

Dioxins on Land Around a Chemicals Waste Incinerator and Assignment of Source

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1.0 Introduction On 21 February 1996, in Leicester Crown Court, Coalite Chemicals pleaded guilty to discharging dioxins into the atmosphere from plant near Bolsover in Derbyshire, UK. This was the culmination of an investigation which began in 1991 when routine surveillance by the Ministry of Agriculture Fisheries and Food⁽¹⁾ revealed the presence of dioxins in milk of cows grazing within about 2 km of the Coalite Works.

In August 1991, Her Majesty's Inspectorate of Pollution (now part of the Environment Agency) commissioned AEA Technology to monitor flue gases in several discharge stacks at the Coalite Works where smokeless fuel and various toiletries were produced. As a follow-up, dioxins were measured in soil samples taken at up to 5 km from the Works.

This paper describes and discusses:

- spatial distribution pattern of dioxins on land around the Works and how this was used in source assignment;
- levels of dioxins on/in soils and how this was used in source assignment;
- the environmental significance of the dioxin levels on/in soils in relation to UK background in terms of both mass and TEQ;
- the potential and limitations of congener and congener group ratios in source assignment.

2.0 Flue Gas Monitoring Dioxins were measured in the flue gases of three potential sources in the Works complex. An unusual profile with elevated concentrations of TCDD was found in emissions from the CWI.

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3.0 Dioxins on/in Soil around the Works Soil samples were taken from each of 46 sites where the soil had remained undisturbed for many years.

As in flue gas at the CWI, total TCDD was found to always be prominent in soil and was selected as a marker for assessment purposes. Within 1 km of the Works, the concentration of total TCDD in soil was up to 9400 ng kg⁻¹ and even 4-5 kilometres away, several hundred ng kg⁻¹ were found. Concentrations of total TCDD in the soil samples and the sampling positions are shown in Figure 1.

3.1 Radial Distribution of Total TCDD: Statistical Considerations and Source Assignment

By considering five radial zones (1 km intervals) around the Works and the concentrations of total TCDD in each of the zones, it was shown that the probability of getting such differences by chance was less than 1 in 10,000. Even when the samples where total TCDD exceeded 1000 ng kg⁻¹ and where samples from the 0 - 1 km zone were excluded, the correlations were significant.

3.2 Prevailing Winds and Spatial Distribution of Deposited Total TCDD Around the Works

It was apparent that most of the deposition occurred to the NE of the Works and this was in-line with the direction of the prevailing wind (SW to NE). A comparison between wind direction and deposition in each of four quadrants around the Works is shown in Table 1.

Table 1 Comparison of Wind Directions and Total TCDD on/in Soil Around the Works (excludes sites where total TCDD = > 1000 ng kg⁻¹)

Quadrant	Mean Wind Frequency 1981-90 (Sheffield) (%)	Mean TCDD in Soil up to 5 km from Works (ng kg ⁻¹)	TCDD in Soil as Fraction of Total Deposited (%)
NE	43	603	42
SE	28	315	22
SW	19	269	19
NW	10	244	17

Analysis of the data in Table 2 using the software package Statistical Analysis System⁽²⁾ indicated that the chances of this spatial distribution pattern being due to chance alone was less than 1 in 10,000.

4.0 A Comparison of Observed Levels of TCDD in Soils and the UK 'Background': A Perspective

In order to put the concentrations of dioxins found in the environs of the Works into some perspective, they were compared with a UK Background Survey⁽³⁾. As an indicator of the highest concentrations which might be expected without a local source of dioxins, the mean plus 3 standard deviations (SD) was calculated for the ten congener groups and for two individual congeners (2,3,7,8-TCDD and 1,2,3,7,8-PeCDD). The range maximum for each of the congener groups was also noted. The data are shown in Table 2.

Table 2 PCDD and PCDF Concentrations in 65 UK Background Soils⁽³⁾

	Concentration (ng kg ⁻¹)				
	Range	Median	Mean	S.D.	Mean + 3 x S.D.
TCDD	<0.5 - 69	6.0	9.4	11	42.4
2,3,7,8-TCDD	<0.5 - 2.1	<0.5	<0.5	0.5	1.9 est.
PeCDD	<0.5 - 46	4.6	6.6	8.4	31.8
1,2,3,7,8-PeCDD	<0.5 - 2.4	<0.5	<0.5	0.5	1.9 est.
HxCDD	2.8 - 165	31	38	27	119
HpCDD	7.5 - 234	55	66	46	204
OCDD	29 - 832	143	191	162	677
TCDF	<0.5 - 237	16	25	32	121
PeCDF	<0.5 - 185	17	23	27	104
HxCDF	4.3 - 212	32	41	32	137
HpCDF	1.5 - 138	15	26	27	107
OCDF	<2.0 - 144	15	27	33	126

The salient points to note in Table 2 are:

