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Exploring the Balance between Sources, Deposition, and the Environmental Burden of PCDD/Fs in the U.K. Terrestrial Environment: An Aid To Identifying Uncertainties and Research Needs

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The United Kingdom is used as a study area in which to examine (i) the relationship between primary and potential secondary emissions of PCDD/Fs; (ii) the balance between atmospheric emissions and deposition; and (iii) the contemporary environmental burden of PCDD/Fs and possible historical input profiles. This critical review exercise is seen as an important aid to identifying gaps in knowledge and research needs and directing a scientifically sound strategy for PCDD/F risk reduction. The paper focuses on two key compartments, air and soil, as these play an important role in the movement and storage of PCDD/Fs. The terrestrial agricultural food chain supplies the majority of human exposure to PCDD/Fs via the pathway air—deposition—crop/pasture/soil—grazing animals—meat/dairy products—human diet. Primary emissions of PCDD/Fs to the atmosphere are expected to decline in the future following the implementation of new legislative controls. This should be reflected by a further decline in ambient air concentrations, as our calculations indicate that primary emissions are currently the main PCDD/F sources to air. The soil burden will take much longer to decline, due to the extreme persistence of these compounds in this environmental matrix. The paper highlights uncertainties and future research needs concerning the environmental sources, fate, and behavior of this group of compounds.

Introduction

The U.S. Environmental Protection Agency (U.S. EPA) recently published a detailed draft re-assessment of the sources, environmental behavior, human exposure, and effects of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs or dioxins) (1). Following a period of public consultation and review, the final report is scheduled for publication in late 1996/early 1997. This report has stimulated the interest of the U.K. Government concerning the sources and significance of PCDD/Fs in the U.K. environment. As a consequence of

the U.S. EPA document and of strategies instigated in Europe to reduce primary combustion sources of PCDD/Fs, several strands of research are currently being undertaken in the U.K. and elsewhere to help provide a sound scientific basis from which to direct government policy for the regulation, source reduction, and control of PCDD/Fs. Key to this approach is the need for a reliable source inventory. In the U.K., Her Majesty's Inspectorate of Pollution (HMIP) recently published an inventory of primary PCDD/F atmospheric emissions (2), focusing on those sources that come under their regulatory control. In this paper we examine (i) the relationship between primary (i.e., fresh combustion-derived inputs and chemical industrial processes) and potential secondary (i.e., remobilized/recycled PCDD/Fs) emissions of PCDD/Fs; (ii) the balance between atmospheric emissions and deposition; and (iii) the contemporary environmental burden of PCDD/Fs. This has helped identify gaps in our knowledge and research needs and can assist in directing a scientifically sound strategy for PCDD/F risk reduction.

This paper focuses on two key environmental compartments, air and soil, as these play an important role in the movement and storage of PCDD/Fs. Air receives both primary and secondary emissions and is the main transport medium from source to sink. The soil holds the bulk of the contemporary PCDD/F terrestrial environmental burden. Importantly, the terrestrial agricultural food chain supplies the majority of human exposure to PCDD/Fs via the pathway air—deposition—crop/pasture/soil—grazing animals—meat/dairy products—human diet (3, 4).

The paper is structured as follows: first, estimates of the primary and secondary sources of PCDD/Fs to the U.K. atmosphere are discussed. Estimates of the contemporary annual atmospheric emissions are then compared to estimates of the national annual atmospheric deposition. Other inputs to the U.K. terrestrial environment are then discussed to set deposition inputs in context. Next, the burden of PCDD/Fs held in the U.K. terrestrial environment is calculated, the loss processes discussed, and the burden compared to contemporary and possible past inputs. This involves a brief review of evidence and speculation about possible historical PCDD/F sources/inputs. Finally, we speculate about possible future changes in emissions and environmental burdens in light of impending changes in legislative controls. We stress that considerable uncertainty surrounds many of the esti-

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TABLE 1. Some Potential PCDD/F Sources to Air

potential source	estimated emissions	additional information	ref
accidental releases	1.1–2.2 kg Σ PCDD/Fs <3 mg Σ TEQ/yr	a b	5 7
volatilization from CA-treated wood	1.2 g Σ TEQ/yr	c	
volatilization from soils	<0.15 kg Σ TEQ/yr	d	
soil resuspension	3 g Σ TEQ in air at any one time	e	12
contamination of commercial products	unquantifiable	d	

^a Large-scale fire at a plastics warehouse involving 500–1000 t of PVC. ^b Fire at a carpet factory, which involved 200 t of PVC and 500 t of carpeting; calculation was based on deposition measurement after the fire. ^c Estimates based on (a) a total of 290 t of PCP and NaPCP being used annually—until recently—by the U.K. timber industry (8) and a further 1000 t of NaPCP being imported each year into the U.K. via treated timber (9); (b) typical commercial PCP and NaPCP mixtures are as those reported in ref 10, i.e., 2.4 and 0.7 mg Σ TEQ/kg, respectively; (c) assuming 0.1% of the PCDD/F content of PCP mixtures volatilizes during timber treatment (11). ^d See text for further details. ^e 4% of the ambient air PCDD/F concentrations originates from re-entrained PCDD/F-containing dust (12).

mates made in the paper. Nonetheless, the exercise is a useful one at this stage of the debate in highlighting where research efforts should be targeted. We also believe that the situation in the U.K. may serve as a useful 'model' for other industrialized countries, with respect to the potential sources and historical input profiles of PCDD/Fs in the environment. We have chosen to quantify inputs, fluxes, and burdens in terms of total toxicity equivalent (Σ TEQ) units. This is because emission control strategies are based on these units and because data are often just reported in these terms. It is acknowledged that using the Σ TEQ masks important differences in source patterns and environmental fate and behavior. Reference will be made to congener/homologue-specific data where appropriate.

Contemporary Inputs of PCDD/Fs to Air in the U.K.

PCDD/Fs are formed and released into the environment primarily either through combustion processes or through the production, use, and disposal of chlorinated aromatic (CA) compounds. Combustion processes involve thermal reactions that form PCDD/Fs and include municipal waste incineration, metal smelting activities, and the burning of fossil fuels. The production of CA compounds such as chlorophenols (CPs), chlorobenzenes (CBs), polychlorinated biphenyls (PCBs), and chlorophenoxy herbicides can lead to the inadvertent formation of PCDD/Fs, which can enter the environment when the CA compounds are used, disposed of (deliberately or accidentally), or combusted. Other sources of PCDD/Fs, which are thought to be minor in the U.K., include paper pulping and recycling plants and production of PCDD/Fs via enzymatically mediated reactions with CPs in compost or sewage sludges.

Combustion Sources. The most obvious sources of PCDD/Fs to the atmosphere are the direct emissions from point and diffuse combustion sources. HMIP (2) have estimated current U.K. atmospheric emissions from industrial and non-industrial processes to be 560–1100 g Σ TEQ/year. Industrial processes account for approximately 90% of the total inventory. The incineration of municipal solid wastes (MSW) is the dominant source assessed, accounting for approximately 70% of the total emissions from industrial sources (460–580 g Σ TEQ/year). The remaining 30% was predominantly due to emissions from the combustion of coal and clinical waste; emissions from iron, steel, and sinter plants; and non-ferrous metal operations. Ten percent of the total emission inventory was from non-industrial sources (i.e., crematoria, domestic wood and coal combustion, traffic, and natural fires). Clearly, these estimates are of variable quality. HMIP (2) assessed the quality of their emission estimates (high, medium, low). Because of the lack of available data, the results for most of the sectors are generally classified under medium to poor data quality ratings (i.e., medium = large numbers of measurements made at a small number of representative sites or an engineering calculation based on a number of relevant facts, low = estimate based on a

calculation derived only from assumptions). Thus, these emissions estimates were considered to be the best that could be derived from the available data, but due to the many uncertainties they should not be assumed to be correct.

Comparison of the study conducted by HMIP (2) with other national inventories suggests that most industrial point sources currently considered as potentially significant sources of PCDD/Fs to the atmosphere have been accounted for, albeit with limitations regarding quality and quantity of the data included in the inventory. However, some sources are very difficult to quantify and were therefore not considered. The HMIP (2) inventory did not address the following sources: (i) diffuse/fugitive emissions from industrial processes; (ii) introduction of PCDD/F into the atmosphere through the distribution and use of chemicals, as opposed to emissions during the manufacturing process; and (iii) unregulated sources such as accidental fires.

