Biomass burning and Polychlorinated Dibenzo-p-Dioxins & Furans in Soil

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Introduction

Biomass burning is a known, highly dispersed source of polychlorinated dibenzo-p-dioxins & furans (PCDD/F) with up to 4% of the earth's land surface area being burnt annually and greater than 50% of the world's households using 1kg of fuelwood per person-day[5].
Straw combustion within the U.K., was until 1992, estimated to be 6-7 million tonnes a year. With an estimated 450g of TCDD emitted into the UK atmosphere every year from straw field burning alone[3]. Straw furnace emissions were found to be equivalent to those of municipal waste incinerators (1.7 ng/m^3 of TCDDs)[7]. Indicating a probable notable source of PCDD/Fs from biomass burning in rural areas. On-field prescribed burning of biomass undoubtedly effects PCDD/Fs within the soil surface layer. And as the bulk of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) in the UK environment are contained within the soil compartment and any transformation or destruction of PCDD/Fs within this medium will result in a change to the overall environmental mass balance of PCDD/Fs[3].
There have been several surveys in the UK assessing the concentrations of PCDD/F in soil. Source appointment and identification have been carried out using a variety of methods but no attempt has yet been made at investigating the sinks and transformations of PCDD/Fs in UK soils[2,4].

Soils were monitored before and after a straw field fire and the degree and nature of formation/destruction and transformation processes occurring during the biomass burning process were assessed.
Principle components analysis (PCA) is a statistical technique that enables the inherent degree of variability within a multivariate data-set to be quantified, reducing the large number of variables within a data-set to a single point per sample. Such statistical tools were used to examine PCDD/F isomer distributions and enabling us to determine the degree of intercorrelation between pre- and post-burn soil samples.

Experimental

Three straw field burning events were attended in Norfolk UK during August 1990 and August 1991 in 1990.

Soil from the field fires were sampled immediately before and after burning along with ash, after one and two years weathered soils were also collected from the post-burn fields. All samples were then analysed for polychlorinated dibenzo-p-dioxins & furans. Analysis for PCDDs and PCDFs was carried out using a Hewlett-Packard GC/MS (HP5890/ HP5970). The method of sample collection and analysis are detailed elsewhere [9].
Principle components analysis was used to examine the differences between PCDD and PCDF isomer arrays of the pre- and post-burn soils.

Results

PCDD/F concentrations of post- burn soils showed a slight relative reduction with respect to the corresponding pre-burn soils. The change in concentration is, in some cases, small compared to the precision of the analytical measurements at these concentrations.
The field burn ash also reflected the very low concentrations of PCDDs and PCDFs of the post-burn soils.
This reduction may be attributed to the high temperature achieved during the burn leading to vaporisation and destruction of PCDD/Fs in the surface layer of the soil. The overall PCDD/Fs TEQ was seen to decrease after the straw fire. This may be explained by the increasing concentration of OCDD and decrease in 2,3,7,8-TCDD compared with pre-burn soils. It is probable that thermal destruction and vaporisation occurs for 2,3,7,8-TCDD, with the simultaneous production of OCDD within the burn process.

Table 1 PCDD/F Toxic Equivalents Concentrations (TEQ) for the pre-, post-burn and straw ash samples.

PRE-BURN SOILS	POST-BURN SOILS	FIELD BURN ASH
TEQ /ng kg^{-1}	TEQ /ng kg^{-1}	TEQ /ng kg^{-1}
1.26	1.86	0.304
1.59	1.38	0.126
2.85	2.00	0.896
1.50	2.22	1.07
2.54	1.29	6.66
1.01	1.59	
Mean TEQ 1.61	1.72	1.81

The concentration of PCDD/Fs in pre- and post- burn soils when compared with background concentration of these compounds in rural and urban UK soils (Tables 2 and 3) indicate TEQ values at the low end of the range observed for uncultivated rural soils. The uncultivated soils samples were from a compacted surface soil core depth of 5cm, whereas the cultivated soils were a 5cm core depth of ploughed soil layer (ploughed to a depth of 25cm) giving a dilution effect of 5.
The lighter and more volatile 2,3,7,8-PCDD/F isomers decreased in the post-burn soils whereas the concentration of OCDD increased. Chlorination of the lower 2,3,7,8-isomers to OCDD does not fully explain the extent of this increase in OCDD. This is evident as the change in OCDD in the post-burn soils is in excess of the total concentration of all other 2,3,7,8-isomers present in the pre-burn soils.

Thus OCDD was produced through either chlorination of non-2,3,7,8 isomers or in-situ production of during the combustion process. The latter would invariably result in a soil surface layer of OCDD, of which, a large proportion would undergo rapid photolytic dechlorination to the lower congeners. These would then be susceptible to vaporisation and transport deeper into the soil.