- (i) The median and the mean values are similar, indicating that the mean values with the corresponding standard deviations are a reasonable guide to typical distributions and range in the UK.
- (ii) The mean concentrations of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD both fell below the lower limit of detection, 0.5 ng/kg, and clearly these compounds make only a minor contribution to the total TCDD and PeCDD congener group concentrations.
- (iii) Since the means for 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were below the lower limit of detection, a nominal mean of 0.4 ng kg⁻¹ has been assumed in calculating the mean plus 3 S.D.s. In practice, if either of the extreme values of 0 or 0.5 had been taken as a nominal mean, there would be only minor alterations to the data in Table 2.
- (iv) When the data are expressed in terms of the concentration per unit mass of soil, the density of the matrix (i.e. the soil) is critical. Since the density of UK surface soils varies by a factor of about three, the range of measured concentration values will always be greater than when values are expressed in terms of mass per unit area of soil surface.

Many environmental measurements show natural variation which follows a Gaussian distribution; that is, most of the measurements are close to the mean and their frequency falls off symmetrically with distance above and below the mean in a characteristic way. If it is assumed that the measurements made in the UK Background Survey are from a normal distribution, it can be calculated from standard tables how often another measurement from the same distribution is likely to exceed the survey mean +3 standard deviations. The tables show that only 1 sample in 667 (0.15%) should exceed this value. If samples from the Coalite survey are more frequently excessive it can be said that they are not part of the natural variation measured by the Background Survey and are therefore abnormal. Some environmental measurements follow a log-normal distribution in which the logarithm of the measurements shows the characteristic pattern of the normal distribution. In that case it would be expected that rather more samples, 1 in 55 (1.88%), would exceed the mean +3 standard deviations. Whichever distribution is apposite, in 46 samples

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only 1 or fewer excessive measurements would be expected for each congener. The frequencies and magnitude by which the soil concentrations in this Coalite survey exceeded multiples of the 'mean plus 3 standard deviations' calculated from the UK Background Survey are shown in Table 3 for one congener and five congener groups. The table also shows the frequency of exceedence of the various range maxima found in the UK Background Survey⁽³⁾.

Table 3 Results from the Coalite Survey: Frequencies of Exceedence of Various Values Derived From UK Background Survey

	Numbers of Samples Exceeding Values of:-					
	(a) mean + 3 S.D.s	(b) 5 x (mean + 3 S.D.s)	(c) 10 x (mean + 3 S.D.s)	(d) 20 x (mean + 3 S.D.s)	(e) 100 x (mean + 3 S.D.s)	(f) Range Max
TCDD	46	33	21	11	2	45
2,3,7,8-TCDD	23	4	2	2	1	21
PeCDD	36	13	11	5	3	29
HpCDD	3	1	1	0	0	2
OCDD	1	1	0	0	0	1
TCDF	32	4	2	2	0	15

Total number of samples = 46

Table 3 shows that:

- (i) In all 46 samples, the total TCDD concentrations exceeded the mean + 3 S.D.s of the UK Background Survey and two samples exceeded this value by more than two orders of magnitude.
- (ii) All but one of the 46 values for total TCDD in the Coalite Survey exceeded the range maximum found in the UK Background Survey.
- (iii) The 2,3,7,8-TCDD congener, the total PeCDD and the total TCDF congener groups were also prominent in the majority of samples. In one case, the 2,3,7,8-TCDD exceeded the mean + 3 S.D.s by more than two orders of magnitude and in three cases the total PeCDD exceeded the mean + 3 S.D.s by two orders of magnitude.
- (iv) The concentrations of the hepta- and octa-chlorinated groups differed little from background.

5.0 Congener Ratios as an Aid to Source Assignment Locally, where a single source of dioxins is dominant, it might be expected that the ratios of congeners might be similar to that in the flue gas ie we may have a means of source identification. However, such a "fingerprinting" approach may be insufficiently robust since (i) the ratios in the flue gas may not be constant, (ii) lifetimes and/or mobilities of the various congeners in the soil may vary and (iii) the distribution between particles and vapour in the atmosphere may differ from congener to congener and this would influence deposition rates.

In the UK Background Survey⁽³⁾, OCDD was found to be dominant with both TCDD and TCDF being smaller but significant contributors. By contrast, in the flue gas from the CWI, the greatest single group of congeners (in terms of mass) was the TCDD and TCDF. In general, the ratios of congener groups in the soil was not unlike that in the flue gas. However, for a fair comparison, it is necessary to deduct the 'natural background' from the soil samples before comparing with the flue gas samples but when this was done negative values were often obtained for the HxCDD and the OCDD since the background values carried large uncertainties and these groups were of low abundance in the flue gas. Although the dominance of the

TCDD in the soils and the flue gas was obvious, the uncertainty associated with background levels prevented unequivocal source assignment.