Other Potential Sources to Air. There is considerable interest in the extent to which the primary emissions quantified in the HMIP (2) inventory are supplemented by the sources just listed and other secondary sources. Some of these potential sources are briefly considered below.

(a) Accidental Releases. Accidental fires may lead to emissions of PCDD/Fs from a variety of materials containing CA compounds (5). Over 90 thousand fires in homes, factories, and elsewhere occur in buildings in the U.K. each year (6). Due to the wide range of combustion conditions and types of chemicals—e.g., pentachlorophenol (PCP) in treated wood and PVC—often involved, it is very difficult to estimate the overall contribution from this source to the U.K. environment. This is highlighted by the results presented in Table 1, showing PCDD/F data from two such fires. Further research is needed to obtain more accurate measurements of emissions from a range of accidents and on the frequency at which such releases occur before the annual emissions to the atmosphere can be estimated.

(b) Volatilization from CA-Treated Wood. During the production of PCP and its derivatives—e.g., sodium pentachlorophenoxide (NaPCP)—PCDD/Fs are inadvertently formed. PCP has been used widely in the past in the U.K. and elsewhere as a wood treatment/fungicide. Restrictions on the manufacture and use of PCP in the U.K. have been imposed with lesser quantities imported directly or indirectly. However, presumably there is a substantial 'stock' of old PCP-treated wood still in use. Based on current information, atmospheric emissions from this source are not believed to be significant (see Table 1), but studies are needed to verify this.

(c) Volatilization and Environmental Recycling. Later in this paper, soils are shown to be the major terrestrial PCDD/F environmental repository. A potentially important secondary source of PCDD/Fs to air is therefore the environmental recycling of previously emitted and deposited material from the soil compartment. This could take two forms—either volatilization of gas-phase PCDD/Fs or resus-

TABLE 2. Results from Two Simple Models To Predict the Likelihood of Compounds Revolatilizing from Soil to Air

compound	fugacity quotients ^a		simple model to predict soil to air transfer ^b	
	soil/air urban	soil/air rural	annual flux: soil to air (kg yr ⁻¹)	annual flux as a percentage of the total soil burden ^c
2,3,7,8-TCDD	7.38 (7.67*)	1.91 (1.98*)	0.03	0.84
1,2,3,7,8-PeCDD	0.04	0.02	0.001	0.02
1,2,3,4,7,8-HxCDD	0.05 (0.05*)	0.04 (0.04*)	0.004	0.02
1,2,3,6,7,8-HxCDD	0.06	0.06	0.01	0.03
1,2,3,7,8,9-HxCDD	0.03	0.02	0.003	0.03
1,2,3,4,6,7,8-HpCDD	0.02 (0.02*)	0.01 (0.01*)	0.10	0.02
OCDD	0.20	0.06	0.32	0.01
2,3,7,8-TCDF	6.97	7.57	0.54	1.69
1,2,3,7,8-PeCDF	4.80	5.92	0.49	0.23
2,3,4,7,8-PeCDF	0.75	0.23	0.04	0.24
1,2,3,4,7,8-HxCDF	0.97	0.54	0.1	0.21
1,2,3,6,7,8-HxCDF	1.26	0.25	0.05	0.11
1,2,3,7,8,9-HxCDF	0.32	0.20	0.003	0.11
2,3,4,6,7,8-HxCDF	0.67	0.22	0.03	0.11
1,2,3,4,6,7,8-HpCDF	1.15	0.21	0.16	0.08
1,2,3,4,7,8,9-HpCDF	0.33	1.51	0.04	0.08
OCDF	0.39	0.04	0.04	0.004
ΣTEQ			0.15	

^a Assumptions made to estimate fugacity quotients: soil fugacity capacity, soil density = 1500 kg m⁻³; organic matter content = 2%; vapor particle partitioning of PCDD/Fs was calculated from field data presented by McLachlan (4). An asterisk (*) indicates selected values calculated at 13 °C (see text for details). ^b Assumptions made to predict soil to air fluxes: U.K. surface area = 2.5 × 10¹¹ m², 10% of which is urban, the remainder rural; the air compartment above the soil = 1 km; there is instantaneous equilibrium between the chemicals in this air mass and those in the soil compartment (an assumption used in generic fugacity models for assessing the environmental fate of organic chemicals); the atmospheric residence time = 100 h; this residence time results in an advective inflow and outflow from the air compartment of 2.5 × 10¹² m³ h⁻¹; the incoming air contains a zero PCDD/F concentration, this assumption is unrealistic, but will give an indication of a worst case flux. ^c The percent of the total flux from soil to air gives a better description of the proportion of each individual congener moving from the soil to the atmosphere. Comparison between actual fluxes for individual PCDD/F concentrations can be misleading; for example, the annual flux for TCDD is lower than OCDD because the soil concentration of OCDD is 3 orders of magnitude higher than TCDD. However, a higher proportion of TCDD will revolatilize relative to OCDD.

pension of soil dust particulates. Secondary inputs (recycling) are believed to currently exceed primary emissions as a source of PCBs to air in the U.K. (13). However, there are important differences between PCBs and PCDD/Fs. First, PCBs have higher vapor pressures and are more volatile; second, PCDD/Fs are still being formed, whereas the PCB problem can essentially be viewed as a legacy of their use in the 1960/1970s (13). The tetra- and penta-CDD/Fs are known to have a significant vapor phase component in air, while the hepta- and octa-CDD/Fs are thought to be almost exclusively associated with aerosols under ambient conditions (14–16). The higher toxicity equivalent factor (TEF)-rated PCDD/Fs are therefore more likely to undergo soil–air vapor phase transfer. Two simple approaches have been used here to assess the potential order of magnitude significance of PCDD/F volatilization from soil to air:

(1) *The fugacity quotient concept* has recently been applied by McLachlan (4) to study the bioaccumulation of organic compounds in agricultural food chains. Air and soil PCDD/F concentrations, presented later in the paper (see Table 4) have been used to calculate fugacities of a range of PCDD/Fs between the air and soil compartments. Fugacity quotients (air–soil) are then calculated by dividing the fugacity estimated for air by that estimated for soil. The various calculated fugacity quotients are displayed in Table 2. The fugacity of a compound in a particular phase can be calculated from the concentration C (g m⁻³) using the following equation:

$$f = C/zM$$

where M is the molecular mass (g mol⁻¹) and z is the fugacity capacity of the phase for the compound (mol m⁻³ Pa⁻¹). The fugacity capacity for air is defined by

$$z_A = 1/RT$$

where R is the gas constant and T is the absolute temperature. The fugacity capacity of soils can be estimated using the following equation:

$$z_S = f_{oc}psK_{oc}Z_w$$

where f_{oc} is the fraction of organic carbon, ps is the soil density (in g mL⁻¹), K_{oc} is the organic carbon/water partition coefficient, defined according to Karickhoff (17) as

$$K_{oc} = 0.41K_{ow}$$

where K_{ow} is the octanol/water partition coefficient. Z_w , the fugacity capacity of water, is calculated from

$$Z_w = 1/H$$

where H is the Henry's law constant (Pa m³ mol⁻¹). The average ambient temperature in the U.K. ranges from ~20 °C in the summer to ~6 °C in the winter months with a mean temperature of approximately 13 °C. As most available physicochemical data are reported at 25 °C (18), it was fairly straightforward to calculate fugacity quotients at this temperature, and these data are displayed in Table 2. However, for three PCDDs, fugacity quotients were calculated at 13 °C, and these data are also included in Table 2. Calculation of a temperature-adjusted fugacity capacity for air was straightforward, but calculating a temperature-adjusted fugacity capacity for soil required some additional data. The two terms in the equation for calculating fugacity that are likely to be temperature dependent are K_{oc} and H . All K_{oc} data used in the calculations were calculated from K_{ow} data at 25 °C, and no temperature correction was applied. Temperature-corrected values of H were calculated, however, by calculation of temperature-corrected values of solid vapor pressures and water solubilities, since H is strongly correlated with these properties and is usually calculated simply as

$$H = P/S$$

where P is vapor pressure and S is water solubility. The solid vapor pressure can be corrected for temperature using the Clausius–Clayperon equation:

$$\ln (P_1/P_2) = -\Delta H_{\text{sub}}(1/T_1 - 1/T_2)/R$$

where ΔH_{sub} is the enthalpy of sublimation (in KJ/mol); data were obtained from Gobas (19). A similar correction was performed for solubility data having the analogous form:

$$\ln (S_1/S_2) = -\Delta H_{\text{sol}}(1/T_1 - 1/T_2)/R$$

where ΔH_{sol} is the enthalpy of solution; data were obtained from Gobas (19).

