

# FORMATION AND SOURCES: FIELD CASES

## PCDD/Fs IN THE ATMOSPHERE AND COMBUSTED MATERIAL DURING A FOREST FIRE IN QUEENSLAND, AUSTRALIA

Joelle A. Prange,<sup>1,2</sup> Melinda Cook,<sup>1</sup> Olaf Pöpke,<sup>3</sup> Jochen F. Müller<sup>1</sup> and Roland Weber<sup>4</sup>.

<sup>1</sup>Nat. Res. Centre for Environ. Tox., 39 Kessels Road, Coopers Plains 4108, Qld, Australia.

<sup>2</sup>School of Public Health, Griffith University, Nathan 4111 Queensland, Australia.

<sup>3</sup>Ergo Forschungsgesellschaft mbH, Geierstrasse 1, 22305 Hamburg, Germany

<sup>4</sup>Universität Tübingen, Inst. for Org. Chem., Auf der Morgenstelle 18, 72076 Tübingen, Germany

### Introduction

Forest fires are suggested as a potential source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in Australia<sup>1</sup> and elsewhere (eg. <sup>2,3</sup>). Due to the erratic nature of fires, a limited number of studies have been able to measure the atmospheric PCDD/F concentrations during a forest fire<sup>4</sup>. As a consequence levels in soil and sediments pre and post fire have been used to assess forest fires as a source of PCDD/Fs. The results from some of these studies have concluded that in soils, there is an interim increase in some PCDD/Fs congeners, however over time soils return to their original PCDD/F concentration<sup>5,6</sup>. Recent investigations in Queensland, Australia have identified elevated concentrations of PCDDs (in particular OCDD) in soils from the coastal region<sup>7</sup>. The source of this contamination remains unknown, however natural formation processes or anthropogenic pre-cursor inputs have been suggested as a possible source of this contamination<sup>7,8</sup>. In Queensland, industrial activities are relatively low compared to other industrialised countries and the majority of the population and industry is concentrated in the south-eastern sector of the state. Forest fires on the other hand are a significant component in the Queensland environment due to the local land management practices and approximately 5000 km<sup>2</sup> are burnt on an annual basis. In a previous study, it was estimated that forest fires could potentially contribute between 70 – 90 % (on an I-TEQ basis) of the known PCDD/Fs emissions in Queensland<sup>9</sup>. However, these calculations were based on emission estimates from woodstove combustion studies (from overseas) and therefore may not provide an accurate emission estimate for fires in Queensland. The aim of this study was to investigate the PCDD/F concentration in the atmosphere during a prescribed burn in Queensland and to assess forest fires as a potential source of PCDD/Fs in the coastal region.

### Material and Method

#### *Sampling Site*

In August 2001 a 'prescribed burn' event in the central coastal region of Queensland, Australia was measured for the analysis of PCDD/Fs. The 'prescribed burn' encompassed an area of approx. 5000 hectares in the Doongul region of the Wongi State Forest, approx. 45 km inland from Maryborough, situated on the coast in central Queensland. The Wongi State Forest is subject to regular fires called 'prescribed burns'. The forest fire took place in Eucalypt sclerophyll forest and the fire consumed approximately 15-18 tonnes of biomass per hectare consisting primarily of ground litter.

#### *Atmospheric PCDD/Fs Sampling*

Sampling of atmospheric PCDD/Fs was performed in the Wongi State forest during a 'prescribed burn' (August 2001) and a 'control' sampling event (September 2001) after the cessation of the fire

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season. Sampling of atmospheric PCDD/Fs was performed using a high volume pump (collecting approx. 35 m<sup>3</sup>/hr) located at 1.5 m off the ground and trapping onto XAD 2/PUF traps and a filter (GFF, Schleicher and Schuell No. 9). The sampling device was located in a clear area in the center of the burned area, and was stationary during the sample collection period. The samples were collected over a 7 hour period (10am – 6pm) both for the ‘prescribed burn’ and ‘control’ sampling, resulting in the collection of 260 m<sup>3</sup>/sample.

