volume containing > 5 g of carbon above ambient concentration would contain sufficient material for accurate PCDD/PCDF analysis. Because the CO<sub>2</sub> concentration was measured on-line it was possible to continue sampling through a single trap until the required amount of smoke carbon had been trapped. Hence samples consisted of multiple fires collected on a given evening and/or even when necessary over several days to achieve enough sample material. For the field sampling system was mounted onto a 4WD utility and powered from a 3.5kVA generator and thus the sampling unit was sufficiently mobile to follow the fire front. In total two field samples were collected.

### Laboratory sampling

Laboratory combustion experiments were carried out at the CSIRO firetesting facility (CSIRO Manufacturing and Infrastructure Technology). The combustion chamber consists of a corridor framed with galvanised steel and lined with ceramic fibre board, (10 m long, 2.1 m high and 1 m wide) connected to an adjacent burn room (3.6 m x 2.4 m x 2.4 m) (Fig. 1). 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 1: Schematic diagram of the laboratory fire-test room.

Burn room is to the right, smoke collection facility is to the left.



Sugar cane fuel was sourced from produce suppliers in Queensland where green cane trash is baled for use as mulch in horticulture. Fuel was preconditioned at 22°C 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 kg 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. Tests were carried out with and without assisted ventilation which affected the spread of the fire (i.e. with forced ventilation, the rate of spread increased by a factor of four).

Table 1 Combustion properties of laboratory test burns.

Sample ID	Ventilation	Duration of burn (min)	Rate of spread (m.min <sup>-1</sup> )	Max.Temp. av. 12 pts (°C)	Mean temp.of burning fuel (°C)
L-cane_1	natural	28	0.97	592	205.6
L-cane_2	natural	29	0.80	601	236.7
L-cane_3	natural	30	1.04	604	203.6
L-cane_4	forced	20	1.13	620	271.0

Analysis of the dioxin-like chemicals collected on the filter and adsorbent (combined) and in the sugar cane straw and ash was carried out at AGAL Laboratories (the only NATA accredited laboratory in Australia to carry out the analysis) using isotope dilution technique and HR-MS detection based on US-EPA methods.

### Results and Discussion

Dioxin-like chemicals were detectable in both the field measurements and the laboratory experiments where sugar cane straw was combusted. Emission factors expressed as TEQ combining PCDD/PCDF and PCB ranged from about 1 pg TEQ g<sup>-1</sup> carbon to about 20 pg TEQ g<sup>-1</sup> carbon. The emission factors observed in the field burns were the lowest of all the samples with 1.2 and 2.9 pg TEQ g<sup>-1</sup> carbon whereas the emission factors in the laboratory samples ranged from 3.7 to 20 pg TEQ g<sup>-1</sup> carbon and were on average about a factor of 3 higher than those observed in the field burns (Figure 2). The key difference between the emission factors obtained in the field burns and the laboratory burns is related mainly to the contribution of PCDF to the TEQ. In the laboratory burns on average the PCDF contributed about 52 % to the TEQ whereas in the field burns they contributed only about 8 % to the overall TEQ (Figure 2 inset).

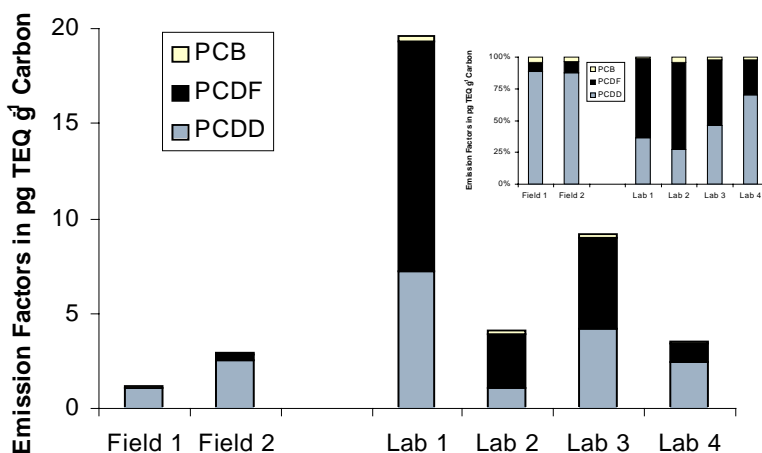


Figure 2 Emission factors of dioxin-like chemicals expressed as TEQ in field burns and laboratory burns. Inset shows the contribution of PCDD, PCDF and PCB to the total TEQ. (Inset shows the percentage contribution of PCDD, PCDF and PCB to the TEQ)

The difference between laboratory and field burns is also apparent in the congener and homologue profiles. PCDFs dominate both the congener and the homologue profiles in the laboratory burns whereas their contribution is very low in the field results. While the congener profiles observed in the laboratory tests are consistent with profiles observed in emissions from wood combustion in domestic heaters and small industrial furnaces, the field measurements<sup>5</sup>, particularly from SE Queensland, are consistent with published field measurements from prescribed fires. The field measurements are also similar to soil congener and homologue profiles.

