# SURVEY OF PCDD/F LEVELS IN UK SEWAGE SLUDGES

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## Introduction

From January 1999 the UK Water Industry ceased the sea dumping of sewage sludge, closing off one potential outlet. At the same time, increasing amounts of sludge are being generated due to improvements in sewage treatment standards in line with the 1991 EC Directive on urban wastewater treatment. Agricultural land is presently the main outlet for sludge in the UK and the amount of sludge applied to land is likely to increase(1). Trace amounts of PCDD/F are present in sludge (2-7) and there has been speculation about the possible transfer of PCDD/Fs into the human food chain via food crops or grazing livestock.
A survey was conducted to determine the concentrations, homologue profile and I-TEQs of several UK sludges and these are reported and briefly discussed here.

## Materials and Methods

Samples of digested sewage sludge were collected from fourteen wastewater treatment works in England during June, July and August 1998. The works were chosen to represent various catchment sizes and varying proportions of industrial effluent. Five litres of sludge were collected and centrifuged at 12000 rpm for 20 minutes and the supernatant liquid discarded. Approximately 5g samples of sludge were then mixed with 50g anhydrous sodium sulfate. The samples were spiked with 20 13C-labelled di- to octa-CDD/F congeners, then extracted with toluene for 16 hours and the extract subjected to a clean-up involving the following steps: Digestion with 3x50 ml concentrated sulphuric acid, followed by adsorption chromatography with a mixed column of acid treated, base treated and activated silica gel, gel permeation chromatography (S-X2 Biobeads) and reaction with activated copper turnings to remove elemental sulphur. Fractionation was carried out on basic alumina and the PCDD/F fraction subjected to additional carbon column clean-up. Samples were quantified by HRGC/HRMS (HP 6890/Micormass Autospec Ultima) using a HP5-ms capillary column for quantification of the homologue groups and the 2,3,7,8-substituted congeners were quantified on a SP-2331 column. Sub-samples of the centrifuged sludges were dried to constant mass at 100°C to determine their solids content. Details of the catchment type and population equivalent of each works are shown in Table 1.

**Table 1: Catchment type, population equivalent, ∑PCDD/F and I-TEQ for each wastewater treatment works in the survey**

| Works No. | Catchment Type | Population Equivalent | ∑PCDD/F (ng/g dw) | I-TEQ (pg/g dw) |
|---|---|---|---|---|
| 1 | Urban/Industrial | 1128029 | 17.5 | 53 |
| 2 | Urban | 68417 | 124 | 225 |
| 3 | Urban/Heavy Industrial | 149041 | 12.3 | 49 |
| 4 | Urban/Industrial | 137737 | 428 | 23 |
| 5 | Domestic/Rural | 9217 | 103 | 153 |
| 6 | Urban | 42228 | 49.8 | 20 |
| 7 | Urban/Industrial | 280253 | 194 | 41 |
| 8 | Urban/Industrial | 192471 | 24.2 | 30 |
| 9 | Urban/Industrial | 530311 | 28.9 | 45 |
| 10 | Urban/Industrial | 155099 | 8.88 | 40 |
| 11 | Urban/Industrial | 420364 | 15.8 | 29 |
| 12 | Urban/Industrial | 108124 | 22.4 | 25 |
| 13 | Domestic | 14139 | 16.7 | 152 |
| 14 | Domestic/Light Industry | 65854 | 9.24 | 20 |

**Results and Discussion**

Homologue Groups

The mean PCDD/F concentrations and range of values for each homologue group are shown in Table 2. It was noted that the di-furans make up the highest proportion of the total PCDD/F. This is not of toxicological significance as di-furans are not thought to be biologically active but could be indicative of a particular source of PCDD/Fs to wastewater and/or a degradation product of the higher chlorinated congeners.

The mean profile of the tetra to octa-chlorinated homologue groups is shown in Figure 1 with the homologue concentrations shown as a percentage of the total tetra- to octa-PCDD/F. The profile is typical of sewage sludges, dominated by the hepta and octa-PCDDs and to a lesser extent by the hepta and octa-furans (2,3).

I-TEQs

Table 2 shows the mean I-TEQs and range for each of the 2,3,7,8-substituted congeners. 1,2,3,7,8-PeCDF and Hepta and OCDD make the biggest contribution to the total I-TEQ. Table 3 shows the I-TEQs from this study in comparison to other studies in the literature (4-7). The I-TEQs from this study are at a comparable level to other sludges and are slightly higher than those of another study of UK sludges conducted in 1994 (5).

It is interesting to note that the sludges from catchments with a high proportion of industrial effluent are not the sludges with the highest total I-TEQs and the sludge with the second highest I-TEQ value is from a rural/domestic site (see Table 1). This could indicate that catchment-based, diffuse sources rather than a point source is the most important contributor

of PCDD/Fs to sludge and that the large amount of trade effluent coming into the more industrial works dilutes the PCDD/Fs in the sludge.

