Are There Natural Dioxins? Evidence from deep soil samples

Nicholas JL Green[1], Ruth E Alcock[1], AE Johnston[2] and Kevin C Jones[1]

[1]Institute of Environmental and Natural Sciences, Lancaster University, LA1 4YQ. UK
[2]Institute of Arable Crop Research, Rothamsted Experimental Station, Harpenden, Hertfordshire AL5 2JQ. UK

INTRODUCTION

There have been an increasing number of observations which appear to indicate that dioxins may have been present in the environment for considerably longer than the onset of the chlorine industry (*eg* .1;2;3), and that they may – in fact – be formed through non-anthropogenic activities (4:5:6). In this paper we present new data which i) confirms the integrity of UK archived soils for observing historical environmental levels of PCDD/Fs, and ii) provides further evidence to support the hypothesis that PCDD/Fs have been produced naturally.

STUDIES ON THE INTEGRITY OF SAMPLES IN THE ROTHAMSTED ARCHIVE

Further to the investigation of Alcock *et al.* (2), we have looked again at ways in which soils in the Rothamsted archive could have become contaminated by PCDD/Fs of more recent origin. Details of these experiments are published elsewhere (7) and the results are summarised here.

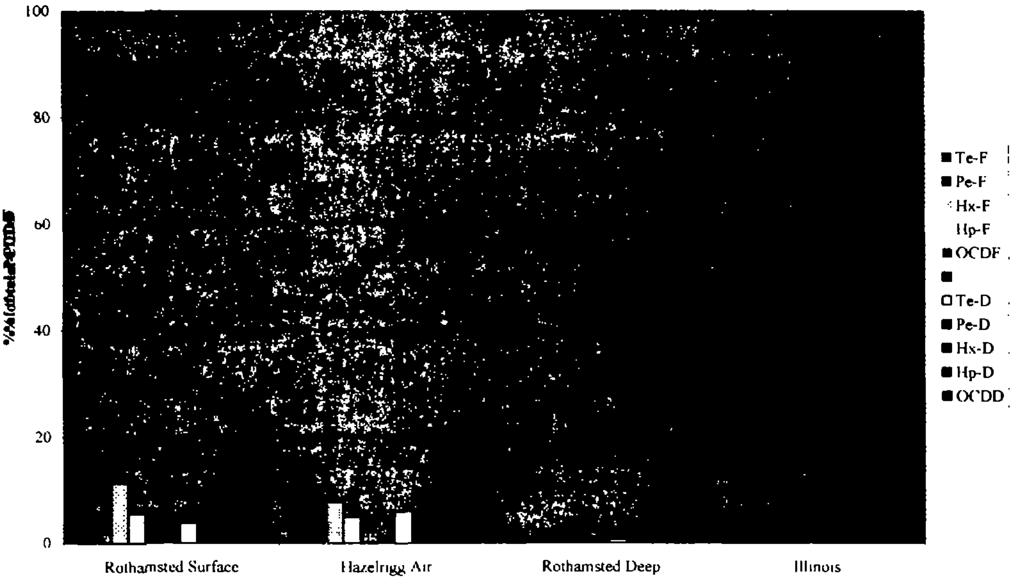
PCBs provide a useful gauge for assessing the contamination of stored samples on account of their intentional introduction, wide spread use, persistence and volatilities that are higher than PCDD/Fs. We analysed four soil samples from jars that had never been opened since their collection. These glass jars were tightly sealed with cork bungs which, in turn, were sealed with wax and covered with a similar lead seal to that employed by vintners. The lead seal still bore the stamp of its patent holders. The four soils were taken from sequential 23cm depths from an experimental, ploughed field in 1876. No PCB congeners were found in any of these four samples above the limits of quantitation, set at three times the amount in the blank.

The same result was obtained for another surface soil sample collected from a separate field three years later (1879). The soil contained $<0.0002\mu g/g\ \Sigma PCB$ and 0.11ng/g $\Sigma_{(4\text{-}8)}$PCDD/F (ratio <2). As no PCBs were found in the soil whereas PCDD/Fs were, diffusion does not appear to account for the soil results. Dust from the bottles was also analysed and found to contain $15\mu g/g\Sigma PCB$ and 110ng/g $\Sigma_{(4\text{-}8)}$PCDD/F. The PCB:PCDD/F ratio in the dust (>100) is very much higher than the maximum possible value for the soil (<2), so contamination by dust is not likely. This is confirmed by considerable differences in the PCDD/F homologue profile of the dust and soil. Collectively this evidence confirms that, in general, the soils from the Rothamsted archive have not been contaminated by dioxins of more recent origin.

