

HUMAN SOURCES AND ACTIVITIES ASSOCIATED WITH DIOXIN-LIKE COMPOUNDS AND POPs IN THE ENVIRONMENT

A CONGENER-SPECIFIC PCDD/F EMISSIONS INVENTORY FOR THE UK: DO CURRENT ESTIMATES ACCOUNT FOR THE MEASURED ATMOSPHERIC BURDEN?

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INTRODUCTION

Issues regarding the uncertainty of primary sources versus secondary sources and the large uncertainties associated with secondary source emission estimates have arisen during PCDD/F inventory development. From our own studies, for example, we have detected the presence of PCDD/Fs in environmental samples collected and stored from the late-1800s (Alcock *et al.*, 1998a) and believe this is consistent with the emission of trace quantities of PCDD/Fs from combustion of coal/wood and/or metal smelting activities prior to the development of the 'Chlorine Industry' during this century. Previous UK inventories have estimated only the Σ I-TEQ emissions. However, in order to compare with the measured atmospheric loadings of PCDD/Fs and to model foodchain transfer/human exposure effectively, it is necessary to consider the individual 2,3,7,8-substituted PCDD/F congeners.

The objective of this study was therefore to: 1). produce a congener specific emission inventory for individual PCDD/F congeners (both concentrations and WHO-TEQ) from a number of regulated source categories for which emission data was available (notably MSWIs, chemical waste incinerators, clinical waste incinerators, cement kilns, sinter plants and sewage sludge incinerators); 2). calculate the significance of 'unregulated sources' (such as traffic, natural and accidental fires, domestic combustion of coal and wood) of emissions to the UK atmosphere; 3). consider the likely relative importance of regulated primary sources, nondioxin-regulated/diffuse primary sources and secondary/re-cycling sources of PCDD/Fs to the contemporary UK atmosphere and 4). compare the estimated congener-specific emissions with the loadings measured in air, to assess how closely the estimated emissions match field observations. Additionally, a mass balance model has been used to examine the behavior and distribution of PCDD/F congener emissions, based on the inventory information. We have used it to investigate whether known sources (both primary and secondary) can account for observed congener levels and patterns in different environmental compartments.

Estimating congener-specific primary source sectors to the UK atmosphere

Of the regulated source categories, a reasonable set of measured emission data was available for MSWIs, chemical waste incinerators, clinical waste incinerators, cement kilns, sinter plants, power generation plants and sewage sludge incinerators. These data formed the basis of the most recent TEQ inventory in the UK (Alcock *et al.*, 1998). The amount of each selected congener released into the atmosphere was calculated for the reference year 1996 by combining known throughputs of waste and gas volumes generated with the ranges in measured emissions for each process. Where possible, individual site ranges were calculated and added to provide the whole sector range. Several regulated industrial processes within the inventory classification do not have recent measured congener specific emission data available. These include coke and industrial coal combustion, waste oil combustion, industrial wood combustion and iron and steel production, crematoria and tyre combustion. In the absence of measured data, emission factor ranges were used as summarized by the recent US EPA Inventory of Dioxin Sources Draft Review (1998). Figure 1 shows the total congener-specific emission pattern associated with summing all sources.

ORGANOHALOGEN COMPOUNDS

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Figure 1: Estimated emission profiles for individual PCDD/F congeners as a) grammes and b) as grammes TEQ. Solid bars represent minimum and maximum ranges for each congener.

Figure 1a

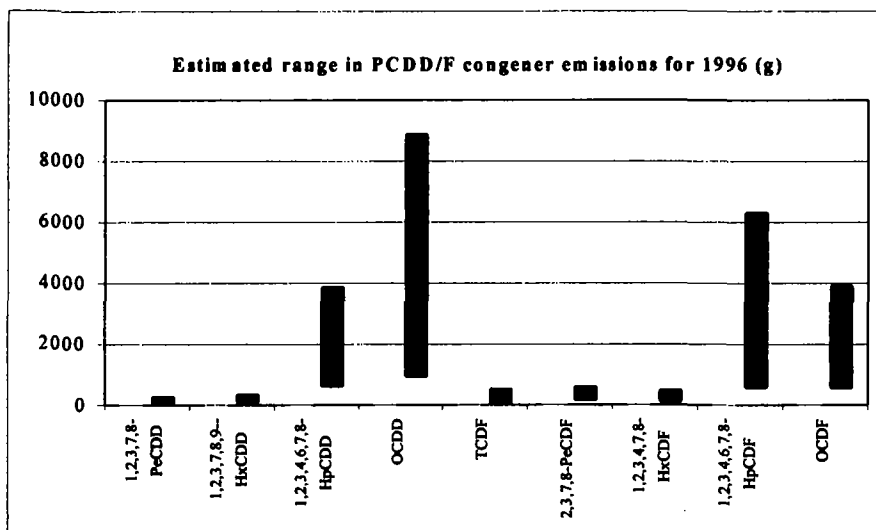
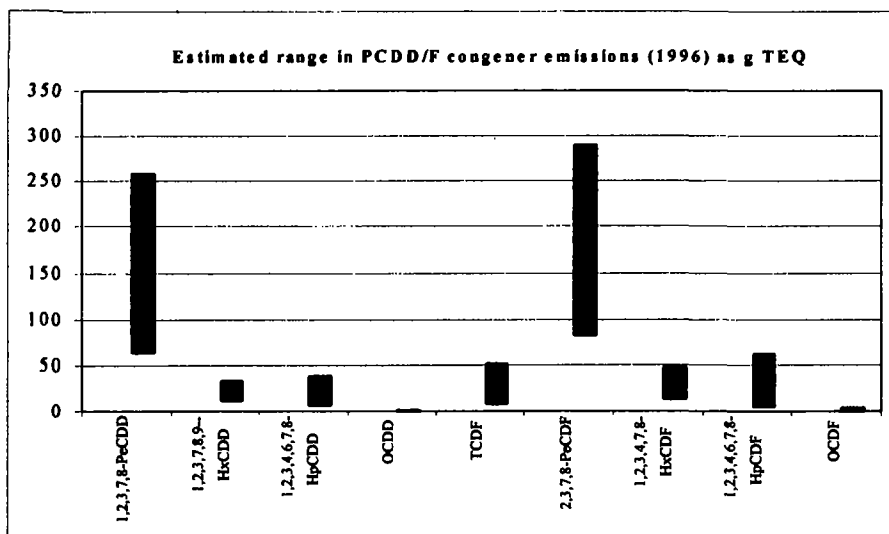