Comparison of the fugacity quotients calculated at 13 and 25 °C, respectively, displayed in Table 2 reveals only a small difference in the values. This is because the temperature-adjusted values of H for PCDDs were almost the same as the H values at 25 °C, and consequently, the soil fugacity capacities at the two different temperatures were also nearly the same. In reality, temperature may have a more pronounced effect on soil fugacity capacities of PCDD/Fs. Hippelein and McLachlan (20) have shown that the fugacity capacities of PCBs in soils are strongly correlated with temperature.

Fugacity quotient values near 1 show equilibrium between air and soil, values >1 indicate a tendency for compounds to volatilize from soils, while those <1 indicate a tendency to remain in the soil. The fugacity quotients displayed in Table 2 show that the PCDFs and 2,3,7,8-TCDD may be close to soil-air equilibrium in the U.K. at the present time. The remainder of the PCDD congeners generally fall well below 1, suggesting that soil is currently a net recipient of gas phase inputs of these compounds in the U.K. environment rather than a source of gas phase PCDD/Fs to the air. These results are similar to those reported for Germany (4), where the tetra- to hexa-PCDD/Fs had fugacity quotients close to 1, but all other PCDD/Fs had fugacity quotients below 1. However, it is stressed that there are important uncertainties in these calculations, most notably over physicochemical data for PCDD/Fs (18) and the fine-scale distribution of PCDD/Fs in surface soils. Experimental studies on air-soil exchange of PCDD/Fs are urgently needed to verify these calculations.

(2) *Simple Model To Predict Soil to Air Fluxes.* A very simple equilibrium partitioning model can be constructed of the U.K. to calculate the possible 'worst case' fluxes of PCDD/Fs that may volatilize from soil to air. The ratio of the soil and air fugacity capacities are used to derive an air-soil partition coefficient. Typical U.K. rural and urban soil concentrations (from Table 4) are then used to predict equilibrium air concentrations. Further details of the modeling procedure are given in the footnote of Table 2. The model predicts that 0.15 kg Σ TEQ would be revolatilized from soils to air each year under the conditions specified (i.e., the worst case scenario). If this estimate were correct soil revolatilization of PCDD/Fs would be a relatively large source as compared to estimated contemporary primary emissions. However, the model will overestimate soil-air fluxes because (1) it assumes that PCDD/F concentrations in air are zero and (2) no account has been taken of resistance to PCDD/F transport out of the soil (i.e., instantaneous soil to water and soil-air to overlying air is assumed). Both of these assumptions will be in error and probably substantially so, largely because the prolonged desorption of recalcitrant organics from soils is kinetically constrained (21). In summary, even though the fugacity quotient and the equilibrium partitioning models are rather simplistic, taken together they suggest that soil outgassing of PCDD/Fs is unlikely to make a significant contribution to the total annual atmospheric emissions for the U.K. nationally at the present time. Obviously if primary emissions are reduced in the future, recycling of previously emitted PCDD/Fs back to the air will assume greater relative importance as a source.

(d) *Soil Particle Resuspension.* Soil is the major repository for PCDD/Fs (see later). As a consequence, soil particle resuspension has been postulated by some to act as an

important source of PCDD/Fs to the atmosphere. Kao and Venkataraman (12) have estimated that up to 4% of the ambient air PCDD/F concentrations and between 70 and 90% of the total PCDD/F deposition to environmental surfaces in urban areas and between 20 and 40% in rural regions could be associated with this source (see Table 1). Their approach has been applied to the U.K. PCDD/F data by using the data reported in Table 4 and the ambient concentrations for aerosols in rural and urban regions given by in Kao and Venkataraman (12). Resuspended soil particles are estimated to contribute only 1.2–5.8% of particulate PCDD/Fs to the air in urban areas of the U.K. and 1.1–3.6% in rural locations.

(e) *Contamination of Commercial Products.* Σ TEQ concentrations in CA chemical formulations (such as chlorophenoxy herbicides, pesticides, PCP mixtures, etc.) can vary over several orders of magnitude. For example, Fiedler (22) has reported PCDD/F levels of 0.11, 0.68, and 23 ng Σ TEQ/kg for Clophen A 30, 2,4,6-trichlorophenol, and trichlorobenzene (TCB), respectively. The list of chemical formulations with PCDD/F impurities may increase as new sources are identified, despite the fact that changes in the industrial processes and purification efficiencies are resulting in a reduction in PCDD/F contamination in some of these formulations (22). However, it is extremely difficult to estimate the Σ PCDD/F concentrations likely to be released into the U.K. environment from contaminated products, especially as there is little information on (1) typical PCDD/F concentrations in chemical formulations, (2) total U.K. production of CA chemicals, and (3) the amounts likely to be released into the environment during the manufacture and use of these chemical formulations. If PCDD/Fs are formed by these processes, they have a greater potential to be released to water and land than to the atmosphere, either via the waste streams from the process, subsequent use of the chemical formulation, or via secondary entry into the environment through the disposal of sewage sludge. The amounts being emitted directly to the atmosphere are therefore likely to be small.

Some General Comments on the Sources of PCDD/Fs to Air. As we have seen, there are numerous potential sources of PCDD/Fs to the atmosphere. The situation is complex because (1) several of these potential sources are very poorly quantified at present and will be difficult to accurately quantify in the future and (2) different sources will vary in importance for different individual TEF-rated compounds. It is pertinent at this stage to make a few observations, drawing on literature data. One of the most recent and detailed studies on PCDD/Fs in air showed a seasonal variation in industrialized countries, with levels during the winter months exceeding those in the summer (16) for a rural part of Germany. This suggests that seasonally-related primary combustion source(s) is/are important (dominant) contributors to the PCDD/F air burden, while volatilization from soil or treated timber (for example) are not. Secondly, that study also reported very little change in the congener profile of PCDD/Fs in air seasonally. Thirdly, although the mixture of PCDD/Fs in air sampled in close proximity to a source can be 'unusual' (i.e., characteristic of the source), the mixture is generally quite consistent in ambient rural and urban air from the same country and even from different countries. PCDD/Fs are known to be rather unreactive in the atmosphere (23) (although photodegradative loss may be greater in summer than winter), so the consistency of the mixture probably reflects a consistency of source. Finally, it is interesting to note that the air mixture is unlike that of municipal waste incinerator emissions from Germany (no congener-specific U.K. data has been published), even though MSW emissions were quantified in the HMIP (2) inventory as the dominant source of PCDD/Fs to the atmosphere. Similarly, the mixture in air is unlike that in technical PCP mixtures (10) or soil (24). These observations are rather difficult to reconcile when taken together, unless one considers a seasonally-consistent mixture

TABLE 3. PCDD/F Deposition Fluxes in the U.K. Environment

	urban deposition flux at 4 U.K. sites ^a (pg m ⁻² day ⁻¹)	rural deposition flux ^b (pg m ⁻² day ⁻¹)	annual national deposition flux ^c (kg)
2,3,7,8-TCDD	6	0.6	0.10
1,2,3,7,8-PeCDD	10	1.8	0.24
1,2,3,4,7,8-HxCDD	8	2.4	0.27
1,2,3,6,7,8-HxCDD	15	7.3	0.73
1,2,3,7,8,9-HxCDD	26	8.3	0.91
1,2,3,4,6,7,8-HpCDD	147	100	9.5
OCDD	640	486	45
2,3,7,8-TCDF	24	5.5	0.67
1,2,3,7,8-PeCDF	32	4.9	0.68
2,3,4,7,8-PeCDF	55	6.0	0.98
1,2,3,4,7,8-HxCDF	27	7.1	0.82
1,2,3,6,7,8-HxCDF	24	7.2	0.80
1,2,3,7,8,9-HxCDF	5	2.3	0.24
2,3,4,6,7,8-HxCDF	24	7.9	0.86
1,2,3,4,6,7,8-HpCDF	96	47	4.7
1,2,3,4,7,8,9-HpCDF	7	4	0.37
OCDF	99	54	5.3
ΣTCDD	194	24	3.7
ΣPeCDD	177	23	3.5
ΣHxCDD	228	85	9.0
ΣHpCDD	278	181	17
ΣTCDF	427	98	12
ΣPeCDF	400	58	8.3
ΣHxCDF	231	77	8.3
ΣHpCDF	152	74	7.4
ΣPCDD/F	2825	1160	120
ΣTEQ	48	12	1.4

^a Due to the high number of nondetect values reported for urban deposition (15), the values presented here have been estimated from the median OCDD concentration reported for four U.K. urban samples, by making the assumption that the U.K. deposition PCDD/F pattern is similar to that reported for Germany by Hiester *et al.* (27). ^b Rural deposition data as reported by Hiester *et al.* (27). ^c The national deposition flux was derived by assuming that the U.K. surface area is 2.5×10^{11} m²; 10% is defined as urban and the remainder as rural (28).

of sources operating in different countries to produce the characteristic air PCDD/F mixture.