INTERPRETATION OF PCDD/Fs IN SOILS FROM THE ROTHAMSTED ARCHIVE

This being so, we can attempt to interpret our observed data as being representative of the soils when they were collected. The first set of four soils described above were a depth series from surface to 23cm, 23 – 46cm, 46 – 69cm and 112 – 135cm at the Stackyard experimental site. The $\Sigma P_{(4\text{-}8)}$CDD/F concentrations decreased with depth from 43pg/g dry weight at the surface to 9pg/g dry weight in the deepest sample. The homologue pattern also changed with depth from a pattern resembling modern day rural air samples at the surface, to one that is dominated by OCDD at depth (Figure 1). For some of the homologues the congener patterns also changed with depth. For example, the HxCDD congener pattern in the surface soil resembles modern day air, whereas in the deepest soil the pattern resembles the 'ball clay pattern' published by Rappe *et al.* (8).

Figure 1: Homologue profiles for Surface soil (UK, 1893), UK rural air (1999), Deep soil (UK, 1893) and Surface soil (Illinois, 1882)



Another soil depth series collected in 1893 from Broadbalk, a different long-term field experiment and location from the first set, were also analysed for PCDD/Fs, though not for PCBs. In this series the same homologue pattern variation was observed with depth, as was the change in HxCDD congener pattern. However the $\Sigma P_{(4-8)}CDD/F$ concentrations increased from 43pg/g dw at the surface to 150pg/g dw in the deepest sample.

The PCDD/Fs found in the surface soils (1:2:7) are interesting observations but we do not interpret them as suggesting a natural source. By the late 1800s there was a considerable history of coal burning and metal smelting, among other industries, throughout the UK. It is likely that the PCDD/Fs in the surface soils are influenced by cumulative atmospheric deposition, derived from anthropogenic sources of this type that had been active up to that time.

The results for the deep soils are less straightforward to account for. Four possible explanations for the presence of PCDD/Fs at depth might be postulated: i) previous exposure to anthropogenic atmospheric PCDD/F inputs, ii) downward translocation of PCDD/Fs from the surface soils, iii) enzymatic formation from either natural or anthropogenic precursors *in situ*, or iv) they were already associated with the soil matter when the soils were formed. PCDD/Fs are considered to be highly recalcitrant in soils and are not likely to percolate from the surface to any significant extent. Possibly, PCDD/Fs might travel through the soil associated with very small particles, or with colloidal material, although this could only mobilise a minute fraction of the surface material. This does not fit with the observation that Hp/OCDD concentrations *increased* with depth at one of the sites. The samples were collected many years before the introduction of PCP, or similar compounds, that might percolate more easily through the soil before undergoing transformation to PCDD/F congeners at depth. If they have not been transported from the surface then we are at a loss to explain our findings in terms of anthropogenic sources. It is possible that these dioxins may be very old indeed, or that they have been formed by poorly understood processes in the sub-surface soil environment.

The Rothamsted archive also contained a few samples of surface soils that had been collected from various locations around the world in 1882. A sample from the then Belgian Congo and another from Illinois, USA contained relatively high PCDD/F concentrations, 1.3 and 0.4ng/g dw respectively. The homologue profiles of these samples were very similar to the deepest soils from the Stackyard and Broadbalk fields described above. In contrast, soil from Brandon, Manitoba contained 0.002ng/g dw $\Sigma P_{(4-8)}$CDD/F, as compared to a blank value equivalent to 0.0001ng/g, and showed no resemblance to other congener patterns in this study.

CONCLUSIONS

We have presented observations that might provide evidence for the existence of naturally produced PCDD/Fs. Our results are highly consistent with the reports of PCDD/Fs in Mississippi clay, German kaolinite and Australian sediments. Taken together, these studies provide a strong indication that PCDD/Fs are formed by natural processes. This could have considerable consequences for dioxin inventory estimates, dioxin abatement policy, and possibly for potential foodchain contamination along similar lines to the 'ball clay' incident. It would now be most timely and appropriate for a rigorous investigation to assess how widespread the phenomenon of natural dioxins might be, and to investigate the mechanism of formation that could account for these observations.

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