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# Dioxins in the Environment: A Review of Trend Data

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A comprehensive review of available PCDD/F time trend data is presented. This focuses on industrialized countries, drawing heavily on those countries that have been actively involved in PCDD/F monitoring and research, notably Germany, the United States, Sweden, The Netherlands, and the U.K. Information on temporal trends comes from the analysis of dateable deposits (e.g., sediments), retrospective analysis of preserved or archived samples, and ongoing monitoring programs. The data on changes in air concentrations, deposition, sediments, soil, biota, food, and human tissues are reviewed. The evidence for natural input/formation of PCDD/Fs is also briefly reviewed and discussed. Human activity has dominated PCDD/F inputs to the environment this century. Conceptually, it is probably appropriate to consider a 'pulse' of PCDD/Fs arising from human activities entering the environment in the 1930/1940s, peaking in the 1960/1970s, and continuing to a lesser degree today. A series of measures introduced in the past, recently, and anticipated for the future have reduced emissions to the atmosphere of industrialized countries and are projected to continue to reduce emissions over the coming decade. Comprehensive monitoring programs are required to confirm the interpretation of past changes and projected future declines presented here.

## Introduction

The polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are two groups of tricyclic, planar, aromatic compounds. They are nonpolar, poorly water-soluble, lipophilic (fat loving), stable chemicals. PCDD/Fs are not produced intentionally but are released into the environment in ultra-trace amounts from various combustion processes and as a result of their occurrence as unwanted byproducts in various chlorinated chemical formulations (e.g., pentachlorophenol, PCP) (see refs 1 and 2 for a review of sources).

To set the current environmental inputs and loadings of PCDD/Fs in context and to assess the significance of any future declines, it is appropriate to examine the information available on past changes. This paper therefore presents a comprehensive review of available PCDD/F time trend data. This draws heavily on those industrialized countries that have been actively involved in PCDD/F monitoring and research, notably Germany, the United States, Sweden, The Netherlands, and the U.K. It is also appropriate to discuss other issues. One such topic is the debate over whether PCDD/Fs are formed naturally, thereby providing a base level of 'pre-industrial' PCDD/Fs in the environment. This is important in providing context to current levels and to expectations about future levels in light of source reduction measures.

Another important theme relates to the *mixture* of PCDD/Fs present in environmental samples and how these may have changed over time. Different PCDD/F sources may be characterized by different PCDD/Fs-specific congener patterns, often the non-2,3,7,8-substituted congeners may be used as markers or 'fingerprints' of specific sources to the environment (e.g., ref 3). Some environmental samples may reflect these differences, provided that the PCDD/F mixture remains largely unaltered by degradation and weathering processes. This issue can become complicated, however, because sources and emission rates of PCDD/Fs have presumably changed over time.

**PCDD/F Mixtures in Sources and the Environment.** The mixture or 'pattern' of PCDD/Fs can differ between sources, and this can be reflected in air, soils, vegetation, and sediments impacted by the source(s). Differences in mixtures may be apparent when the data are plotted as homologue groups (the homologue profile), as the ratio of homologues, or as the 2,3,7,8-substituted PCDD/Fs. Ideally, however, all three approaches should be considered (3–5). Because different sources introduce complex mixtures of PCDD/Fs into the environment, no single congener can be used to attribute the occurrence of PCDD/F in a sample to a specific source (3). Data interpretation therefore involves finding structure in large multivariate (congener/homologue) sets of numerical information. This often involves recourse to principal components analysis (PCA) or cluster analysis techniques (5–7) as tools for identifying correlations between patterns and sources.

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The patterns of PCDD/Fs found in air, soils, vegetation, and sediments are likely to be similar in an area where a strong atmospheric signal reflects a source or mixture of sources; this will include both non-2,3,7,8-substituted and 2,3,7,8-substituted PCDD/Fs. However, biotic samples tend to only contain the 2,3,7,8-substituted congeners, since the non-2,3,7,8-substituted congeners are readily metabolized. These observations suggest the following: (a) Abiotic media may ultimately be helpful in providing clues as to the significance of different PCDD/F sources. This will require reliable source characterization of the PCDD/F mixture and detailed knowledge of the environmental fate and persistence of individual congeners. (b) Biotic media point to the existence of similar sources of PCDD/Fs into the environment of the industrialized countries.

