Environmental Levels P14

Concentrations of PCDD/PCDFs in Soil Around a Point Source, 1992 - 1997

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Introduction

In 1991 elevated concentrations of PCDD/PCDFs were discovered in cows milk near to a point source of emission in Bolsover, Derbyshire, UK. The source, a waste chemicals incinerator used in the destruction of chlorinated phenolic wastes, ceased operation in November 1991¹.

As part of a larger project, soil samples have been taken from several locations within 2 km of the source since 1992. This paper comments on the congener profiles of the samples and reports the changes in concentration of PCDD/PCDFs between 1992 and 1997.

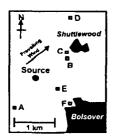


Figure 1. Plan of the sample area showing the location of the six soil samples (A - F) relative to the point source.

Experimental

The 1992 soil samples were taken by AEA Technology on behalf of Her Majesty's Inspectorate of Pollution from which sub-samples were donated in 1994 for this project. Repeat samples were taken from, as far as has been practicable, the exact locations in 1994, 1995, and 1997.

The samples comprised of 5 x 50 mm diameter cores extracted with a bulb planter - one from each corner and the centre of a square of 1m length sides. The cores were cut to 50 mm depth and air dried before sieving to < 2 mm and storage at -20 °C (the 1992 samples have been stored at this temperature only since 1994).

A plan of the sampling sites from which the soils were analysed and other key geographical features is shown at Figure I.

Analytical

Soil was extracted in soxhlet apparatus for 16 hours using toluene. The extract was cleaned using adsorption chromatographic techniques and thermally aided digestion using concentrated sulphuric acid. Quantification was performed by isotope dilution methods using high resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS). Samples were analysed on two capillary GC columns of different polarities (a 30m DB5 and 60m SP2331).

Results and Discussion

The concentration of PCDD/PCDFs for each homologue group is shown in Table I and of selected 2,3,7,8-congeners in Table II. There was no sample available from 1992 for site E.

The \sum PCDD/PCDFs compared to the typical UK mean concentration² of 433 ng/kg are elevated at all sites in both years, however only two sites (D and E) are significantly higher than the typical U.K. urban concentration ² (30 ng/kg) in terms of the I-TEQ value (see Figure II). All sites except site D have a similar and unusual congener profile compared to the typical U.K. soils characterised by the dominant TCDD, PeCDD, TCDF and PeCDF homologues compared to OCDD. At site D, however, although exhibiting high concentrations in terms of its I-TEQ value, the homologue profile was very different from the other sample sites (See Figure III).

| Sample/Year | A92 | B92 | C92 | D92 | F92 | A97 | B97 | C97 | D97 | E97 | F97 |
|---------------|-------|-------|-------|--------|-------|-------|-------|-------|-------|--------|-------|
| Di-dioxins | 28 | 33 | 51 | 29 | 25 | 22 | 32 | 35 | 22 | 209 | 26 |
| Tri-dioxins | 110 | 159 | 232 | 194 | 83 | 86 | 148 | 175 | 91 | 1,116 | 74 |
| Tetra-dioxins | 384 | 673 | 1,290 | 994 | 317 | 732 | 1,314 | 1,032 | 623 | 10,254 | 568 |
| Penta-dioxins | 255 | 624 | 676 | 748 | 204 | 228 | 628 | 626 | 328 | 5,254 | 293 |
| Hexa-dioxins | 83 | 106 | 114 | 638 | 54 | 91 | 131 | 142 | 247 | 828 | 65 |
| Hepta-dioxins | 63 | 54 | 80 | 1,176 | 34 | 61 | 66 | 144 | 1,174 | 133 | 56 |
| OCDD | 124 | 124 | 164 | 4,914 | 56 | 114 | 87 | 268 | 4,814 | 165 | 84 |
| Mono-furans | 24 | 82 | 112 | 42 | 65 | 7 | 32 | 1 | 2 | 81 | 15 |
| Di-furans | 144 | 199 | 267 | 139 | 157 | 112 | 182 | 173 | 82 | 616 | 155 |
| Tri-furans | 175 | 263 | 369 | 230 | 154 | 153 | 264 | 307 | 146 | 845 | 172 |
| Tetra-furans | 287 | 536 | 730 | 573 | 231 | 224 | 541 | 551 | 261 | 3,530 | 134 |
| Penta-furans | 66 | 174 | 145 | 167 | 55 | 66 | 196 | 152 | 91 | 471 | 76 |
| Hexa-furans | 43 | 89 | 68 | 499 | 32 | 44 | 104 | 74 | 198 | 170 | 45 |
| Hepta-furans | 39 | 61 | 39 | 1,122 | 21 | 33 | 68 | 55 | 467 | 82 | 23 |
| OCDF | 22 | 58 | 27 | 278 | 16 | 22 | 36 | 35 | 154 | 67 | 21 |
| ∑ PCDD/PCDF * | 1,848 | 3,237 | 4,366 | 11,743 | 1,505 | 1,996 | 3,830 | 3,771 | 8,700 | 23,822 | 1,806 |