Table 2 PCDD/F (TEQ) concentrations for the UK National Rural Soils Survey samples.[2]

Survey UK Rural Soils Total TEQ/ng kg^{-1}
5.64
10.46
14.89
8.54
2.81
6.30
15.84
21.83
5.11
4.79
3.02

Table 3 PCDD/F (TEQ) concentrations for the *UK National Urban Soils Survey samples.*

Survey UK Urban Soils Total TEQ/ng kg^{-1}
6.08
35.04
35.11
18.07
56.66

High temperatures of the straw burning induced initial evaporative losses with subsequent condensation of PCDD/Fs formed during biomass combustion. It is possible that a thermal destruction mechanism or vaporisation occurs for TCDD, accompanied by production of the OCDD within the burn process.
No significant difference was found between the TEQ of PCDD/Fs in pre- and post burn soil concentrations, as analysis of post- burn soils did suggest a slight reduction in the post-burn soils PCDD/F TEQ concentrations. Though this change in concentration was small with respect to the precision of the analytical measurements at the ppt detection range.

Principal Components

A significant difference between the pre-burn and post-burn soils was identified in the Principle Components of the pre-and post-burn soils.

Fig. 1 First Two Principal Components of PCDD's for Straw Burn Soils

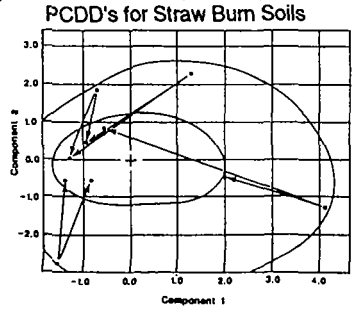
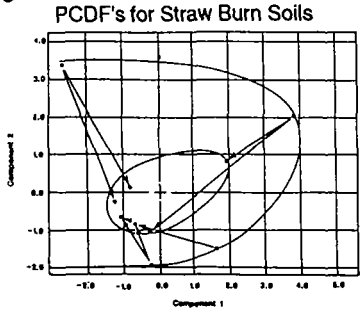
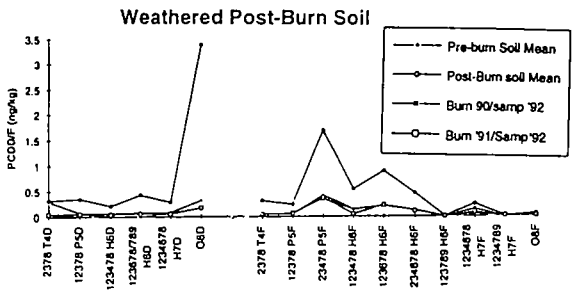


Fig. 2 First Two Principal Component of PCDF's for Straw Burn Soils



Both the dioxin and furan plots of Principle Components 1 and 2 of pre-and post-burn soils (Fig.'s 1 and 2) had a wider spread of values for pre-burn soils which enclosed within them a much narrower distribution of their associated post-burn soils.
The vectors in figures 1 and 2 associate the relationship between a individual sample soil before and after a burn has taken place from a particular field. Illustrating how the individual variance of the soil is reduced in the post-burn sample. This cluster of post-burn soil scores around zero is an indication of the relative decrease in the variability of these samples relative to their pre-burn soils.
With the pre-burn soils displaying a wide variation and bearing no relation to one another with the post-burn soils clustering around zero, displaying a marked decrease in their variability.

Fig. 3



Weathering of PCDD/Fs in Rural Soils

Soils collected one and two years after the field fires, weathered post-burn soils, (Fig. 3) showed a lost of OCDD and resembled an isomer distribution pattern and concentration of a pre-burn soil. With a tendancy towards a reduction in the concentrations of octa-dioxin, penta-furans and hexa-furans in comparison with the concentrations of these congeners immediately after the straw fire.

Conclusions

The data to date suggests that straw burning does not contribute to significantly to the PCDD/F burden in agricultural soils and may actually lead to a slightly reduced burden. This reduction may be attributed to the high temperature achieved during the burn leading to vaporisation and destruction of PCDD/Fs in the surface layer of the soil.
Thus the original estimation of PCDD/Fs generated from straw field fires were over estimated[3], as the straw furnace data[7], from which the initial measurements were taken, were not representative of the combustion conditions of a straw field fire[9].
Though the pre- and post-burn soils had similar TEQ concentrations their PC's showed characteristic differences. Transformation of all the PCDD/Fs in the post-burn soils occurred with the process of biomass burning giving them an interrelated PCDD/F isomer array. Thus the burning process appears to destroy the natural variability of the original PCDD/F signature in the pre-burn soils.
This is quite different from the strong change in the statistical character observed when there is a specific input from an external source[6], where single source related samples form a distinct cluster with respect to the main body of samples.

It would be expected that over time the post-burn soils would return to a greater degree of natural variation with an overall decrease in their tetra-chlorinated dibenzo-p-dioxin and an increase in their octa-chlorinated dibenzo-p-dioxin concentrations. This is to some extent confirmed by the results obtained from the analysis of one and two year weathered post- burn soils (Fig. 3) which when compared to their related pre- and post-burn soils can be seen to be regaining some of their pre-burn isomer array characteristics.

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