**Analytical Problems.** The trace level analysis of PCDD/Fs in environmental samples presents a significant analytical challenge. Different laboratories have developed different procedures for the determination of PCDD/Fs in different sample matrices and may have modified them over time. In addition, considerable advances have been made over the last 20 years in high-resolution mass spectrometry, with marked improvements in detection limits being achieved. All these factors lead to problems when comparing data collected at different points in time and analyzed by different laboratories using different methods. These factors need to be borne in mind when comparing data obtained in long-term monitoring programs. For example, some countries have programs on the PCDD/F content on human milk, foodstuffs, or air where data from the 1980s is compared with data from the 1990s (see later). It is necessary for the laboratory concerned to be able to demonstrate comparability between the two data sets. This may be done by re-analysis of a subset of samples from the first batch of samples with the second batch. In addition, laboratory intercomparison exercises and various intralaboratory procedures can provide a good check on performance.

The World Health Organisation (WHO) initiated an interlaboratory calibration on the analysis of PCDD/Fs in human milk and blood that included 19 laboratories from 14 countries (8), the largest controlled intercalibration exercise to date. The study showed that the laboratory is the single most important determinant of data precision and accuracy. Factors such as cleanup method, replicate number, use of high- or low-resolution mass spectrometry, and sample matrix were not correlated with the accuracy or precision of reported values. Rather, the laboratories that had well-established and carefully followed quality assurance programs produced superior results. Both milk and blood analyses from 11 of the 16 laboratories showed similar mean coefficients of variation (CoVs) for both repeatability and reproducibility of between 20 and 30%. The remainder had CoVs significantly higher, ranging from 55% to 130%. It is important to bear these factors in mind when examining time trend data obtained as part of an ongoing program by a given laboratory.

The choice of media for studying PCDD/F trends over long time scales may itself determine the accuracy of the final data. In depositional environments (such as sediments), annual inputs can accumulate. Nevertheless, the PCDD/F flux in any one year may be very small and difficult to detect. However, surface soils effectively reflect a longer-term integral of deposition; atmospherically derived PCDD/Fs are persistent in soils, and soils have a large capacity for

PCDD/F storage and are the major environmental repository for PCDD/Fs. Consequently, it may be easier to detect PCDD/Fs in old (archived) soils than ancient sediment slices because any pre-industrial emissions would accumulate there. Similarly, it may be easier to detect trace concentrations of PCDD/Fs in preserved fatty biological specimens because of the bioconcentration phenomena.

**Environmental Matrices.** The following section reviews and evaluates each environmental media used for PCDD/F time trend studies. The merits and limitations of the various techniques employed to obtain data on PCDD/F time trends are briefly discussed at the beginning of each section as a prelude to a more detailed examination of the data itself.

**Sediment Record—Evidence of Long-Term Change.** Depositional media such as sediment cores (lacustrine, estuarine, and marine), polar ice, and peat profiles have all been used in historical pollutant monitoring studies (9), but only sediment cores appear to have been used for PCDD/Fs to date. Dated sediment cores have the potential to provide detailed chronologies of pollutant input as long as resuspension, bioturbation, biotransformations, molecular diffusion, and transport with infiltrating water are (or may be considered to be) negligible. However, there is some disagreement in the literature over the importance of biotransformations. On the one hand, Kjeller and Rappe (10) reported that PCDD/Fs in buried sediments from the Baltic Proper were very stable, with PCDF half-lives decreasing with increasing level of chlorination. OCDF had the lowest value but was still very persistent, with a half-life of 30 years. In contrast, Beurskens *et al.* (11) reported microbially mediated anaerobic dechlorination of 1,2,3,4-TCDD in sediments in the River Rhine. *In situ* reductive dechlorination of PCDD/Fs spiked into sediments has also been observed by Adriaens *et al.* (12). Segstro *et al.* (13) attributed a decline of PCDD spiked into sediments to diffusion of DOC-associated PCDDs in pore water.

