

## PCDDs AND PCDFs IN AMBIENT UK URBAN AIR

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### Introduction

PCDD/F air concentrations have been monitored at three major UK cities (London, Manchester and Cardiff) and a busy industrial town (Stevenage) from the beginning of 1991, as part of an ongoing project to provide the most comprehensive set of data for PAHs, PCBs and PCDD/Fs in UK ambient air. Before this monitoring programme started, virtually no air data was available for PCDD/Fs in this country.

This paper summarises the results obtained for PCDD/Fs to date, and comments on the temporal trends obtained during this period. The  $\Sigma$ 2,3,7,8-substituted compounds, non-targeted isomers and  $\Sigma$ TEQ values for the four sites are reported.

### Sampling and methodology

Sampling was carried out using Hi-volume air samplers. Each Hi-Vol was positioned in the city/town centre at roof top level. PCDD/Fs have been sampled on alternative weeks since the beginning of 1991, yielding 26 samples at each site through a year. The Hi-Vol pumps have been programmed to

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sample for 30 minutes in every hour, aspirating *ca.* 500 m<sup>3</sup> of air through the week.

Sample preparation and analysis involved chromatographic separation and solvent exchange on a Florisil™ column and analysis of the appropriate extract using techniques detailed in Clayton *et al.* (1992). High resolution mass spectrometry has been used to quantify the full range of 2,3,7,8-substituted PCDD/Fs.

## Results and discussion

### PCDD/F concentrations

The median and range values for the total 2,3,7,8-substituted PCDD/Fs in London, Manchester, Cardiff and Stevenage are summarised in Table 1. The Manchester and Cardiff samples contain additional information on non-targeted homologue groups (ie.  $\Sigma$ TCDD,  $\Sigma$ PCDD etc). Non-targeted isomers include both the 2,3,7,8- and non-2,3,7,8- components for each isomer group.

Concentrations reported for the 2,3,7,8-substituted PCDDs are mainly due to the hepta- and octa-CDD, the later congener accounting for over 76% of the total 2,3,7,8-substituted PCDDs. The tetra-, penta- and hexa-substituted congeners were generally below the detection limits.

Results generally suggest that all four sites have relatively equal amounts of the 2,3,7,8-substituted compounds. Comparison of the non-targeted isomers for Cardiff and Manchester, however, show that in general Manchester is perhaps the more contaminated of the 2 sites. The median 2,3,7,8-substituted  $\Sigma$ PCDD/F concentrations at each site are 3.1, 3.2, 2.7 and 2.1 pg/m<sup>3</sup> at Cardiff, Manchester, London and Stevenage respectively, if 'nd' values are taken as 'zero'. These values are very similar to those reported by Eitzer and Hites (1989) for two US urban areas (1.9 and 5.1 pg/m<sup>3</sup>), and by Broman *et al.* (1989) for Stockholm (1.4 pg/m<sup>3</sup>). König *et al.* (1993) detected average annual  $\Sigma$ PCDD/F concentrations in six German sites in the range 3.2 - 8.8 pg/m<sup>3</sup>, when taking concentrations below the detection limits (DL) as being equal to half the DL.

### PCDD/F $\Sigma$ TEQ values

The  $\Sigma$ TEQ values for the air samples are also summarised in Table 1. These

values, however should be interpreted with considerable caution, given that a very large number of non-detect values were reported for the tetra-, penta-, and hexa-CDDs. The median TEQ values for Cardiff and Manchester were essentially the same, *ca.* 0.1 pg  $\Sigma$ TEQ/m<sup>3</sup>, with the values for London and Stevenage computed as lower, 0.06 and 0.04 pg  $\Sigma$ TEQ/m<sup>3</sup> respectively, because of the differences in DLs. The furans make a greater contribution to the  $\Sigma$ TEQ than the dioxins, these accounting for an average of ~ 90% for Cardiff and Manchester, and 74% for London and Stevenage. The compounds that tend to contribute greatest towards the  $\Sigma$ TEQ concentration are the 2,3,7,8-TCDF and 1,2,3,4,7,8-, 1,2,3,6,7,8- and 2,3,4,6,7,8-HxCDFs. The annual average  $\Sigma$ TEQ values derived by König *et al.* (1993) for their German sites ranged between 0.05 - 0.15 pg/m<sup>3</sup>, again consistent with the data reported here.

## Seasonal trends in PCDD/Fs

Because of the high proportion of non-detects, the compounds which occurred most frequently, *ie.* 1,2,3,4,6,7,8-hepta-CDD and OCDD, have been used to illustrate the general trends. Figures 1a and 1b show the pattern distribution for London of these two congeners with time. This site shows higher concentrations of these two congeners in the winter months - when some weeks gave clear peaks above the general levels - and lower concentrations in the summer - when the frequency of non-detects increased. Generally the 'highs' and 'lows' coincide for the two compounds. Similar broad trends were also observed for the other three sites and when the data was expressed as  $\Sigma$ TEQ values.

