An updated UK PCDD/F atmospheric emission inventory based on a recent emissions measurement programme

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Introduction

During the last 5 years, three principal estimates of UK national PCDD/F emissions to the atmosphere have been made (Eduljee and Dyke 1996; APARG 1995; Harrad and Jones 1992). Large uncertainties were acknowledged since in some cases source emissions were estimated from a very limited measured data-set, often employing information from non-UK studies. Total estimated emissions to the atmosphere ranged from 560-1100 g I-TEQ a^{-1}. MSW incinerators were the dominant source of PCDD/F emissions to the atmosphere and were responsible for up to 80% of the inventory.

The objective of this work is to survey the current data on dioxin emissions made available as a result of a comprehensive monitoring survey undertaken by the UK Environment Agency. Such monitoring has been driven by the need to demonstrate compliance with emission standards. This study updates previous estimates using measured emission data from a variety of industrial sectors collected during 1995, 1996 and early in 1997. It represents the most comprehensive survey to date of measured UK PCDD/F emission data. Distinctive mixtures of 2,3,7,8-substituted congeners have been used several times as 'fingerprints' for environmental source apportionment studies. This comprehensive survey of PCDD/F profiles in the UK will help to determine if this type of source identification work is valid and if broad process-based signatures are evident within a range of industrial plants within the same process sector.

PCDD/F data acquisition

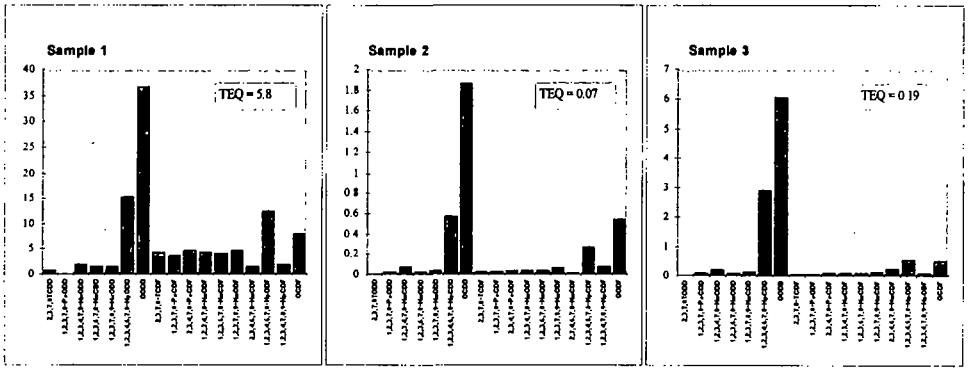
To date, the UK Environment Agency monitoring programme has provided a large amount of data for the following industry sectors; MSW incinerators, sinter plants, cement kilns, chemical waste incinerators, clinical waste incinerators and metal processing. The majority of sites have been sampled only once so far, but a proportion of MSWI plants have been sampled on more than one occasion between 1995 and 1996. Data included here refers only to those periods when the plant operators indicated that the plant was operating normally during the periods of testing. Sampling dates in the survey range from 1995 through to early 1997. All PCDD/F analyses were carried out using high resolution gas chromatography - mass spectrometry (GS-MS). Strict quality control procedures were required at each stage of the analysis and recovery spike concentrations associated with both sampling and extraction were provided by each contractor.

In only ~60% of sampling events were iso-kinetic flue gas sampling conditions achieved. This is primarily due to limitations imposed by the flue design and position of the sampling points, particularly in older installations. In general, a high degree of similarity was seen in both ΣTEQ concentrations and congener profiles during duplicate sampling events at a given site. However, despite the high degree of quality control measures employed, ΣTEQ concentrations in stack emissions collected within hours of each other on the same day could, in some cases, be very different. For example, the first sample collected from a cement kiln stack measured 4.2 and the second collected 5 hours later only 0.06 ng I-TEQ m^{-3}. During the time stack gas was sampled the plant was running normally and spike recoveries of both the samples were within the normal range. This highlights the importance of quality control at all points within the sample collection/storage, extraction and analysis protocol. This also implies the need for caution when extrapolating emissions from a single sample to then provide emission factors for a whole industrial process sector.

PCDD/F emissions

MSW incineration plants represent the sector which has generated the most data to date (total of 14 MSW sites). The broadest range of TEQ concentrations measured was found in the municipal waste incineration sector (0.07 to 74.4 ng I-TEQ m^{-3}). This range does not seem to reflect the age of the incinerator, type of gas cleaning system used or correlate with particulate releases. Despite the broad range in observed ΣTEQ, profiles of individual 2,3,7,8-substituted congener concentrations were quite similar. OCDD and 1,2,3,4,6,7,8-HpCDD dominated, followed by 1,2,3,4,6,7,8-HpCDF and OCDF. There is a high degree of profile consistency within an individual plant and also between sites, despite the large range in ΣTEQ concentrations. Figure 1 present the concentration profiles (ng/kg) of 3 samples collected at one MSWI and shows a high degree of profile consistency, despite the range in TEQ.