The majority of temporal trend studies using lake sediment cores have been carried out in the North American Great Lakes (10, 11, 14–21). Data from these studies are generally presented as either  $\Sigma$ PCDD/F, total homologue group, or  $\Sigma$ TEQs, with very little congener-specific data.

**North American Studies.** Czuczwa *et al.* (14) were probably the first authors to report temporal PCDD/F trends in sediments. They studied inputs to the core from Lake Siskiwit, a remote site on Isle Royale in Lake Superior, which only receives inputs via atmospheric deposition (i.e., no direct discharges). In slices of the core dated as pre-1940 PCDD/Fs were 'virtually absent' when quantified using the relatively low-resolution GC/MS available in the authors' laboratories at the time (14). In contrast, surface sediment slices contained the full range of PCDD/F homologues, dominated by OCDD and HpCDDs. Czuczwa and Hites (22) subsequently published more detailed data for Siskiwit Lake, in which the  $\Sigma$ PCDD/F flux to the sediment rose from  $<5 \text{ pg cm}^{-2} \text{ year}^{-1}$  pre-1940 to peak at ca.  $30 \text{ pg cm}^{-2} \text{ year}^{-1}$  in the late 1960s/early 1970s (see Figure 1a). There was some evidence of a decline between the 1960/1970s and the mid-1980s. They also presented evidence of a similar trend, but much higher fluxes, to a core from Lake Erie. Data cores from Lake Huron, Lake Erie, and Lake Ontario (22, 23) all showed a similar trend.

Smith and co-workers have published a series of papers on the historical record of PCDD/F deposition preserved in the sediments of the northeastern United States (17, 18). Their early work (17) focused on Green Lake in New York

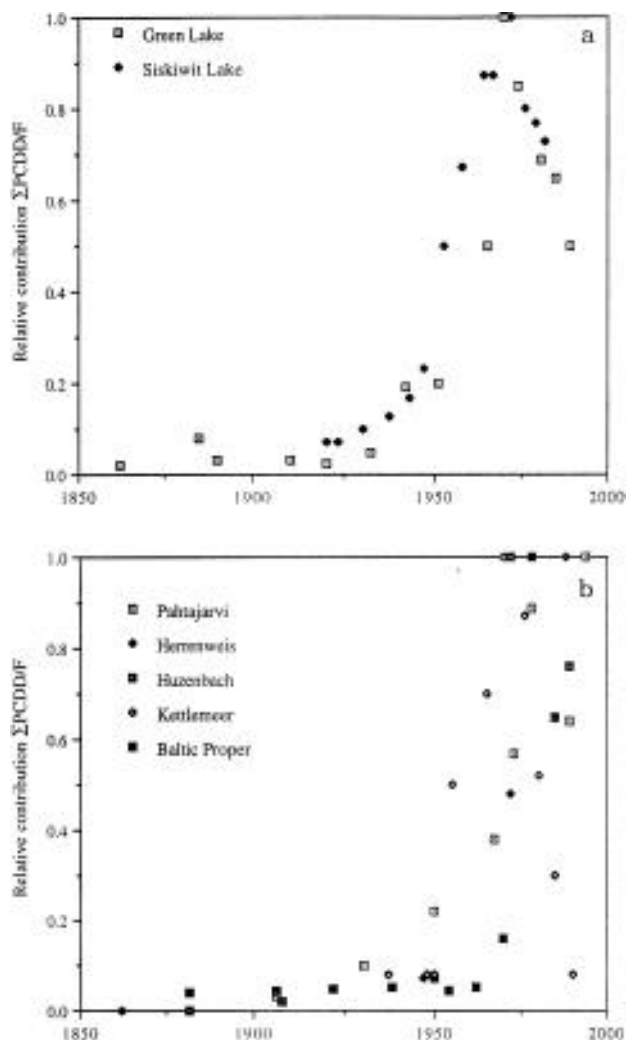


FIGURE 1. (a) Generalised plot of  $\Sigma$ PCDD/F trends from Green Lake and Siskiwit Lake. Data scaled relative to the peak year (set at 1.0) in each study. (b)  $\Sigma$ PCDD/F trends from European sedimentary studies. Data scaled relative to the peak year (set at 1.0) in each study.