6.0 Results Expressed as Toxic Equivalent: Comparison with UK Background Levels The UK Background Survey⁽³⁾, established a mean background TEQ of about 1.0 ng/kg from the mean values (Table 3) for 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, OCDD and OCDF if the concentrations of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD are assumed to be 0.4 ng/kg. From the range maxima, a Total TEQ of 4.3 ng/kg was derived. When further analyses were carried out on soils from the UK Background Survey, Cox and Creaser⁽⁴⁾ derived a TEQ of 6.19 ± 3.71 ng/kg dry soil from eleven rural samples and a TEQ of 30.19 ± 19.21 from five urban soils.

From Cox and Creaser's data, the mean + 3 S.D.s of the eleven rural background samples was calculated to be 17.32 ng (TEQ)/kg. However, it may be unreasonable to compare the rural background with the aged industrial area around the Coalite Works. Nevertheless, if we compare the total TEQ values obtained in this survey around the Coalite Works with the value of 17.32 ng (TEQ)/kg it does put the results into some perspective in that only about 20% of the soil samples exceeded this value.

It may be more appropriate to compare the aged industrial area around the Coalite Works with an urban rather than a rural background, in which case a comparison with the urban value of 30.19 ± 19.21 ng (TEQ)/kg is more appropriate. In fact, only four samples exceeded this mean value and only two exceeded the mean + 3 S.D.s. Thirty-seven samples (80%) were less than 50% of the mean urban value.

7.0 Conclusions

- The spatial distribution pattern of dioxins on surrounding land implicated the Works as the likely source;
- The correlation between deposition and wind direction suggested that the TCDD reached the ground via the atmosphere over a long period of time and the probability that the Works was not the source was less than 1 in 10,000;
- Forty-two of the forty-six soil samples showed similar congener ratios (fingerprints) which in turn resembled those from the CWI;
- No soil samples showed a congener ratio pattern resembling that found in a UK Background Survey;
- In terms of mass, the soils contained levels of dioxins well in excess of the UK background, but in terms of TEQ the levels were much less significant;
- The Coalite Works was very likely the source of the dioxins found on the land around the Works.

8.0 References

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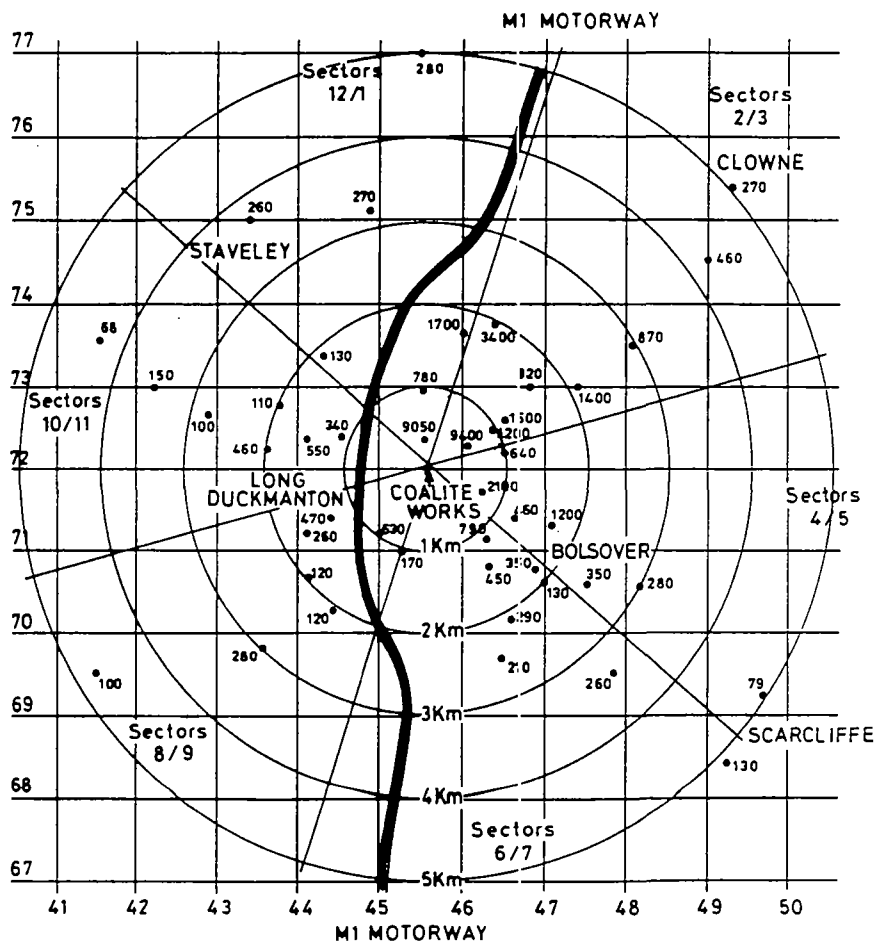


FIGURE 1. TOTAL TCDD CONCENTRATIONS (ng/kg) IN SOIL SAMPLES AROUND COALITE WORKS