### *Leaf litter*

Ground litter samples were collected at the atmospheric sampling site immediately before and after the area was burnt. The initial litter comprised of fallen and partially degraded eucalyptus leaf, while the sample collected after the area was burnt consisted of partially or completely combusted leaf (ash). Ground litter samples were collected using stainless steel sampling equipment and stored in the freezer prior to analysis.

### *Analysis*

Samples were analysed at ERGO Forschungsgesellschaft mbH, Hamburg, Germany, for the 2,3,7,8-substituted PCDD/Fs using a standardised method<sup>10</sup>. In brief, the atmospheric samples (XAD2/PUF and filter) were extracted for 20 hours in toluene, a blank (consisting of pre-cleaned XAD2/PUF and filter paper) was included for each of the sampling periods. The analytes were subject to a pre-treatment using H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> and SiO<sub>2</sub>, the filtrate was further subject to clean-up using acid-base, alumina (Alox B-super) columns in series followed by activated carbon. The ground litter samples were extracted for 10 hours with acetone/hexane (1:1) and 20 hours with toluene. Samples were subject to cleanup on activated carbon. Analysis of tetra- to octaCDD/Fs was performed on a GC (DB-5 fused silica column, 60 m, 0.25 mm i.d., 0.1 µm film thickness) interfaced to a VG Autospec mass spectrometer operating on a resolution of approximately 10 000. Identification of 2,3,7,8-substituted PCDD/Fs was performed using retention times of the <sup>13</sup>C-labelled standard and isotope ratios M<sup>+</sup> and M<sup>2+</sup>. Non-2,3,7,8 substituted PCDD/Fs were determined using the relative retention time of these compounds on a DB-5 column as provided by Rappe (unpublished data).

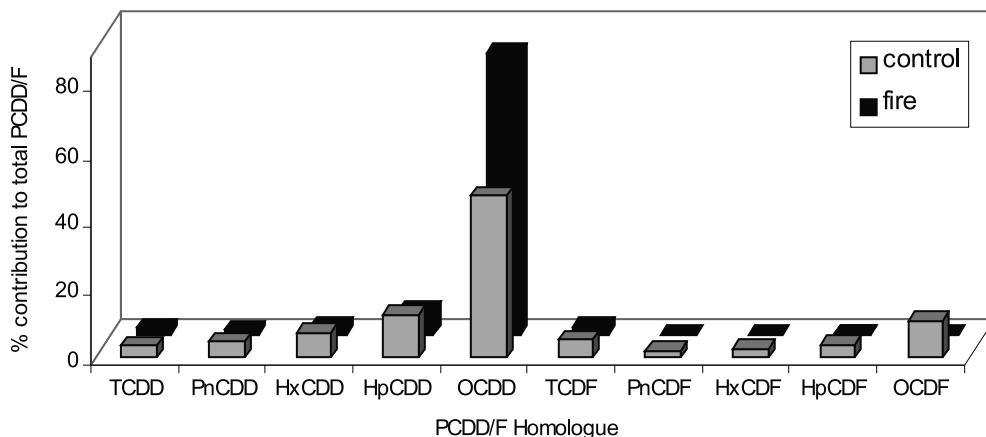
## Results and Discussion

PCDD/Fs were detected in the atmosphere during both the ‘control’ and the ‘prescribed burn’ in the Wongi State Forest (Figure 1). The ΣPCDD/Fs detected in the ambient atmosphere during the control period was 400 fg m<sup>-3</sup>, and the homologue profile was dominated by OCDD (47 % of ΣPCDD/Fs). The PCDD/F concentration and congener pattern is similar to typical atmospheric PCDD/Fs for a rural environment, with rural environments typically showing a higher contribution of OCDD<sup>11</sup>. In contrast the ΣPCDD/Fs that could be detected during the ‘prescribed burn’ was 21500 fg m<sup>-3</sup>, and the congener profile was again dominated by OCDD (87 %). Therefore, the ΣPCDD/Fs that may be attributed to the fire was 21 000 fg m<sup>-3</sup>. The results of the ΣPCDD/Fs detected in the atmosphere during a forest fire in this study are similar to a study by Tashiro et al. 1990, who detected concentrations up to 17 600 fg m<sup>-3</sup> in atmosphere during a fire in Canada<sup>4</sup>.