State, which is located in a rural setting with no known sources of local PCDD/F contamination. This lake has little or no mixing between sediment layers, with stratified compact sediment that is ideal for dating purposes. In the sediment deposited prior to 1900, Smith *et al.* noted that there was little or no PCDD/F (concentrations not reported) in the Green Lake sediments. However, increased fluxes began in the 1930s, continued to increase through the 1940s and 1950s, reaching a sharp peak in the 1960s when  $\Sigma$ PCDD/F concentrations reached a maximum of  $\sim 1550$  ng/kg (pre-1900 values were  $\leq 10$  ng/kg). The concentrations then declined, with the surface (1986–1990) sample containing ca. 50% of the peak value (750 ng/kg). PCDDs dominated the mixture of PCDD/Fs in recent samples, with OCDD predominating in a mixture that remained constant post-1970. These workers later published a somewhat more detailed account of their data from Green Lake (17). Here they noted that PCDD/F ‘were present in sediment from 1860, although the concentrations were very low’ (at or below 10 pg/g). They also adjusted the dating profile, indicating that they now believed the onset of the rise in concentrations commenced after 1916–1923.

Later work on the Hudson River, New York (18), supported the earlier trend data from Green Lake. The

oldest sediment ( $\sim 1907$ –1924) contained  $< 1100$  ng of  $\Sigma$ PCDD/F/kg, with the highest concentrations in subsurface sediments dated between 1950 and 1980. OCDD again dominated the PCDD/F content; there were relatively small quantities of the tetra- to hexa-CDD/Fs and significant quantities of the Hp- and OCDFs. These observations concur with those of Hites and co-workers discussed earlier.

Pearson and Swackhamer (16) presented summary data from an important study spanning several sites in the Great Lakes region (Lakes Superior, Michigan, and Ontario). In addition, cores from control inland lakes, assumed to receive their inputs from only the atmosphere, were analyzed. Their study was in broad agreement with the earlier U.S. work, namely, (i) most of the cores exhibited maximum subsurface concentrations in the early-to-mid 1970s; (ii) accumulation onset occurred in the 1930–1940 horizon for all lakes; (iii) remote lakes have received lower inputs ( $\sim 5$ – $10$  pg  $\text{cm}^{-2}$  year $^{-1}$  at the peak), and anthropogenic impacted lakes have received higher inputs ( $\sim 300$ – $575$  pg  $\text{cm}^{-2}$  year $^{-1}$  peak input to Lake Ontario); (iv) current inputs to Lakes Ontario and Michigan have fallen by  $\sim 50\%$  from the 1970s; (v) the deepest slices of the cores contained low but detectable quantities of PCDD/Fs (R. F. Pearson, personal communication, 1995); (vi) Lake Ontario had a different homologue profile from the other studies, indicating significant nonatmospheric sources to the lake. Figure 1a presents a summary ‘input  $\Sigma$ PCDD/F profile’ from the North American studies. Some of the papers reported sediment concentrations; others reported fluxes. Figure 1a therefore simply normalizes the peak input in each study to 1.0 and scales other data to that point. The picture is broadly consistent between study locations.

**European Studies.** In addition to their U.S. studies, Czuczwa *et al.* (24) also investigated PCDD/F time trend profiles in three Swiss lakes. They used annually laminated (and therefore reliably dated) cores sampled from Lakes Zurich, Baldeg, and Lugano. PCDD/Fs were not detected above the blank controls in any of the pre-1945 samples. Thereafter, concentrations increased, but with no evidence of a decline post-1960/1970s. The authors commented on a similarity in the mixture of PCDD/Fs detected in the Swiss and U.S. cores and suggested that this implied similar sources to the environment in both regions. Hagenmaier *et al.* (19) studied a core collected from Lake Constance in 1982 and detected PCDD/Fs in the oldest (1945–1954) slice. Concentrations increased significantly between 1955 and 1976 and decreased in the 1976–1981 layers. Beurskens *et al.* (11) studied a 50-year core taken from Lake Ketelmeer, a sedimentary area of the River Rhine in The Netherlands. They presented congener-specific data for three slices, dated as 1945, 1965, and 1985. 2,3,7,8-TCDD showed a dramatic increase and subsequent decrease, ranging from  $< 10$  ng/kg in 1945 and 1985 to 360 ng/kg in 1965. By comparing the core data with that from an air-dried sample collected in 1972, these authors argued that there was evidence for post-depositional microbially mediated dechlorination of some of the higher chlorinated CDD/Fs.