The information that we need to take forward from this section on sources to air is that contemporary U.K. primary emissions have been estimated at between 560 and 1100 g ΣTEQ/year and that this may be supplemented by several potential secondary inputs. These are very difficult to quantify at present, but are probably smaller than the primary emissions, perhaps collectively in the range of grams to <0.5 kg ΣTEQ/year.

Balance between Emission and Deposition

This section compares estimated contemporary U.K. atmospheric emissions to limited measurements of deposition. Measurements of reliable atmospheric deposition fluxes for PCDD/Fs and other semivolatile organic contaminants are notoriously difficult to make, due to the large number of uncertainties that arise during sample collection and analysis. Levels are often near or below detection limits, particularly for the low molecular weight PCDD/Fs which have a higher vapor phase component in air and therefore may not be as readily deposited/sampled by conventional deposition collectors as the higher molecular weight compounds. PCDD/Fs may be deposited by dry gaseous deposition, dry particle-bound deposition, and wet deposition. Partitioning between the gas and particle phases influences the relative importance of deposition processes (3, 4, 14).

An additional problem in balancing estimated regional-scale emissions with estimates of national or regional-scale deposition is that deposition measurements tend to be made in urban locations that are higher than national average values (25, 26). This was a problem in a previous U.K. study (6), where inadequate deposition data were extrapolated to give 'average U.K.' fluxes, which were probably too high. A larger

U.K. deposition flux data set now exists, which allows an improved estimate of the U.K. annual deposition flux to be made.

Monthly PCDD/F deposition fluxes have been measured in four U.K. city centers and a rural location as part of an on-going monitoring program (15). Unfortunately, the lighter PCDD/Fs were often not detected after 1 month exposure; the higher chlorinated compounds dominated the congener profile. As the air and deposition mixtures measured at the U.K. sites are similar to those reported for other industrialized countries, the data have been normalized using OCDD to that measured by Hiester *et al.* (27) for seven urban German sites to derive fluxes for the lower chlorinated congeners. Similarly, the rural data used are that reported by Hiester *et al.* (27) for a rural location, as no U.K. rural deposition flux data are available for a whole year. The national annual contemporary deposition flux to the U.K. surface is estimated as 1.4 kg ΣTEQ/year (see Table 3). This is in close agreement with the primary emission estimate of 0.56–1.1 kg ΣTEQ/year mentioned earlier, especially given the large errors associated with each estimate. The contribution of potential secondary emissions (noted above to be perhaps a few grams to <0.5 kg ΣTEQ/year) will supplement the primary emission estimates given here. While accepting the large uncertainties on these estimates, one interpretation of the good agreement between the estimated emissions and deposition is that the major emission sources to air have been accounted for (29). Another interpretation is that the agreement is largely by chance, because in addition to the uncertainties noted earlier with regards to PCDD/F measurements in deposition samples, other factors will influence the balance, notably (1) possible atmospheric transformation/degradation of PCDD/Fs between source and deposition; (2) long-range transport to/from the U.K.; and (3) elevated deposition in close proximity

TABLE 4. Typical or Representative PCDD/F Concentrations in Different Environmental Compartments

	air ^a (pg/m ³)		river water ^b (pg/m ³)	soil ^c (ng/kg)		herbage ^d (ng/kg) rural	sludge ^e (ng/kg)	river sediment ^f (ng/kg)		human adipose tissue ^g (ng/kg)
	urban	rural		urban	rural			rural	urban	
2,3,7,8-TCDD	0.01	0.002	<22	1.7	0.1	0.07	2.1	0.3	1.1	<9
1,2,3,7,8-PeCDD	0.04	0.01	<30	2.2	0.2	0.07	3.3	0.7	6.2	19
1,2,3,4,7,8-HxCDD	0.05	0.01	27	5.4	0.9	0.09	3.6	0.9	5.6	31
1,2,3,6,7,8-HxCDD	0.10	0.02	60	11.9	2.9	0.27	24	3.8	26	154
1,2,3,7,8,9-HxCDD	0.08	0.02	38	5.4	0.6	0.19	18	1.1	4.4	23
1,2,3,4,6,7,8-HpCDD	1.06	0.22	225	246	23	3.07	1498	63	623	129
OCDD	3.80	0.73	1395	2690	161	24	15231	238	3032	686
2,3,7,8-TCDF	0.10	0.02	24	9.2	1.9	0.89	31	3.9	25	<9
1,2,3,7,8-PeCDF	0.12	0.02	19	55	13	0.24	12	2.4	11	12
2,3,4,7,8-PeCDF	0.12	0.02	17	8.5	0.5	0.28	19	3.1	7.6	20
1,2,3,4,7,8-HxCDF	0.18	0.04	24	19	2.0	0.21	21	14	265	21
1,2,3,6,7,8-HxCDF	0.08	0.03	23	20.8	1.5	0.09	20	3.6	19	12
1,2,3,7,8,9-HxCDF	0.01	0.01	11	0.7	0.2	0.04	7.0	<0.45	1.1	13
2,3,4,6,7,8-HxCDF	0.10	0.02	14	14	0.8	0.08	29	0.9	8.2	nd
1,2,3,4,6,7,8-HpCDF	0.39	0.07	107	121	4.2	1.20	301	17	134	29
1,2,3,4,7,8,9-HpCDF	0.04	0.01	44	3.6	3.7	0.10	17	0.5	10	<17
OCDF	0.31	0.06	255	598	15	1.3	556	<44	<80	38
ΣTCDD	0.28	0.06	67	48	6	1.24	15	34	155	
ΣPeCDD	0.49	0.10	94	47	5	3.12	67	39	173	
ΣHxCDD	1.05	0.22	400	121	23	2.94	134	48	274	
ΣHpCDD	1.92	0.41	405	501	40	6.75	2290	155	1196	
ΣTCDF	1.65	0.37	220	139	17	3.55	50	87	351	
ΣPeCDF	1.36	0.28	170	131	17	2.62	41	89	265	
ΣHxCDF	1.05	0.22	180	155	25	1.24	144	84	500	
ΣHpCDF	0.55	0.11	265	230	16	1.97	675	32	214	
ΣPCDD/F	12	2.5	3450	4660	324	49	19694	805	6160	
ΣTEQ	0.18	0.04	38	26	3.3	0.49	61	6.2	54	48

^a Due to the high number of nondetect values reported for urban air, the values presented here have been estimated from the median OCDD concentration reported for four U.K. urban samples, by making the assumption that the U.K. air PCDD/F pattern is similar to that reported for Germany. Rural air data are the mean of that reported by refs 16 and 37 for Germany. Note that the rural data from ref 16 was calculated by dividing the urban concentration by 2. ^b Ref 38. ^c 2,3,7,8-Substituted mean concentrations from refs 24 and 39. Homologue group concentrations from ref 39 only. ^d Ref 40. ^e Refs 41 and 42. ^f Ref 43. ^g Ref 44.

to sources. The results obtained here differ from those reported earlier by workers who found a large (10-fold) discrepancy between the emissions and deposition ΣPCDD/F fluxes; emissions being much lower (6). This was attributed—probably incorrectly—to the existence of unquantified secondary sources. There is an urgent need for more reliable measured urban and especially rural deposition flux data (25, 26) for the U.K. In summary, further measurements of improved sensitivity and quality are needed, together with an improved understanding of the processes of deposition to vegetation, soil, and water bodies to increase confidence in the comparison of national emission and deposition estimates.