 Table I
 Concentration of PCDD/PCDFs (ng/kg dry weight) in Bolsover soil samples 1992 and 1997

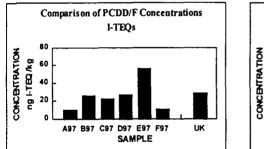
* Note The \sum PCDD/F concentration shown is $\sum C_1$ to C_8 CDD/CDF congeners

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| Sample/Year | A92 | B92 | C92 | D92 | F92 | A97 | B97 | C97 | D97 | E97 | F97 |
|-----------------|------|------|------|------|-----|-----|------|------|------|------|-----|
| 2.3.7.8-TCCD | 3.5 | 14.2 | 8.3 | 8.1 | 3.1 | 2.7 | 7.3 | 7.5 | 2.8 | 14.8 | 2.4 |
| 1,2,3,7,8-PeCDD | 2.9 | 5.2 | 4.2 | 7.2 | 2.6 | 2.9 | 6.1 | 5.1 | 3.2 | 19.4 | 3.7 |
| 2,3,7,8-TCDF | 5.4 | 12.5 | 10.6 | 5.1 | 4.8 | 5.5 | 15.9 | 11.3 | 4.8 | 16.5 | 7.2 |
| 1,2,3,7,8-PeCDF | 6 | 15.3 | 12.5 | 8.1 | 5.2 | 6.4 | 18.9 | 13.6 | 5.8 | 24.3 | 7.3 |
| 2,3,4,7,8-PeCDF | 4.3 | 11.8 | 8.7 | 5.9 | 3.7 | 4.8 | 14.4 | 9.4 | 4.2 | 9.9 | 5.3 |
| Total I-TEQ | 11.7 | 31.6 | 22 | 54.6 | 9.7 | 11 | 27.5 | 23.5 | 28.5 | 57.5 | 12 |

Table II Concentration (ng/kg dry weight) of selected congeners and total TEQ values in 1992 and 1997

This may have been due to a very local source, such as the location of a bonfire. The homologue profiles of soils from the other five sample locations have a good resemblance of those found on vegetation and in the air around the time the contamination was arising.



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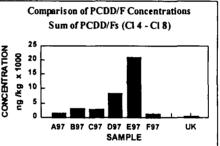
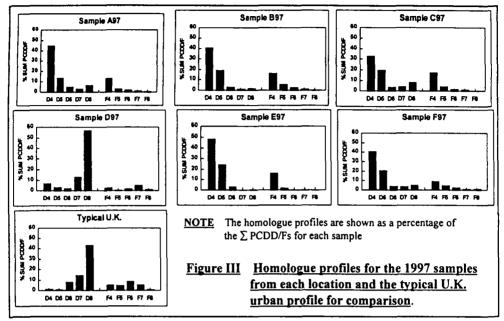


Figure II Comparison of PCDD/F concentrations for the 1997 samples compared with the typical U.K. urban concentration.

The concentrations found in the 1997 samples are generally unchanged at the four sites having the similar homologue profiles (A,B,C and F) from those measured in 1992. For the $\sum TCDD$ homologue, three of these four sites (A,B and D) showed an increase by almost a factor of two. This is consistent with the presence of a continuing diffuse source of $\sum TCDD$ in the area as suggested by Jones et al³ from air monitoring undertaken at several sites in the vicinity during 1993, although this is not found for other key homologue groups. At site D there is evidence of a reduction in concentration across all homologue groups and a fall in the $\sum PCDD/PCDFs$ by 25%. This site is the furthest from the source and exhibited an atypical homologue profile for the area.

The difference in the homologue profiles for samples from each of the locations for 1997 and that of the typical U.K. profile is illustrated in Figure III



Conclusions.

The soils analysed contained dioxins of a distinguishable and unusual homologue profile. One site exhibited elevated PCDD/Fs compared with typical UK urban concentrations in soil in 1992 but of a completely different profile to the other sites.

All sites showed elevated Σ PCDD/PCDF concentrations in both 1992 and 1997. The soil at two sites (D and E) was found to have elevated concentrations of approximately double the typical U.K. urban mean concentration, one of which was of a completely different profile to the other sites. The I-TEQ values are, with the exception of site E, in the typical range for the U.K.

Generally, there has been no change in the concentration of PCDD/Fs as homologues and individual congeners at the selected sites between 1992 and 1997, confirming the persistence of these compounds in soils.

Acknowledgements.

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References.

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- 2. Sandalls F.J, Berryman R.J, Bennett S.L, McCrorie S.K.C, Ambridge P.J. and Coleman P.J A Survey of Dioxins and Furans in Surface Soil in the Vicinity of the Coalite Works, Near Bolsover, Derbyshire. Published by The Environment Agency 1997
- 3. Jones K.C and Duarte-Davidson R. Environmental Monitoring of Dioxins and Furans in Air, Deposition and Herbage around the Coalite Works, Bolsover, Derbyshire. Published by The Environment Agency 1997