Figure 1b



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Estimating congener-specific 'unregulated' emissions to the UK atmosphere

Important nondioxin-regulated/diffuse primary and secondary sources of PCDD/Fs include releases from domestic combustion sources, vehicle emissions, natural and accidental fires and the use of pentachlorophenol and other chloroaromatics. For this assessment, 'nondioxin-regulated sources' refers to the following process categories: Traffic; Domestic coal/wood combustion; Natural and accidental fires. Emissions were estimated for the same congeners as for the primary emission estimates.

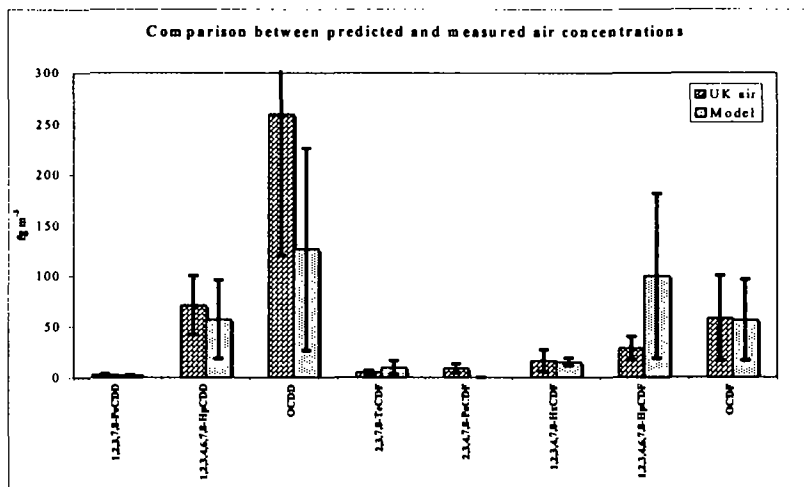
The following conclusions can be drawn from this assessment of congener emissions:

- during 1996 it was estimated that the total amount of PCDD/Fs released ranged from ~3 to ~22 kg. This translates to between 0.19 and 0.6 kg on a Σ TEQ basis.
- higher chlorinated PCDD/F congeners dominate the Σ PCDD/F emissions from both regulated and nondioxin regulated sources. The inventory profile is dominated by OCDD (~30-40%), 1,2,3,4,6,7,8-HpCDD (~15-19%) and 1,2,3,4,6,7,8-HpCDF (~14-19%).
- the 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF congeners dominate the Σ TEQ composition.
- Nondioxin-regulated sources contribute a significant proportion of the 1,2,3,7,8-PeCDD and 2,3,7,8-TCDF congener emission estimates, between ~44-66% and ~53-81% respectively. Accidental fires are estimated to be major contributors for both congeners, while domestic coal combustion is estimated to be important for TCDF.

Mass balance modeling

The atmospheric emission estimates from earlier in the paper were 'introduced' into the box model and subjected to atmospheric reaction and deposition processes as detailed above. Steady state air concentrations were then derived and are shown in Figure 2, where they are compared to observed concentrations collated from several UK studies conducted in 1997 (Lohmann and Jones, 1998; Lohmann *et al.*, 1999a). Results suggest that the predicted congener pattern is similar to the observed, with absolute concentrations generally being estimated within a factor of 2.

Figure 2: Comparison between predicted and measured air concentrations based on 1996 source inventories



Concluding remarks

1. To our knowledge, this is the first congener-specific PCDD/F atmospheric emission inventory. It has highlighted that for most regulated primary sources at the present time there is adequate

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measured information in the UK to compile reasonable emission estimates. The data suggest that primary emissions could account for between 30-86% of the total PCDD/F emitted into the atmosphere in 1996. Of the nondioxin-regulated sources (e.g. traffic, domestic combustion and accidental fires) only very crude estimates of contribution can be made, based on estimated emission factor ranges. Given these uncertainties, we have estimated that these sources could account for between 13–70% of the total PCDD/F emission.

2. The emission estimates were introduced into a multi-media model, incorporating loss processes mimicking those occurring in the UK atmosphere. Estimates of ambient concentrations were in reasonable agreement (i.e. generally within a factor of 2) with measurements. This provides an important measure of encouragement that major sources have been quantified reasonably well.

3. Modeling shows the congener-selective influence of deposition/atmospheric reaction processes on the stability of the ambient PCDD/F patterns. Weathering and advection generally alter patterns over timescales of a few days. Again, these modeling predictions are consistent with recent field measurements because of the consistency in measured air profiles throughout the UK.

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