The results from the atmospheric analysis of PCDD/Fs in the Queensland forest fire indicate that elevated PCDD/F concentrations could be detected in comparison to the control sampling. The presence of PCDD/Fs in the atmosphere may be attributed to a number of factors a) PCDD/Fs are formed during the forest fire combustion, potentially from dioxin pre-cursors present in the environment or 2) PCDD/Fs are re-distributed from the combustion of PCDD/Fs present in the material combusted. The analysis of combusted material may elucidate this fact.

PCDD/Fs were detected in the ground litter samples collected both before and after burning.

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**Figure 1.** PCDD/F atmospheric homologue profile in the 'control' and 'prescribed burn' in the Wongi State forest.

Concentrations of  $\Sigma$ PCDD/Fs in unburnt ground litter was 45  $\mu\text{g g}^{-1}$  dw and 145  $\mu\text{g g}^{-1}$  dw in the burnt litter. Similar PCDD/F homologue and congener profiles were detected in the burnt and unburnt ground litter material, with a dominance of OCDD (81 % and 82 % unburnt and burnt litter, respectively). However, changes in isomer profiles were evident when comparing the 'control' and 'prescribed burn' atmosphere and the unburnt and burnt ground litter samples. Specifically changes included an increase in the 1234/1269/1236/1237/1238 TCDD, 1469/1678/1234/2368 TCDF, and 12346 PnCDD isomers (Figure 2). Typically, in combustion processes with a chlorine and inorganic carbon source isomer patterns result in an even distribution within the homologue group<sup>12</sup>. In this study, specific isomers were elevated suggesting that the formation of PCDD/Fs from pre-cursors may be occurring in the forest fire.

At this stage the specific process causing these isomers changes is unknown, however the results from this study suggest that there is an increase in the PCDD/F concentration in the atmosphere during a 'prescribed burn'. Although it is yet to be determined if the forest fires produce PCDD/Fs or the results are due to a re-distribution of PCDD/Fs already present in the environment. Further investigations are underway in Queensland to identify the formation process resulting in the changed isomers observed in this study and to assess the contribution of forest fires to the environment PCDD/F burden.

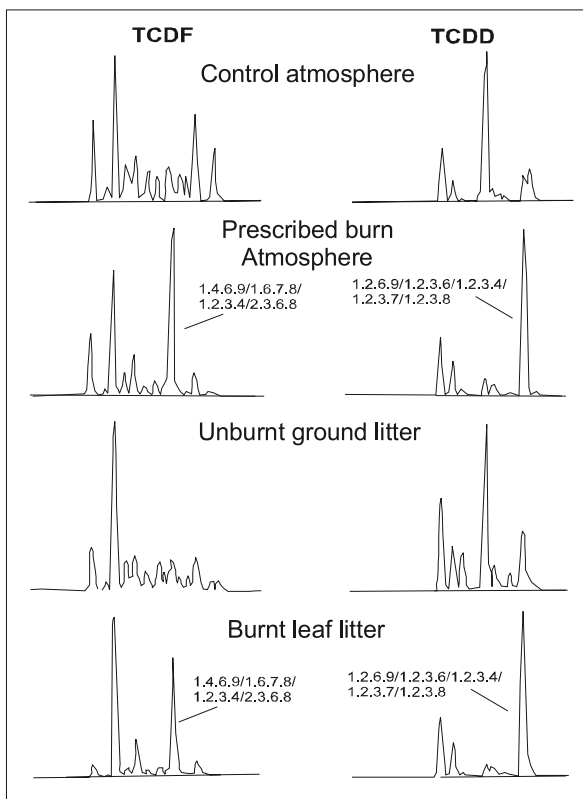
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**Figure 2.** TCDF and TCDD isomer profiles in the atmosphere during the control and prescribed burn sampling and in the unburnt and burnt ground leaf litter.

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