Schramm *et al.* (20) presented data for two lakes in the Black Forest, Germany. In one core (Lake Herrenwiesersee), the surface (1983–1992) layer contained about twice the  $\Sigma$ TEQ of the 1960–1984 layer. Pre-1960 layers contained  $< 10\%$  of the maximum. Kjeller and Rappe (10) obtained a laminated marine core from the Baltic Proper, off the coast of Sweden. PCDD/Fs were detected in all the 1882–1962 slices at 92–234 ng of  $\Sigma$ PCDD/F/kg and did not

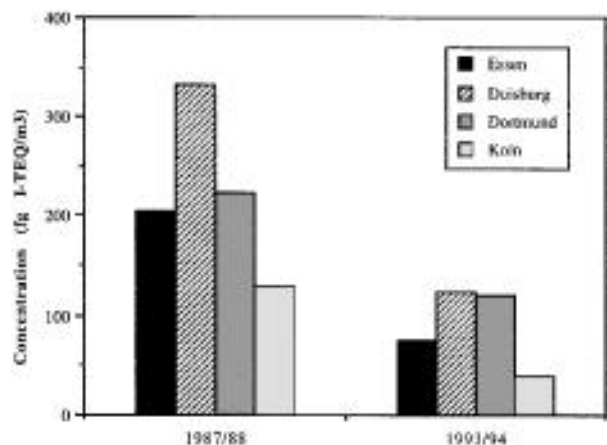


FIGURE 2. Reduction of  $\Sigma$ PCDD/F concentrations in the ambient air of four cities in North-Rhine-Westphalia, Germany.

increase until the 1970–1985 slices (520–1800 ng/kg). The  $\Sigma$ PCDD/F content of the 1985 slice was somewhat lower than that of the 1978 slice. Changes in the homologue distribution were noted by the authors and discussed in terms of possible changes in petroleum, coal and wood combustion activities, paper pulping activities around the Baltic, and use of PCP.

Vartiainen *et al.* (21) presented data from two small sub-Arctic lakes in Lapland, northern Finland. The trends noted here were similar to those reported by Kjeller and Rappe (10), with extremely low (2–20 ng of PCDD/F/kg) concentrations between 1880 and 1965. However, the authors do not present data to enable fluxes to the cores to be determined and the trends to be discussed in a meaningful way.

The only U.K. data published to date presents homologue profiles for two dated slices of a core sampled from Lake Windermere in the English Lake District (15). In 1946–1950, the PCDFs were a significant fraction of the  $\Sigma$ PCDD/F deposition to the lake, while the 1988–1992 slice was dominated by OCDD (and HpCDD). The various European data sets are plotted in Figure 1b. Collectively they present a rather less coherent picture than the two U.S. studies plotted in Figure 1a. This may be because many of the European studies were from more densely populated locations than those from the U.S. such that the European sites may have been more impacted by localized/regional sources. While some of the European studies (e.g., Baltic Sea studies) provided evidence for post-1970 declines (e.g., refs 11 and 19), in line with the U.S. data, others do not (e.g., refs 10, 20, 21, and 24).