The key difference between field and lab burns relates to 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 the cane straw. There are thought to be two pathways by which dioxins are synthesized during combustion; gas phase reactions occurring in a temperature window of 500-700°C and heterogeneous reactions, which occur on particle surfaces in thermal window between 200 and 400°C<sup>6</sup>. In field fires, while the flame temperature are typically 600 to 1000°C (Gould, Cheney and McCaw, pers. comm.) the smoke plume rapidly entrains surrounding air and cools, so that the residence time for gas or particles in either window is very short, probably of the order of a few seconds. In the laboratory burns the flame temperatures are 600-700°C, however, the smoke is retained in the combustion room and, therefore, the residence time for particles in the 200-400°C window is considerable. In the current study the combustion chamber remained within the 200-400°C thermal window for the full duration of the test and probably of the order of a minute rather than seconds. Therefore, it is likely that the high PCDD/PCDF emission rates are the result of heterogeneous chemistry within the combustion chamber and that these processes occur to a much lesser extent in the field. Laboratory tests of open burns, in which the smoke plume entrains ambient air and is immediately cooled, produce congener profiles with high PCDD to PCDF ratios similar to the field burns of our study<sup>4</sup>. Therefore, we should be cautious when using results from the laboratory tests of grass fuels combustion to estimate emissions in the field.

To date there are only few studies reporting emission factors for agricultural and field fires. Gullett and Touati<sup>7</sup> report emission factors for wheat and rice stubble combustion of 0.5 µg TEQ (t fuel)<sup>-1</sup> which is similar to our field measurements of cane fires (0.8 µg TEQ (t fuel)<sup>-1</sup>). However the congener patterns from their tests are distinctly different from our field measurements, which could indicate differences in combustion properties. One particularly interesting outcome is that the field burns had congener profiles dominated by OCDD. This feature has been reported previously by Prange et al.<sup>2</sup> in fire emission studies. The feature also appears in soils of the region<sup>4</sup> and has led to speculation that the presence of high concentration of OCDD in smoke might be due to revolatilisation from OCDD present in the fuel and soil.

Finally the comparison between laboratory and field data suggest that laboratory data obtained in closed system cannot be used to infer emissions from fires in the field. Presently however most emission factors used for estimation of national emission budgets are based on such laboratory data. Hence our study suggests that the role of fires may be overestimated due to artefacts related to the combustion chambers.

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# NONTHERMAL SOURCES AND SOURCE INVENTORIES

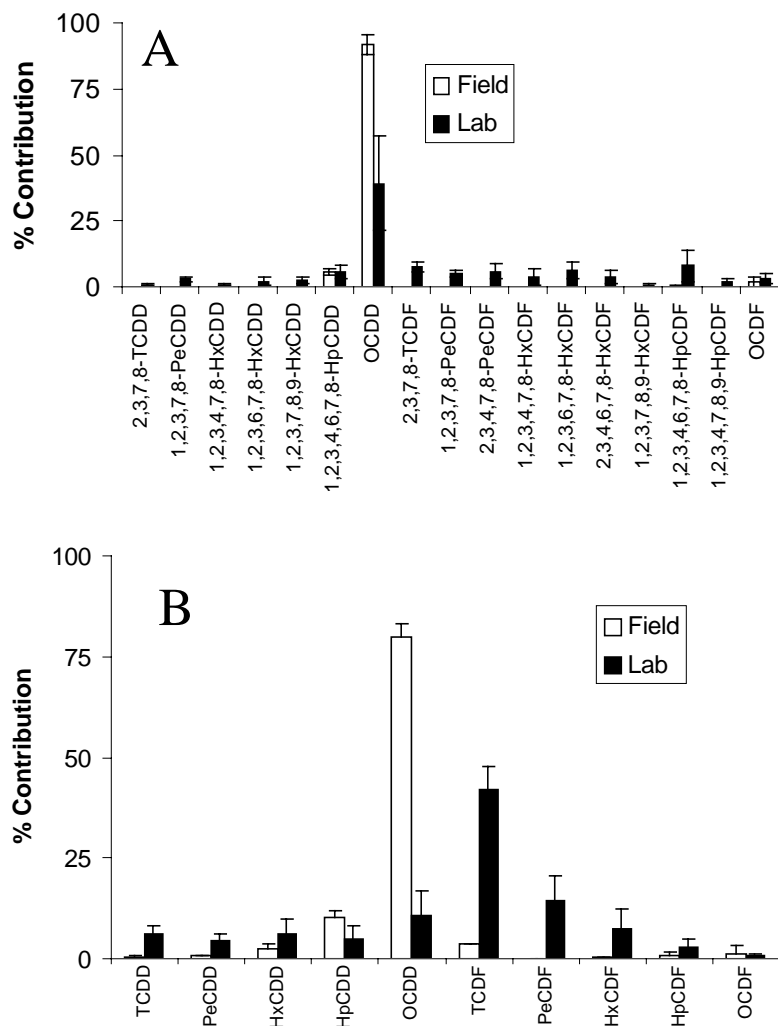


Figure 3 Congener (A) and homologue (B) profiles in the emission samples collected from the two field and 4 laboratory burns of sugar cane straw.

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