Inputs to the Terrestrial Environment

It is now appropriate to assess deposition as a source to surface soil relative to other potential inputs, to put deposition in context. We consider inputs to U.K. surface soils (i.e., rural, urban), not contaminated land, industrial sites, and landfills, which are likely to be impacted by spillages, dumping, etc.

(a) Atmospheric Deposition. Deposition is a source to all agroecosystems (soils/crops/pasture) and non-agricultural land; fluxes are greater in urban areas, resulting in generally higher concentrations in milk from urban locations (30). The estimate of 1.4 kg ΣTEQ/year made above is taken here as the contemporary deposition flux to U.K. soils.

(b) Sewage Sludge Amendments. In the U.K. 1.1 million t (dry weight) of sewage sludge is generated each year, of which about 50% is applied to agricultural land and 8% is landfilled. PCDD/Fs are ubiquitous in sewage sludge. Estimates of the inputs of PCDD/Fs from sewage sludge applied to agricultural land in the U.K. have been made elsewhere (31) and are currently about 25 g ΣTEQ/year and 21 kg ΣPCDD/F per year. Interestingly, the TEQ input is only

about 1.8% of the estimated input derived from atmospheric deposition, but a more significant source of ΣPCDD/Fs (see Table 4), because sludge contains very high concentrations of non-2,3,7,8-substituted and/or low TEF-rated congeners (31, 32).

(c) Farm Yard Manures, Compost, and Paper Pulping Products. Compost is an important amendment of some agricultural soils, and recycled paper pulp is also used as a soil ameliorant in some areas of the country. These materials can contain low levels of PCDD/Fs (33). Farm yard manures (FYM) are also recycled to agricultural land and will presumably contain PCDD/Fs ingested but not absorbed by livestock and PCDD/Fs aerially deposited onto the manure while in storage.

General Comments. The information provided in this section further highlights the large number of uncertainties with regard to inputs of PCDD/Fs to the U.K. terrestrial environment. Despite this, at a national level, available data suggest that deposition is likely to be the most important source to rural and urban soils. Other sources contribute to the national inventory/burden in surface soils, but to a lesser extent. The estimates made here are summarized as follows: atmospheric deposition, 1.4 kg ΣTEQ/year; sewage sludge, 25 g ΣTEQ/year; other soil amendments (FYM, paper pulp, compost), unknown (maybe ~ few grams to tens of grams ΣTEQ/year).

As noted previously, the primary pathways of human dietary exposure to PCDD/Fs is air–deposition–plant–grazing animal–human diet. An increase in the ΣTEQ burden of soils will therefore not necessarily impact human exposure (although it may impact specific wildlife food chains). There are exceptions to this generalization, such as free range chickens whose intake may comprise 10% soil (34). But generally, unless grazing animals ingest substantial amounts

TABLE 5. Burden of PCDD/Fs in Different Environmental Compartments of the U.K.^a

	air (g)	water (g)	soil (case A) (kg)	soil (case B) (kg)	herbage (g)	inland sediment (g)	human (g)
2,3,7,8-TCDD	3.6	<0.54	3	5	4.3	7	<9.3
1,2,3,7,8-PeCDD	15	<0.74	5	7	4.6	21	20
1,2,3,4,7,8-HxCDD	21	0.67	17	28	5.6	21	32
1,2,3,6,7,8-HxCDD	42	1.49	46	83	17	98	159
1,2,3,7,8,9-HxCDD	36	0.94	13	20	12	23	24
1,2,3,4,6,7,8-HpCDD	449	5.57	562	860	197	1936	133
OCDD	1536	35	5125	7208	1541	8408	709
2,3,7,8-TCDF	41	0.59	32	57	57	98	<9.3
1,2,3,7,8-PeCDF	50	0.47	212	380	16	52	12
2,3,4,7,8-PeCDF	50	0.42	16	23	18	58	21
1,2,3,4,7,8-HxCDF	74	0.59	46	72	13	630	22
1,2,3,6,7,8-HxCDF	50	0.57	42	62	5.5	84	12
1,2,3,7,8,9-HxCDF	9	0.27	3	6	2.7		13
2,3,4,6,7,8-HxCDF	39	0.35	26	36	4.8	26	<18
1,2,3,4,6,7,8-HpCDF	155	2.65	196	251	77	470	30
1,2,3,4,7,8,9-HpCDF	17	1.09	45	92	6.6	24	<18
OCDF	121	6.31	902	1090	83		39
total TCDD	126	1.66	121	192	80	745	
total PeCDD	203	2.33	116	183	200	850	
total HxCDD	446	9.90	409	710	189	1141	
total HpCDD	827	10.02	1060	1570	434	4208	
total TCDF	733	5.45	361	581	228	1844	
total PeCDF	573	4.21	351	571	169	1726	
total HxCDF	444	4.46	471	794	79	2037	
total HpCDF	228	6.56	463	670	127	822	
total PCDD/F	5189	85	9380	13570	3131	21782	1261
total TEQ	76	0.94	69	111	32	177	50

^a All units are in g, except for the U.K. soil burden which is in kg. Assumptions: Concentrations reported in Table 4 are representative of rural and urban matrices for the whole of the U.K. The U.K. surface area is $2.5 \times 10^{11} \text{ m}^2$ (28), 90% of which is rural, and the remainder is urban. (a) Mixing height is 6 km (45). (b) Water comprises 1% of the U.K.'s total surface area. (c) Case A, soil depth is 5 cm; case B, soil depth is 5 cm, except for arable land where plow soil depth is 23 cm; soil bulk density is 1000 kg/m³. (d) Dry aerial biomass is 260 g/m². (e) Inland surface sediment comprises 1% of the U.K.'s total surface area (28), the majority of PCDD/Fs reside in the top 5 cm of the sediment profile, and sediment density is 0.13 g DW/cm³ (i.e., sediment moisture content is 87% and solids density is 1 g/cm³). (f) The U.K. population is 55 million; average body fat weight of 18.8 kg/person assumed.

of soil—and under routine agricultural practice in the U.K. they may, but usually do not (35, 36)—and absorb the PCDD/F on it, then the soil can be viewed as having a certain capacity to effectively 'sequester' PCDD/Fs by strong sorption/partitioning.

Given the dominance of deposition to agroecosystems, it is now appropriate to consider (1) the mass balance between emission and deposition and (2) the burden of PCDD/Fs in soils and in other compartments. As this section has shown, deposition can be assumed to contribute essentially all of the PCDD/Fs entering agricultural soils in rural and urban areas, except for unusual situations—e.g., soils situated in the proximity of point sources or accidental releases. This argument is supported by the broad consistency of the soil mixture in urban and rural areas except near known sources (24).

Burdens in the Terrestrial Environment

In this section, the burden of PCDD/Fs in different environmental compartments is estimated, enabling the loading in soil to be put in context and a comparison of the contemporary burden and projected cumulative inputs to be made later.

The contemporary U.K. burdens of PCDD/Fs and ΣTEQ in air, water, vegetation, soil, sediment, and selected biota are calculated by multiplying typical or representative concentrations for the different media, as detailed in Table 4, with volume/mass assumptions made for each compartment. The burdens are presented in Table 5. This exercise demonstrates the overwhelming dominance of the soil compartment in the total inventory. Over 99% of the U.K. terrestrial burden of ~ 70 –110 kg ΣTEQ is estimated to reside in soil. The biggest uncertainties over the soil burden concern:

(i) The assumption that all the PCDD/Fs reside in the top 5 cm of undisturbed soil (46). Another important factor is the PCDD/F levels in plowed agricultural land (soil plow depth ~ 20 cm; 47), which accounts for 29% of all U.K. land. Inclusion of a deeper mixing depth for this land category will raise the ΣTEQ levels up to 111 kg/year (Table 5), with 11 kg residing in urban soil; 68 kg in rural soil (i.e., nonarable to include permanent grassland and woodland); 32 kg arable soils; and an unknown quantity in contaminated sites. The precise burden is uncertain, but is probably in the region of 110 kg ΣTEQ nationally.

(ii) The absence of any U.K. data for PCDD/Fs in woodland or forest soils. Data from Baden-Württemberg (48) shows that such soils dominate the PCDD/F burden in that region of Germany, presumably because the forest canopy effectively scavenges airborne PCDD/Fs. For example, there are higher PCDD/F levels in forest soils relative to agricultural land (30 and 1.1 ng/kg, respectively) (48). As 10% of U.K. land is under forestry or woodland and PCDD/F burdens for woodland soils have not been included, the burden is likely to be underestimated. However, as PCDD/F congener and homologue group profiles in forest soils seem to differ from urban/rural soils (48), it is not currently possible to estimate the ΣTEQ of U.K. forest soils.

