ARE FOREST FIRES A SOURCE OF PCDD/Fs IN QUEENSLAND, AUSTRALIA?

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Introduction

Forest fires have received considerable attention in recent years as a potential source of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs)[1-3]. Despite a lack of evidence from real forest fires, many source inventories now include forest fire emissions as a significant contributor to the environmental PCDD/F contamination[e.g.3, 4].

In Queensland, Australia elevated concentrations of PCDD/Fs have been identified in topsoils and sediments extending along more than 3000 km in the coastal area. The contamination shows a similar PCDD/F congener profile in most samples, dominated by PCDDs, with OCDD contributing 90 - 99% ∑PCDD/Fs. To date, the contamination could not be associated with known PCDD/F industrial or other anthropogenic activities and the source of PCDDs remains unidentified.

Previous investigations in Queensland identified elevated PCDD/Fs in the atmosphere during a ‘prescribed burn’ (an induced forest fire, used as a management tool, to reduce biomass) in comparison to sampling during a period of non-burning[7]. The PCDD/F profiles detected in the smoke were unlike typical combustion profiles, with a high D:F ratio and the elevation of specific non-2,3,7,8-substituted lower chlorinated PCDD/F isomers. Atmospheric measurements however, did not provide sufficient information to determine the source of PCDD/Fs in the fire.

Therefore, the present study was carried out to determine whether forest fires are a source of PCDD/Fs in the Queensland coastal environment. This study was conducted using a combustion chamber to simulate the conditions of a typical Queensland forest fire. The distributions of PCDD/Fs in the pre- and post-combustion components were quantified to assess the role of the fires in the PCDD/F contamination in Queensland.

Materials and Methods

Leaf litter was combusted on a bed of soil in a combustion chamber specifically designed for this study. The forest soil and litter were collected from a location distant to known anthropogenic dioxin sources, but subject to a regular fire regime. For this experiment 25kg of ambient soil was collected within an area unburnt for 9 years. The soil was homogenized using stainless steel sampling equipment and placed into a stainless steel tray (80cm × 80cm) at a depth of 10cm. The fuel consisted of leaf litter, (comprised of fallen and partially degraded eucalyptus leaf, twigs and bark) collected from the forest floor of the Wongi State forest.

A total of 3 kg of the leaf litter was combusted in the chamber on top of the soil. The bulk of leaf ash was collected from the surface of the soil after the combustion of each 1kg avoiding the collection of the surface soil. Following the combustion of the 3kg, the soil was differentiated into soil-ash (the top 5mm soil and remaining ash), burnt soil (top 2cm of soil distinguished by a darkened color due to the burning process), and the underlying soil (remaining soil fraction in the tray). All fractions (leaf litter, leaf ash, and soils) were weighed, homogenized and sub-sampled for PCDD/F analysis. The smoke was collected on the filter/condenser/XAD traps and subsequently analyzed for PCDD/Fs.

Samples were analyzed for all 2,3,7,8-substituted PCDD/Fs and ∑tetra-hepta homologues at ERGO Forschungsgesellschaft mbH, in Hamburg Germany, using a certified method[8]. Non 2,3,7,8-substituted PCDD/F isomers were calculated using ratio of the signal height of the individual isomers to the ^{13}C labeled standards. Isomer verification was performed by analysis on DB5 and SP23-31 columns. Details of the analytical methods have been reported elsewhere [5].

Results and Discussion

The mass of dioxins in the entire system was quantified, before (leaf litter and soil) and after (leaf ash, burnt soil and smoke) combustion. The total mass of individual PCDD/F homologue groups was compared post- and pre-combustion to evaluate the effect of combustion process. For the ∑tetra-octa PCDD/Fs and $\sum TEQ_{WHO}$ basis the results suggest that no formation occurred during the combustion process (Table 1). On an individual homologue basis, the mass of OCDD did not increase post-combustion, therefore these results indicate that forest fires are not the source of the elevated OCDD detected in Queensland soils.

There was an increase, however of the ∑TCDD (2 fold), ∑PnCDD (1.6 fold) and ∑TCDF (1.4 fold) homologue groups, after the combustion process (Table 1), in particular in the burnt soil. Additionally, specific isomers, were elevated post-combustion (i.e. 1,2,3,4-TetraCDD and 1,2,3,4,6-PentaCDD, and 1,2,3,4-TCDF), particularly in the soil (Figure 1). Interestingly similar isomer distributions were detected in the atmosphere during a forest fire monitored in the same region in the previous year[7].

The homologue distribution in the smoke emission in this study was atypical for PCDD/F combustion patterns; they were however, similar to the unburnt leaf and soil PCDD/F homologue profiles and again, similar to the forest fire smoke emissions monitored the previous year. In combustion processes with a chlorine and inorganic carbon source, chlorine substituents are usually evenly distributed between the two aromatic rings and furans dominate the profile (i.e. D:F ratios are <1)[9]. The similarities to the unburnt leaf and soil profiles, the lack of furans and the distinguished isomer distributions in this study suggests that PCDD/F emissions from forest fires in Queensland are influenced by pre-existing PCDD/F concentrations PCDD/F precursors.

