EVIDENCE FOR INCREASES IN THE ENVIRONMENTAL BURDEN OF POLYCHLORINATED DIBENZO-p-DIOXINS AND FURANS (PCDD/PCDFs) OVER THE LAST CENTURY

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ABSTRACT
    Archived soil samples collected from the same semi-rural plot in south east England between 1846 and the present have been analysed for tetra-octa PCDD/Fs. Atmospheric deposition is known to have been the only source of PCDD/F to the site. PCDD/Fs were present in all the samples, typically in the ng ΣPCDD/F per kg range. Concentrations have increased over the last century, by factors of between 2-10 depending on the congeners. Herbage samples from 1960-70 and the 1980s contained 62800 and 40500 pg ΣPCDD/F per kg, respectively, compared to 3700 pg ΣPCDD/F per kg in a sample from 1880-90. This represents a substantial increase in atmospherically-deposited compounds.

INTRODUCTION

    Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) are ubiquitous in the contemporary environment, albeit at very low concentrations. What is still unclear at present, however, is the relative importance of the various anthropogenic sources into the environment, and the possible contribution of natural inputs. This issue needs to be addressed, because it has important implications for the management and control of PCDD/F releases into the environment.

    PCDD/Fs are known to be generated during various chemical and industrial

manufacturing processes, and by a range of combustion activities. The latter are more important because atmospheric transport and deposition processes then result in their widespread dispersal through the environment (1). In an initial attempt at source apportionment in the UK the Department of the Environment estimated the relative contribution to total tetra-CDDs released into the atmosphere from various combustion sources (2). Based on very limited data, their report implicated municipal incinerators, various coal burning activities (domestic, power station and industrial plants), and vehicle exhausts as the major sources. However, this approach can be supplemented by examining evidence for temporal trends in the environmental burden of PCDD/Fs, and relating this to known sources of release. Some workers have undertaken retrospective analysis of archived samples (sewage sludges, human tissues etc. refs. 3-5) or dated sediment cores (6,7) to address this issue, but these data fail to adequately clarify the issue of natural versus anthropogenic sources.

In this paper we describe changes in the PCDD/F content of soils collected from the same experimental plot between the mid-1800s and the present. This approach has been used previously to examine the temporal trends of PAHs (8,9). All the samples originate from an experiment which has been under continuous arable cultivation since 1843 at the Rothamsted Experimental Station, a semi-rural location in SE England. One plot of this agricultural experiment (i.e. the 'control') has not received any additions of soil fertilisers or amendments. Therefore, by comparing the chemical composition of archived soils from this plot with that of recent samples the significance of atmopheric inputs can be determined. On a national or regional basis atmospheric deposition will be the most important source of PCDD/Fs to agroecosystems.

MATERIALS AND METHODS

Location and samples
The sample site and soils have been described in detail previously (8,9). Essentially all the samples have been taken from the cultivated plough layer (0-23 cm), then air-dried, ground and sieved through 2 mm. The samples were subsequently stored in glass jars with cork lids to the present day in a dark room at ambient temperatures. For this study samples from the years 1846, 1856, 1893, 1914, 1944, 1956, 1966, 1980 and 1986 were taken from the archive, transferred to acetone/hexane-rinsed glass jars sealed with similarly rinsed aluminium foil, and then ground in an agate tema mill to produce a fine powder.

Analytical methods
    The extraction, clean-up and analysis will be described in detail elsewhere (10). Briefly, 30-40 g samples were weighed into glassfibre thimbles, spiked with 2.5 ng of 5 13C labelled internal standards (2,3,7,8-TCDF; 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,4,7,8-HxCDF; and OCDF), and Soxhlet extracted with dichloromethane / acetone for 12 hr. The extracts were then reduced by rotary evaporation, and the concentrate passed through 3 column clean-up stages: I. silica/KOH silica; II. a double column with silica/sulphuric acid silica, connected to a basic alumina column; and, III. a Carbopac C column. Tetradecane was added at all the evaporation steps. Finally 2.5 ng of 1,2,3,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF was added to check recoveries, and the samples concentrated into 20 μL of tetradecane. Analyses were performed on a high resolution gas chromatograph with a 60 m Supelco SP2330 column, connected to a VG70-250S mass spectrometer operating on a resolution of 1 to 10000 Daltons. The mass spectrometer was optimised on 35 eV with perfluorocreosen. 3 μL of sample was injected which represented 5-6 g of soil. Recoveries of the 13-C labelled internal standards ranged between 50-150% for the tetra- and hexa- compounds, and between 22-50% for 13-C OCDD. The detection limit of the method is 10-30 pg/kg.

RESULTS AND DISCUSSION

    A full dataset will be presented elsewhere (11), with just the overall trends discussed here.

    Generally, the ΣPCDD/PCDF concentration increased through the twentieth century (Figure 1), with the total tetra- to octa-CDD/F concentration increasing from ca. 30 ng/kg in the 1850-90s to a concentration of ca. 90 ng/kg in the 1980s. This is generally typical of contemporary UK PCDD/F concentrations (2). The profile or mixture of compounds broadly mirrors that for atmospheric aerosols, and confirms that deposition is the source of PCDD/Fs at this site. PCDD/Fs are clearly present in the older samples. The source(s) of PCDD/Fs to the UK atmosphere at that time are unknown, but combustion of coal and coke started many centuries ago in the UK, and was probably an important contributor. Rather higher concentrations were detected in the earliest (1846) sample than for the late-1800s. The reason for this is unclear, but may reflect differences in land management at the site, or may be due to differences in sample collection or storage techniques used for this earliest sample. This sample has also given higher values for PAHs and macro-nutrients (8).

    The PCDD/F concentrations increase most during the twentieth century. This is probably due to increased production and use of chlorinated organic products combined with releases from various incineration and combustion activities such as the smelting of iron and heavy metals, and car exhaust emissions.

These broad trends in the soils are confirmed by further analyses of bulked herbage samples from the Rothamsted Experiments. Four samples were prepared, and the ΣPCDD/F determined as follows: 1880-90 - 3700 pg/kg; 1934-1944 - 5000 pg/kg; 1960-70 - 62800 pg/kg; 1979-88 - 40500 pg/kg. Plant uptake of PCDD/Fs from the soil is known to be very inefficient, and the burden is therefore thought to represent material deposited directly onto the foliage from the atmosphere. The herbage will provide a better indication of temporal trends because it has been harvested and stored annually.

Figure 1: Temporal trends in soil plough layer PCDD/F concentrations at Rothamsted, UK
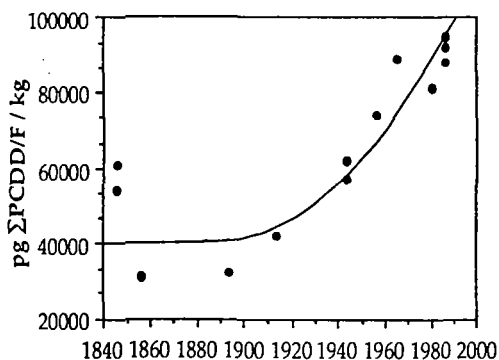
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