(iii) The lack of data for potential 'hot spots' of soil contamination. These have been shown to be important for the U.K. PAH inventory (49) and may be important for PCDD/Fs too. However, the focus of this paper is on the relationship between PCDD/F atmospheric sources and soil rather than on contaminated land affected by spillages/accidents etc., and it is therefore appropriate to ignore potential hot spot sites here.

Points i and ii are important considerations for the inventory, and it is conceivable that they could substantially increase the surface soil inventory estimate of 110 kg Σ TEQ used here.

It is now appropriate to consider the fate and behavior of the large PCDD/F burden in the soil system. Organic compounds may potentially be subject to several loss processes in soils, namely, biodegradation, volatilization, leaching, photochemical transformation, plant uptake, removal by grazing animals, irreversible binding and alteration (humification), and erosion. These loss processes are—collectively—‘slow’ and PCDD/Fs have long half-lives (see ref 31 for review). Measurements/estimates of persistence differ, but data for 2,3,7,8-TCDD indicate a half-life of at least 10 years, with the more chlorinated 2,3,7,8-substituted species probably being more persistent (31). Some authors suggest that PCDD/Fs may—to all intents and purposes—persist in soils ‘indefinitely’. McLachlan et al. (50) presented data on PCDD/F persistence in a long-term sewage sludge amendment trial; ‘effective’ half-lives for all the congeners were ~20 years, but these half-lives probably reflected the rate of physical movement of PCDD/F-contaminated soils out of the sludge-amended plots rather than biologically/chemically mediated losses. In summary, soils can probably be regarded as indicators of the cumulative atmospheric deposition falling on a unit area of land in the long-term, provided there has not been extensive disturbance of the soil (25).

Relationship between Deposition and Soil Burden

Earlier sections have shown that (1) atmospheric deposition supplies essentially all of the PCDD/Fs currently entering rural and urban soils nationally at the present time and (2) PCDD/Fs are extremely persistent in soils. It is therefore hypothesized that the contemporary PCDD/F burden of rural/urban U.K. soils is derived almost exclusively from cumulative atmospheric deposition over time (see also refs 25 and 26). Key questions arise in this context. First, how long have PCDD/Fs been deposited onto soils? Are they essentially all of recent anthropogenic origin or have there been important ‘natural’ inputs that are still present in soils from ‘pre-industrial’ times? Second, is there evidence that deposition fluxes to soils have changed over time as atmospheric sources have changed? Third, exactly how persistent are PCDD/Fs in soils, and can they be formed in soils from other compounds (including other PCDD/Fs)?

It is pertinent at this stage to consider the relationship between current deposition rates (from Table 3) and the soil burden (Table 5) for rural and urban scenarios. This enables the time of accumulation to be calculated, assuming that (a) current deposition fluxes are a representative time-average and (b) there has been no degradation of PCDD/Fs in the soil. This shows interesting patterns between PCDD/F homologue groups (see Table 6). A total of 30–40 years would be necessary at the current rate of deposition to have reached current tetra- and penta-CDD/F soil burdens, while for the hepta- and octa-CDD/Fs it would take between 200 and 800 years for urban soils. This suggests either that the mixture of PCDD/Fs has changed over the years and perhaps higher molecular weight congeners were released at relatively higher concentrations in the past or that there are other sources of the hepta- and octa-CDD/Fs to urban soils. Table 6 shows a difference between the accumulation time for rural and urban soils, namely, that it would have taken longer to reach the current urban levels relative to the rural ones, or that the rural/urban flux measurements used here are disproportionate.

It is now appropriate to refine the deposition input and the soil fate scenario considered here, by considering the issues of natural versus anthropogenic inputs and changing

TABLE 6. Calculation of Accumulation Time To Reach Current PCDD/Fs Soil Burdens at Rural and Urban Locations Assuming That Contemporary Deposition Fluxes Have Remained Constant^a

	accumulation time (years) to reach current soil burden	
	urban location	rural location
Σ TCDD	34	31
Σ PeCDD	36	31
Σ HxCDD	72	38
Σ HpCDD	246	30
OCDD	574	45
Σ TCDF	44	24
Σ PeCDF	45	40
Σ HxCDF	92	45
Σ HpCDF	206	30
OCDF	826	37
Σ PCDD/F	225	38
Σ TEQ	61	39

^a Contemporary deposition fluxes as presented in Table 3; soil burden estimated for the top 5 cm layer by assuming that the soil bulk density is 1000 kg/m³.

deposition fluxes over time as a prelude to a simple model of air–soil interactions over time using different scenarios.

(a) Natural Versus Anthropogenic Inputs. It has been proposed that—because PCDD/Fs are formed during combustion—they will have been present in the environment since the ‘advent of fire’ (51). It should be noted that there is still ambiguity over some of the data used in support of this hypothesis, although it is generally accepted that trace quantities of PCDD/Fs were released in the past from combustion and that releases became greater during the industrial period (52). Data from sediment cores taken in various industrialized countries support the view that recent anthropogenic inputs of PCDD/Fs (recorded in recently deposited surface sediments) greatly exceed natural inputs (detectable in older deeper sediment layers) (see refs 52–54). However, because soil surface layers reflect cumulative deposition (whereas sediment layers do not), it may be appropriate to consider that surface soils had a certain base level of pre-industrial PCDD/Fs that has been substantially supplemented by recent inputs (47). Given the range of combustion activities that are contemporary sources of PCDD/Fs and the long history of industrial activity in the U.K., it is likely that U.K. soils have had a base level of PCDD/Fs prior to the large-scale inputs through this century (47, 52). In summary, considerable uncertainty still surrounds the issue of pre- and post-industrial PCDD/Fs, and it is therefore appropriate to consider more than one input scenario in the modeling exercise later.

(b) Changing Deposition Fluxes over Time. Deposition fluxes have changed over time, most notably in recent decades. There is good evidence for an increase in deposition in industrialized countries and other media commencing in the 1930/1940s from several studies on sediment cores (see refs 52–54). The general picture is of an increase in PCDD/F fluxes through the 1950/1960s, peaking in the late 1960s/early 1970s, followed by a decline through the 1980s/early 1990s. Other studies have reported direct evidence for a recent decline in air concentrations in industrialized countries (40, 52, 55). This general trend is complicated, because some of the long-term trend data show changes in the mixtures of PCDD/Fs over time. For example, archived grass samples from 1861 to 1945 were dominated by PCDD/Fs presumed to have been derived from combustion of coal and wood, while post-1946 samples had a greater influence of PCDD/Fs, which were probably derived from the production and use of chloroaromatic compounds (40). This makes it difficult to derive an estimate of Σ TEQ inputs over recent decades.

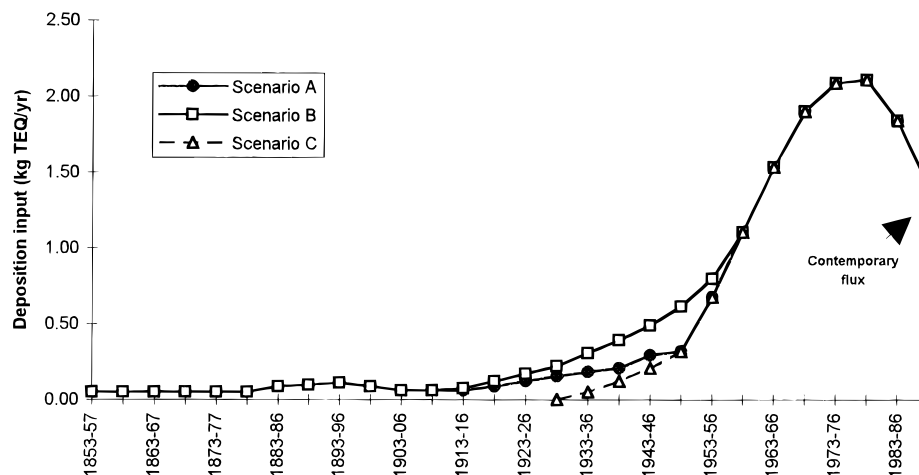


FIGURE 1. Changing PCDD/F deposition inputs since 1850. Scenario A: Pre-industrial base levels, supplemented after 1930 by the CA product/use inputs. Deposition data inputs calculated from changes in sediment core PCDD/F levels; mean values calculated from those reported by Czuczwa et al. (56), Smith et al. (57), Schramm et al. (58), and Beurskens et al. (59) from data bulked into 5 yearly intervals. These were then normalized to the contemporary deposition data reported in Table 2 to predict past deposition fluxes. Sediment cores were assumed to be representative of general/urban sites from western countries (USA and Germany). Scenario B: Pre-industrial level, supplemented initially at the turn of the century by large-scale coal burning/metal mining/smelting in the U.K. and after 1930 as for scenario A. Scenario C: No pre-CA inputs.