To evaluate the fate of PCDD/Fs after combustion, the emission to the smoke and leaf ash were calculated as ∑PCDD/F emitted/kg leaf litter combusted. The emission of ∑PCDD/Fs to the

TABLE 1: Total mass of PCDD/F homologues (ng) in each component, pre- and post-combustion

	Pre-combustion			Post-combustion					
	Unburnt Leaf	Unburnt soil	**Total**	Leaf Ash	Soil Ash	Burnt soil	Under soil	Smoke	**Total**
TCDD	4.3	59	**63**	0.34	14	61	52	4.5	**130**
PnCDD	2.9	30	**33**	0.14	5.2	20	25	2.1	**50**
HxCDD	7.7	130	**140**	0.14	6.4	30	86	6	**130**
HpCDD	8.3	560	**570**	0.77	11	75	350	10	**450**
OCDD	40	8600	**8645**	52	92	950	4870	70	**6040**
TCDF	4.9	19	**24**	0.2	2.5	5.3	22	3.1	**33**
PnCDF	2	4.4	**6.4**	0.04	0.46	1.0	1.0	0.51	**3**
HxCDF	2.8	18	**22**	0.040	0.7	< 2.5	16.0	0.38	**20**
HpCDF	2	< 7.4	**2**	< 0.03	0.34	0.67	1.8	0.50	**3.3**
OCDF	< 2	1.2	**1.2**	< 0.03	< 0.36	< 0.18	< 0.5	< 0.04	**0.77**
∑PCDD	62	9410	**9470**	54	130	1140	5390	94	**6800**
∑PCDF	12	50	**62**	0.31	4.0	11	40	4.5	**60**
∑PCDD/F	74	9460	**9535**	54	134	1150	5430	100	**6860**
TEQ_{WHO}	0.67	6.7	**7.4**	0.072	1.07	3.2	0.67	0.5	**5.5**

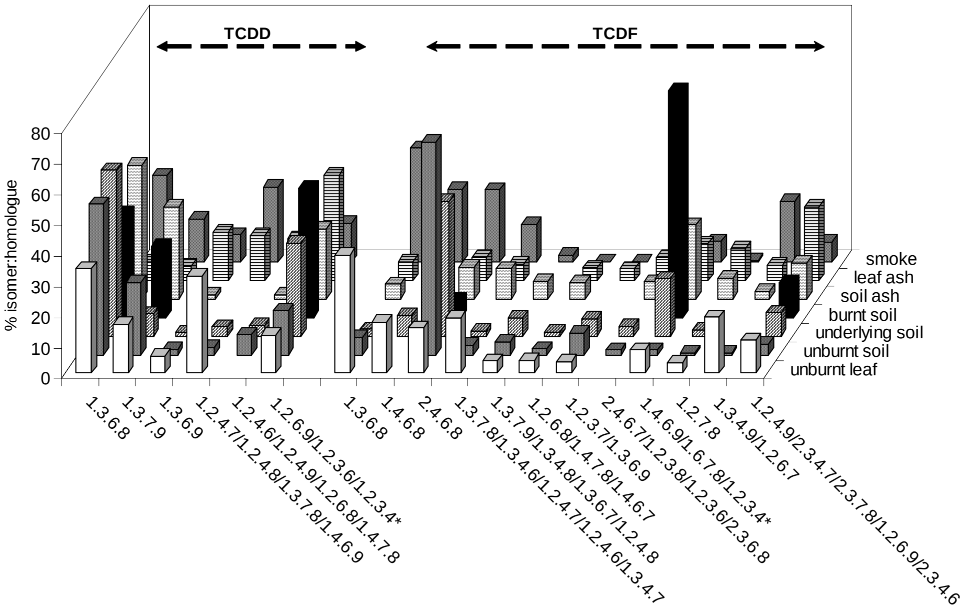

Figure 1: TCDD and TCDF isomers (% contribution to homologue group) in the unburnt and burnt components. *1.2.3.4 isomer was identified as the contributing isomer in these co-eluting isomers.

smoke was 32.6 ng kg^{-1} combusted (0.17 TEQ ng kg^{-1}). Combustion experiments conducted in the US, found an average emissions from biomass of 20 ng TEQ kg^{-1}, these authors identified a 20 times higher emission (on a TEQ basis) compared to the unburnt biomass, suggested to be due to a formation of PCDD/Fs during the combustion[2]. However the results from this study on a TEQ basis suggest an overall loss of PCDD/Fs, whereas on a concentration basis there was an increase of the lower chlorinated homologues. Therefore, TEQ based estimates may not be sufficient to evaluate PCDD/F formation during forest fires.

In comparison to the smoke emissions, in the present study the emission of ∑PCDD/Fs to the ash was lower (32.6 ng kg^{-1} combusted, compared to 17.9 ng kg^{-1} combusted), suggesting that the majority of PCDD/Fs emitted from forest fires enter the atmosphere. Therefore, although these results indicate that forest fires are not the source of OCDD in the coast of Queensland, they represent an important mechanism for the re-distribution of PCDD/Fs, which may have resulted in the widespread distribution of PCDDs identified in soils throughout the Queensland coastal region.

Forest fires have been suggested as a natural source of PCDD/Fs. However, forest ecosystems play a key role in sequestering atmospheric derived PCDD/Fs[10] as well as other compounds[11,12], which may act as PCDD/F precursors. In this study we show that in Queensland, forest fires are not a source, rather they are a process for the re-distribution of PCDD/Fs from existing sources and precursors. Therefore, a quantitative and qualitative evaluation of pre-existing dioxins and their precursors is imperative to assess local and global dioxin emissions from forest fires.

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