Figure 1: PCDD/F profiles from 1 MSWI site in the UK (ng/m^3) together with ΣTEQ data



Cement kilns, sewage sludge incinerators and sinter plants showed the least variation in measured emission TEQ within a given industry sector. The range of measured TEQs for chemical waste incinerators was 0.005 - 1.27 ng I-TEQ m^{-3} and the range of ΣTEQ observed in the 10 chemical waste incinerator sites was 0.009 to 1.27 ng I-TEQ m^{-3}. Congener profiles

were again dominated by OCDD, OCDF followed by 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD. Also, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF are observed in the pattern. The range of ΣTEQ observed in the sinter plant emissions is relatively small (0.43 to 1.08 ng I-TEQ m^{-3}) and the pattern very distinctive and quite different from that seen in other combustion processes, due to the dominance of PCDF congeners. Congener 2,3,4,7,8-PeCDF tended to dominate the profile, followed by 1,2,3,4,6,7,8-HpCDF, 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8-HxCDF.

Table 1. PCDD/F emission estimates for the UK (numbers in bold type represent estimates calculated from measured emissions

PROCESS	1994 estimate (g TEQ/a)*	1997Range/Low (g TEQ/a)	1997 Range/High (g TEQ/a)
Coke production	2	2	2
Coal combustion (industrial)	5-67	5	67
Coal combustion (power generation)			
Waste oil combustion	0.8-2.4	0.8	2.4
Wood combustion	1.4-1.9	1.4	1.9
Straw combustion	3.4-10	3.4	10
Tyre combustion	1.7	1.7	1.7
Landfill gas combustion	1.6-5.5	1.6	5.5
Sinter plants	29-54	**25**	**30**
Iron and steel	3-41	3	41
Non-ferrous metals (1 site)	5-35	**29.8**	**29.8**
Cement manufacture (5 sites)	0.2-11	**0.29**	**10.4**
Lime manufacture	0.04-2.2	0.04	2.2
Glass manufacture	0.005-0.01	0.005	0.01
Ceramic production	0.02-0.06	0.02	0.06
Halogenated chemicals	0.02	0.02	0.02
Pesticide production	0.1-0.3	0.1	0.3
MSW combustion	460-580	**122**	**199**
Chemical waste (10 sites)	1.5-8.7	**0.02**	**8.7**
Clinical waste (5 sites)	18-88	**0.99**	**18.3**
Sewage sludge (5 sites)	0.7-6	**0.001**	**0.37**
Carbon regeneration	0.006	0.006	0.006
Asphalt mixing	1.6	1.6	1.6
PCP in timber processes	0.8	0.8	0.8
Animal carcass incineration**		**0.001**	**0.18**
Crematoria	1-35	1	35
Domestic wood combn (clean)	2-18	2	18
Domestic wood combn (treated)		1	5
Domestic coal combustion	20-34	20	34
Traffic	1-45	1	45
Natural fires (wood)	0.4-12	0.4	12
Fires (accidents)	10	**10**	**81**
TOTAL	560-1100	219	663

* from Eduljee and Dyke 1996

** assumes 71160 carcasses processed to mid-June 1997 (associated with over 30 months scheme)

ΣUK emissions

Measured emission data for each industry sector were compiled and the PCDD/F related ΣTEQ released per year into the atmosphere calculated (from known throughputs of waste and gas volumes generated). Where possible, individual site ranges were calculated and added to provide the whole sector range (e.g. sinter plants). The minimum and maximum emission concentrations represent the range in the measured estimate for a given sector. Where possible, updated measured emissions from the literature were compiled e.g. accidental fires. For comparative purposes, industrial process categories remain the same as the 1996 inventory.

The new emission inventory estimates are presented in Table 1 (bold numbers) along with estimates from the Eduljee and Dyke (1996) study for comparison. Emissions from the incineration of MSW remain a significant source of PCDD/Fs to the atmosphere from the industrial sector, contributing between 30 and 56% to the total PCDD/F emission. This represents a significant decline from the 80% estimated in 1994. Emissions from sinter plants contribute between 5 and 11% to the total estimated primary emission. The metal sector (including sinter plants, iron and steel and non-ferrous metals) contributes a sizeable fraction of emissions from industrial sources contributing in total between 15 and 26%. Industrial combustion of coal increases in significance, contributing about 18% to the total emission. The net outcome of this assessment is a significant reduction in the estimate of annual emissions from 560-1100 g I-TEQ a^{-1} to 220-660 g I-TEQ a^{-1}.

References

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