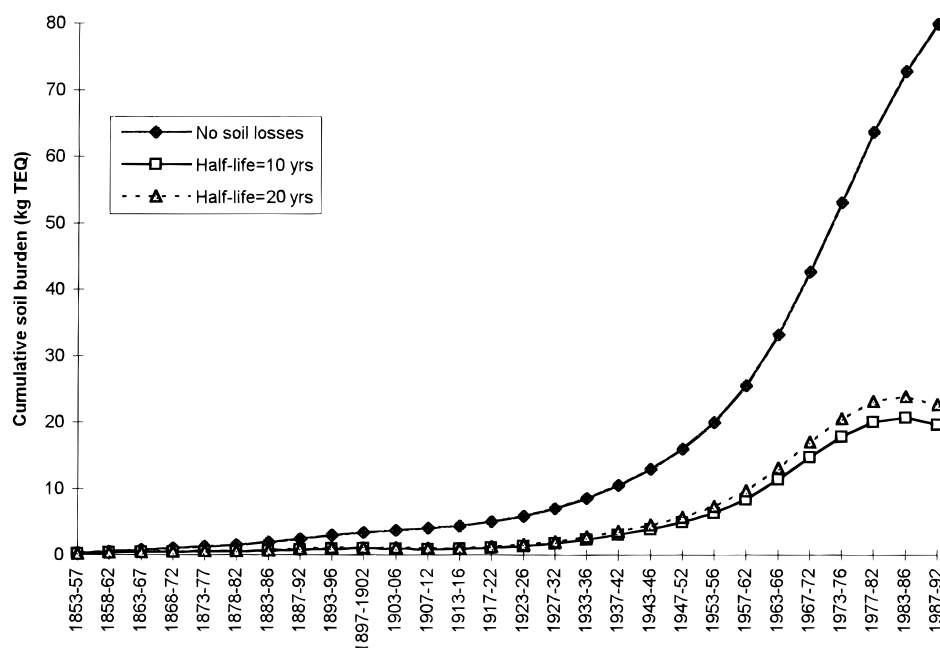


FIGURE 2. Cumulative soil burden assuming (1) no soil losses and (2) soil half-lives of 10 and 20 yr. Soil burdens and half-lives have been estimated solely from annual deposition fluxes using TEQ data from Figure 1, based on average 5-yr intervals.

(c) Simple Modeling of Input/Loss Scenarios. Figure 1 presents three different deposition flux scenarios that may be representative of inputs between 1850 and 1995. Scenario A envisages a baseline input of Σ TEQ due to combustion sources between 1850 and 1930, followed by an increase post-1930 associated with the production, use, and disposal of CA compounds. Scenario B shows a baseline input from 1850 (when U.K. industrialization expanded), supplemented initially by increased fossil fuel combustion inputs and later by the CA signal. Scenario C considers no pre-industrial PCDD/Fs, just the CA signal. In each case, the fluxes between 1960/1970 and 1995 are modeled the same, based on sediment core data (see ref 52). They differ, however, in the scenarios modeled between 1850 and the late 1960s (see Figure 1); note that 1850 was taken as the starting date for scenarios A and B because PCDD/Fs measurements have been made in archived sediment core samples back to that time. Each curve is normalized relative to the estimated contemporary (early 1990s) national deposition flux of 1.4 kg Σ TEQ/year derived

earlier in the paper. The integral of these curves gives three estimates of the cumulative depositional input (kg Σ TEQ) falling onto the U.K. land surface, ranging from 67 kg Σ TEQ (scenario C) through 74 kg Σ TEQ (scenario A) to 80 kg Σ TEQ (scenario B) between 1850 and the present day. In other words, the scenarios give similar cumulative deposition inputs. Furthermore, they compare reasonably well with the Σ TEQ burdens estimated for soils in Table 3 (110 kg), assuming that PCDD/Fs persist indefinitely in soils. If degradation of PCDD/Fs in soils is modeled with half-lives of either 10 or 20 years, the Σ TEQ cumulative soil burdens shown in Figure 2 are obtained. If PCDD/F are assumed to degrade, the Σ TEQ burdens are lower than the estimates made earlier from contemporary soil data. Discrepancies between these values could be due to several factors, notably (1) errors in the deposition flux estimates; contemporary fluxes are based on very few sampling sites, and may therefore not be representative (see earlier discussion); (2) errors in the U.K. soil burden estimation; (3) errors in the historical input models

used. Interestingly, if the soil half-life of PCDD/Fs is assumed to be infinite (scenario 1 in Figure 1), a cumulative soil burden (concentration) similar to that measured in archived soils from southeast England is obtained (47). Further data on the historical input profile of PCDD/Fs to the U.K. environment would be very valuable in helping to reconstruct changes to the environmental burden of these.

Speculation about the Future

The recent and projected future introduction of more stringent controls on PCDD/F emissions is predicted to bring about a marked reduction in PCDD/F emissions from industrial processes. Under Integrated Pollution Control (IPC) in the U.K., all prescribed processes and substances require authorization by HMIP (now the U.K. Environment Agency). Currently, 85% of PCDD/F emissions from industrial processes are believed to arise from prescribed processes, which will have to conform to an emission standard over the next few years. It has been estimated that by the year 2006 primary emissions will have declined by ~70%; from 560–1100 g Σ TEQ/year to 110–350 g Σ TEQ/year (2). A significant decline in ambient air concentrations might therefore be expected following the implementation of abatement measures. While the soil burden may not decline in the short to medium term due to the extreme persistence of PCDD/Fs in this matrix, a greater reduction would be expected in vegetation levels and therefore, by inference, a continued decline in human exposure. The environmental significance of the soil burden remains uncertain at the present time. Data are needed to aid an evaluation of the bioavailability of PCDD/F residues that are held in the soil over long periods of time (60, 61) to assess their potential to impact human and wildlife food chains.

Identification of Research Needs and Uncertainties

This paper has emphasised a number of key areas where major uncertainties remain concerning the environmental sources, fate, and behavior of PCDD/Fs. These are (i) the significance of primary and possible secondary sources of PCDD/Fs; (ii) reliable measurements of atmospheric concentrations and deposition fluxes of PCDD/Fs in rural and urban areas; (iii) data on the relative importance of atmospheric deposition and other sources as an input to surface soils; (iv) data on the PCDD/F burden of forest soils and soil depth distribution data, to improve the estimates of the contemporary soil PCDD/F burden; (v) measurements of the long-term fate, behavior, persistence, and bioavailability of PCDD/Fs in soils; (vi) assessments of the changes in atmospheric deposition flux over time; and (vii) rigorous studies to quantify the significance of natural/pre-industrial PCDD/F inputs relative to anthropogenic inputs.