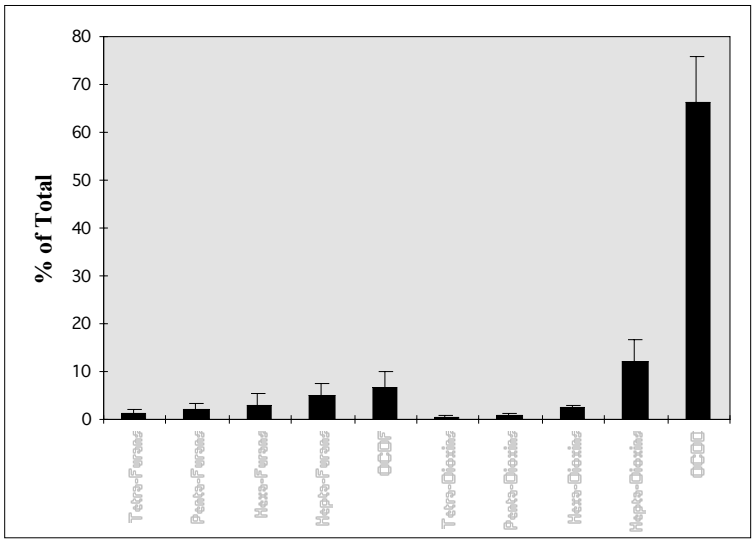
**Table 2: Homologue group concentrations and congener I-TEQs in sludges (pg/g dw)**

| Homologue Group | Mean (n=14) | Range | Congener Name | Mean I-TEQ (n=14) | Range |
|---|---|---|---|---|---|
| **Mono-Furans** | 251 | 8.0-1400 | **2,3,7,8-TCDF** | 1.6 | 0.53-3.7 |
| **Di-Furans** | 57000 | 3300-414000 | **1,2,3,7,8-PeCDF** | 15 | 2.3-67 |
| **Tri-Furans** | 187 | 26-1000 | **2,3,4,7,8-PeCDF** | 0.78 | 0.15-3.4 |
| **Tetra-Furans** | 90 | 40-183 | **1,2,3,4,7,8-HxCDF** | 6.5 | 0.80-43 |
| **Penta-Furans** | 156 | 55-396 | **1,2,3,6,7,8-HxCDF** | 2.3 | 0.57-10 |
| **Hexa-Furans** | 301 | 88-1120 | **1,2,3,7,8,9-HxCDF** | 0.47 | nd-1.5 |
| **Hepta-Furans** | 641 | 167-4150 | **2,3,4,6,7,8-HxCDF** | 1.3 | nd-4.0 |
| **OCDF** | 646 | 192-2590 | **1,2,3,4,6,7,8-HpCDF** | 2.4 | 0.81-12 |
| **Mono-Dioxins** | 19 | nd-55 | **1,2,3,4,7,8,9-HpCDF** | 0.30 | 0.050-1.4 |
| **Di-Dioxins** | 2150 | 793-7230 | **OCDF** | 0.65 | 0.19-2.6 |
| **Tri-Dioxins** | 134 | 11-1470 | **2,3,7,8-TCDD** | 1.8 | 0.67-5.6 |
| **Tetra-Dioxins** | 33 | 3.0-77 | **1,2,3,7,8-PeCDD** | 3.2 | 1.4-7.7 |
| **Penta-Dioxins** | 81 | 36-308 | **1,2,3,4,7,8-HxCDD** | 0.82 | 0.30-3.3 |
| **Hexa-Dioxins** | 371 | 89-2740 | **1,2,3,6,7,8-HxCDD** | 3.1 | 1.1-20 |
| **Hepta-Dioxins** | 2640 | 423-22500 | **1,2,3,7,8,9-HxCDD** | 2.6 | 0.64-12 |
| **OCDD** | 10200 | 2320-51000 | **1,2,3,4,6,7,8-HpCDD** | 12 | 2.3-92 |
| **∑PCDD/F** | 75300 | 8880-428000 | **OCDD** | 10 | 2.3-51 |
| | | | **∑I-TEQ** | 65 | 20-225 |

**Table 3: I-TEQ values for sludges in selected studies**

| Reference | I-TEQ (pg/g dw) |
|---|---|
| Näf *et al.* (1990), Sweden | 31 |
| Hagenmaier *et al.* (1992), Germany | Min=20, Max=177, Mean=47 (n=13) |
| DoE (1994), UK | Min=7.6, Max=192<br>Mean rural =23.3, Mean ind/dom=52.8 |
| Rappe *et al.* (1998), USA | Min=2.26, Max = 1270 |
| This Study (1999) | Min =20, Max =225<br>Mean = 65 (n=14) |

**Figure 1: Mean Homologue Profile of the Tetra to Octachlorinated PCDD/Fs**

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