## References

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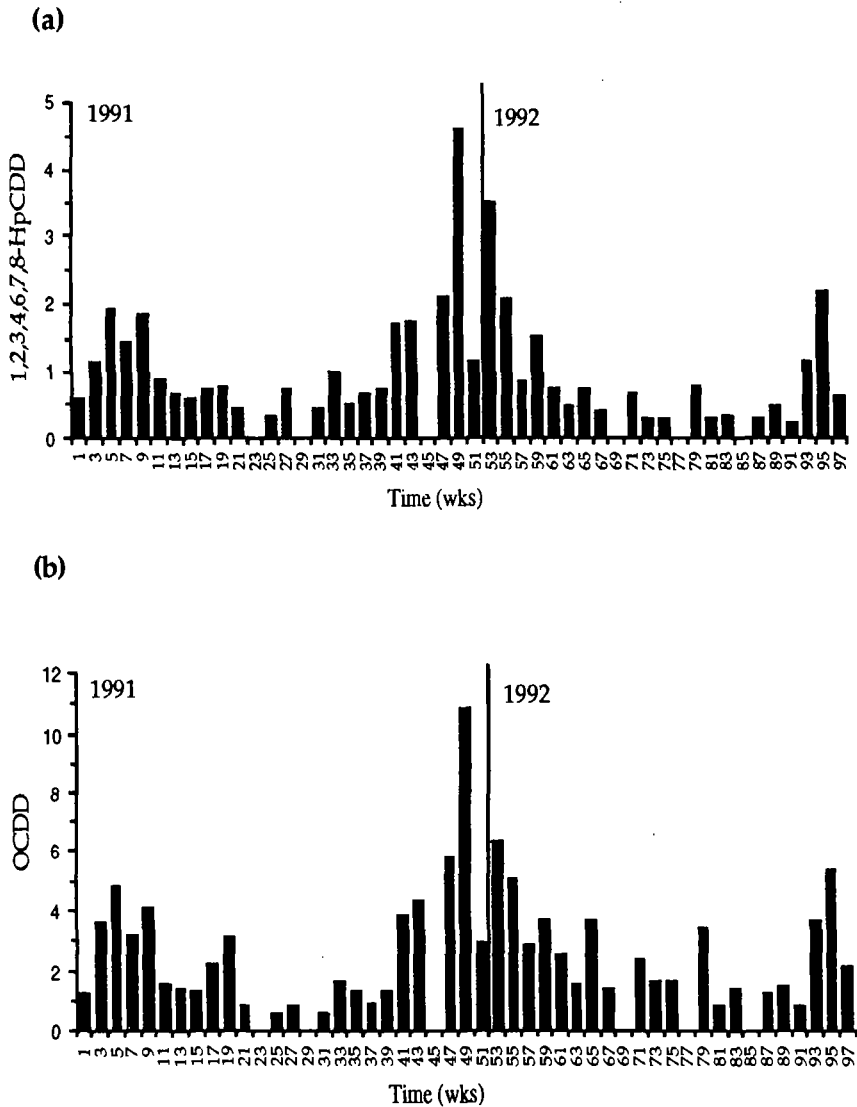
**Table 1: Median (and range) PCDD/Fs concentrations (pg m<sup>-3</sup>) and TEQ values (fg m<sup>-3</sup>) at 4 different UK sites.**

Compound	Cardiff	Manchester	London	Stevenage
Σ <sub>2,3,7,8</sub> -substituted dioxins	2.3 (nd-66)	2.1 (nd-46)	2.2 (nd-17)	1.7 (nd-9)
ΣT <sub>4</sub> CDD	0.2 (nd-2.2)	0.5 (nd-4.2)	na	na
ΣP <sub>5</sub> CDD	nd (nd-4.2)	0.5 (nd-6.0)	na	na
ΣH <sub>x</sub> CDD	0.3 (nd-2.7)	0.4 (nd-6.7)	na	na
ΣHpCDD	0.6 (nd-4.1)	1.1 (nd-17)	na	na
Σ <sub>2,3,7,8</sub> -substituted furans	0.78 (nd-11)	1.1 (nd-18)	0.48 (nd-7.1)	0.36 (nd-7.8)
ΣT <sub>4</sub> CDF	0.66 (nd-7.5)	1.97 (nd-14)	na	na
ΣP <sub>5</sub> CDF	0.4 (nd-5.2)	0.78 (nd-10)	na	na
ΣH <sub>x</sub> CDF	0.74 (nd-5.5)	1.45 (nd-11)	na	na
ΣHpCDF	0.39 (nd-3.1)	0.54 (nd-6.7)	na	na
ΣTEQ values	100 (nd-860)	102 (1.4-1813)	61 (nd-654)	39 (nd-800)

nd = not detected; na = data not analysed.

Median and ranges are based on samples collected and analysed for alternative weeks between January 1991 and September 1992 for Cardiff, January 1991 and April 1992 for Stevenage, January 1991 and November 1992 for London and March 1991 and September 1992 for Manchester.

Figure 1: 1,2,3,4,6,7,8-Hepta (a) and OCDD (b) in London air over time (pg/m<sup>3</sup>).



Week 1 = January 1991; Week 97 = October 1992.