Literature Cited

- U.S. Environmental Protection Agency. *Estimating Exposure to Dioxin-like Compounds*; External review draft; Office of Health and Environmental Assessment, Office of Research and Development, U.S. Government Printing Office: Washington, DC, Aug 1994; EPA/600/6-881/005Ca.
- HMIP. *A Review of Dioxin Emissions in the U.K.* Report to Her Majesty's Inspectorate of Pollution; HMSO: London, 1995; Research Report DoE/CPR2/41/1/38.
- Lorber, M. N.; Cleverly, J.; Schaum, L.; Phillips, L.; Schweer, G.; Leighton, T. *Sci. Total Environ.* **1994**, *156*, 39–65.
- McLachlan, M. S. *Environ. Sci. Technol.* **1996**, *30*, 252–259.
- Meharg, A. A.; Osborn, D. *Nature* **1995**, *375*, 353–354.
- Harrad, S. J.; Jones, K. C. *Sci. Total Environ.* **1992**, *126*, 89–107.
- Marklund, S.; Tysklind, A.; Andersson, R.; Ljung, K.; Rappe, C. *Chemosphere* **1989**, *18*, 1031–1038.
- Consultants in Environmental Sciences Ltd. *Timber preservation chemicals*. Volume 1a-final report. Contract PECD 7/7/238 for Department of the Environment (DoE): 1988.
- Hobbs, S. *Environmental Hazard Assessment: pentachlorophenol*; Directorate for Air, Climate and Toxic Substances, Department of the Environment: Washington, DC, 1991; EPTS/10D.
- Hagenmaier, H.; Brunner, H. *Chemosphere* **1987**, *16*, 1759–1764.
- Eitzer, B. D.; Hites, R. A. *Environ. Sci. Technol.* **1987**, *21*, 924.
- Kao, A. S.; Venkataraman, C. *Chemosphere* **1995**, *31*, 4317–4331.
- Harner, T.; Mackay, D.; Jones, K. C. *Environ. Sci. Technol.* **1995**, *29*, 1599–1606.
- Welsch-Pausch, K.; McLachlan, M. S.; Umlauf, G. *Environ. Sci. Technol.* **1995**, *29*, 1090–1098.
- Duarte-Davidson, R.; Clayton, P.; Coleman, P.; Davies, B. J.; Halsall, C. J.; Harding-Jones, P.; Pettit, K.; Woodfield, M. J.; Jones, K. C. *Environ. Sci. Pollut. Res.* **1994**, *1*, 262–270.
- Hippelein, M.; Kaupp, H.; Dorr, G.; McLachlan, M.; Hutzinger, O. *Chemosphere* **1996**, *32*, 1605–1616.
- Karickhoff, S. W. *Chemosphere* **1981**, *10*, 833–849.
- Mackay, D.; Shiu, W.; Ma, K. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. II PAHs and PCDD/Fs*; Lewis Publishing Co.: Chelsea, MI, 1992.
- Gobas, F. A. P. C. *Sci. Total Environ.* **1991**, *109/110*, 89–104.
- Hippelein, M.; McLachlan, M. *Measuring the fugacity of semi-volatile organic compounds in soil*. Transcript from a poster presented at the SETAC World Conference in Vancouver, 1995.
- Beck, A. J.; Wilson, S. C.; Alcock, R. E.; Jones, K. C. *Crit. Rev. Environ. Sci. Technol.* **1995**, *25*, 1–43.
- Fiedler, H. *Organohalogen Compd.* **1993**, *11*, 221–228.
- Kwok, E. S. C.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **1995**, *29*, 1591–1598.
- HMIP. *Determination of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in soils*. 2nd Technical Report to Her Majesty's Inspectorate of Pollution; HMSO: London, 1995.
- Brzuzy, L. P.; Hites, R. A. *Environ. Sci. Technol.* **1995**, *29*, 2090–2098.
- Brzuzy, L. P.; Hites, R. A. *Environ. Sci. Technol.* **1996**, *30*, 1797–1804.
- Hiester, E. R.; Bruckman, P.; Bohn, R.; Eynck, P.; Gerlach, A.; Milder, A.; Ristow, W. *Organohalogen Compd.* **1993**, *12*, 147–150.
- Geodata. *The World Almanac Gazetteer*, 1st ed.; Kurian, G. T., Ed.; Gale Research Company: Detroit, MI, 1983.
- Thomas, V. M.; Spiro, T. G. *Environ. Sci. Technol.* **1996**, *30*, 824–834.
- MAFF: Ministry of Agriculture, Fisheries and Food. *Dioxins in Food*; Food Surveillance Paper No. 31; HMSO: London, 1992.
- Jones, K. C.; Sewart, A. *Dioxins and furans in sewage sludges*; HMSO: London, 1995; DOE/U.K.WIR. DOE Ref: EPG 1/9/13.
- McLachlan, M.; Horstmann, M.; Hinkel, M. *Sci. Total Environ.* **1996**, *185*, 109–123.
- Fridke, K.; Vogtmann, H. *Toxicol. Environ. Chem.* **1994**, *43*, 95–114.
- Stephens, R. D. *Sci. Total Environ.* **1995**, *175*, 253–273.
- Fries, G. F.; Paustenbach, D. J. *J. Toxicol. Environ. Health* **1990**, *29*, 1–43.
- Wild, S.; Harrad, S.; Jones, K. C. *Environ. Pollut.* **1994**, *83*, 357–369.
- König, J.; Theisen, J.; Gunther, W. J.; Liebl, K. H.; Buchen, M. *Chemosphere* **1993**, *26*, 851–861.
- Rappe, C.; Kjeller, L.-O.; Andersson, R. *Chemosphere* **1989**, *19*, 13–20.
- Ball, D. J.; Creaser, C. S.; Foxall, C.; Lovett, A. A. *Polychlorinated biphenyls, dioxins and furans in the Pontypool environment*; Research Report 21; Fifth Report to the Welsh Office; 1994; ISBN 1 873933 55X.
- Kjeller, L.-O.; Jones, K. C.; Johnston, A. E.; Rappe, C. *Environ. Sci. Technol.* **1996**, *30*, 1398–1403.
- Sewart, A. P.; Harrad, S. J.; McLachlan, M. S.; McGrath, S. P.; Jones, K. C. *Chemosphere* **1995**, *30*, 51–67.
- DoE. *Report on the examination of sewage sludges for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans*; HMSO: London, 1993.
- Rose, C. L.; McKay, W. A. *Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the aquatic environment. Field and experimental studies*; AEA Technology, National Environmental Technology Centre: 1994; Contract AEA/CS/18358014/001/ISSUE2.
- Duarte-Davidson, R.; Harrad, S.; Allen, S.; Sewart, A. S.; Jones, K. C. *Arch. Environ. Contam. Toxicol.* **1993**, *24*, 100–107.
- Wittlinger, R.; Ballschmiter, K. *Chemosphere* **1987**, *16*, 2497–2513.
- Di Domenico, A.; Silvano, V.; Viviano, G.; Zapponi, G. *Ecotoxicol. Environ. Saf.* **1980**, *4*, 327–338.

- (47) Kjeller, L.-O.; Jones, K. C.; Johnston, A. E.; Rappe, C. *Environ. Sci. Technol.* **1991**, *25*, 1619–1627.
- (48) Hagenmaier, H.; Krauss, P. *Organohalogen Compd.* **1993**, *24*, 81–84.
- (49) Wild, S. R.; Jones, K. C. *Environ. Pollut.* **1995**, *88*, 91–108.
- (50) McLachlan, M. S.; Sewart, A. P.; Bacon, J.; Jones, K. C. *Environ. Sci. Technol.* **1996**, *30*, 2567–2571.
- (51) Bumb, R. R. *Science* **1980**, *210*, 385–390.
- (52) Alcock, R. E.; Jones, K. C. *Environ. Sci. Technol.* **1996**, *30*, 3133–3143.
- (53) Cleverly, D. H.; Monetti, M.; Phillips, L.; Cramer, P.; Heit, M.; McCarthy, S.; O'Rourke, K.; Stanley, J.; Winters, D. *Organohalogen Compd.* **1996**, *28*, 77–82.
- (54) Hagenmaier, H.; Walczok, M. *Organohalogen Compd.* **1996**, *28*, 101–104.
- (55) Hiester, E.; Bruckman, H.; Bohn, R.; Eynck, P.; Gerlach, A.; Milder, A.; Ristow, W. *Organohalogen Compd.* **1995**, *24*, 147–152.
- (56) Czuczwa J. M.; McVeety, B. D.; Hites, R. A. *Science* **1984**, *226*, 568–569.
- (57) Smith, R. M.; O'Keefe, P. W.; Hilker, D.; Bush, D. R.; Connor, S.; Liddle, M. *Organohalogen Compd.* **1993**, *20*, 215–218.
- (58) Schramm, K. W.; Jutter, I.; Winkler, R.; Steinberg, C.; Kettrup, A. *Organohalogen Compd.* **1994**, *20*, 179–182.
- (59) Beurskens, J. E. M.; Winkels, H.; de Wolf, J.; Dekker, C. G. C. *Environ. Toxicol. Chem.* **1993**, *12*, 1549–1566.
- (60) Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 2713–2717.
- (61) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1–11.

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