**Evidence for Air Trends by Direct Measurement and Analysis of Vegetation.** *Direct Air Measurements.* Heister *et al.* (25) presented the annual mean air PCDD/F concentrations for four cities in North-Rhine Westphalia (Köln, Duisburg, Essen, Dortmund) in 1987/1988 and again in 1993/1994. During this time period, annual averages  $\Sigma$ TEQs (of predominantly mean monthly data) decreased by between 46 and 69% for the four locations (see Figure 2) as follows: Köln, 0.13 to 0.04 pg/m<sup>3</sup> (down 69%); Duisburg, 0.33 to 0.12 (down 63%); Essen, 0.20 to 0.076 (down 63%); Dortmund, 0.22 to 0.14 (down 46%). It should be noted, however, that the sampling regime was not the same in the two years; there were differences in the number of samples taken and the length of the sampling intervals. There was a decline of ~20% in the average suspended particulate burden in the air between 1987/1988 and 1993/1994.

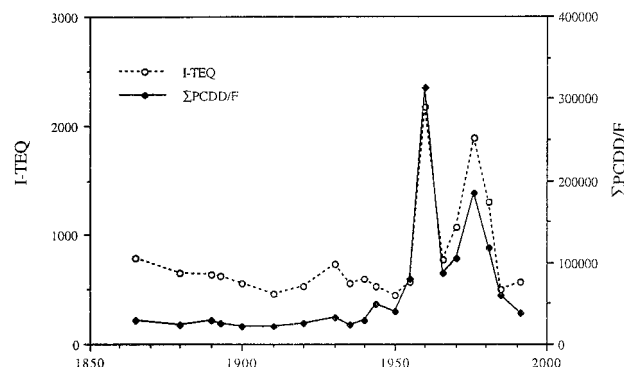


FIGURE 3. Trends in both  $\Sigma$ PCDD/F (ng/kg) and I-TEQ (ng/kg) in archived Park Grass herbage.

Heister *et al.* (25) attributed the PCDD/F declines to abatement measures introduced between the two sampling intervals, citing three changes: (i) prohibition of halogenated scavengers in petrol in 1992; (ii) a 'ban of PCBs' in 1989; and (iii) an upgrading or shutdown of 12 out of the 26 waste incinerators in the region. They also noted that systematic monitoring of PCDD/F emissions from 50 industrial sources would have resulted in reduced inputs. These reductions in air concentrations have also been linked to reductions in milk concentrations in the same region (see later).

*Air Trends Inferred from Vegetation Analysis.* Vegetation may effectively scavenge PCDD/Fs out of the atmosphere (26), retaining vapor-phase PCDD/Fs on the waxy cuticle (27–29) and trapping aerosol-bound PCDD/Fs brought in contact with the leaves by wet and dry deposition (29, 30). With the notable exception of the cucumber (*Cucurbitaceae*) family (31), aboveground plant tissue does not take up soil-borne PCDD/Fs very efficiently. The presence of PCDD/Fs on vegetation surfaces is therefore due almost exclusively to the uptake/retention of airborne PCDD/Fs (32). Changes in leaf (i.e., herbage or leafy crops) PCDD/F concentrations and composition can therefore be used to make inferences about changes in air concentrations and hence changing atmospheric source loadings and types. This needs to be done cautiously, however, because the mixture of PCDD/Fs released from a given source is subject to changes during aerial transport, deposition, and residence in the environment.

Kjeller *et al.* (33) analyzed bulked samples of unwashed vegetation from the long-term Park Grass experiment at Rothamsted Experimental Station, ca. 40 km north of central London. Samples of herbage had been taken from the same plots between 1891 and the present, dried, and stored. These were used to prepare samples from four time intervals (1891–1900, 1934–1944, 1960–1970, and 1979–1988) for PCDD/F analysis. There were large differences in the  $\Sigma$ PCDD/F content of the samples over time and in the mixture of PCDD/Fs present. The bulked samples from 1960–1970 and 1979–1988 were 7–8 times higher than the sample from 1891–1900.

A follow-up study (34) analyzed bulked samples covering the entire time period from 1861–1993. Trends in the  $\Sigma$ PCDD/Fs and  $\Sigma$ TEQ are plotted in Figure 3. A wide array of PCDD/Fs were detected in all the samples well above the method blanks. Concentrations ranged between 21 and 310 ng of  $\Sigma$ PCDD/F/kg DW, although some individual compounds were sometimes below the detection limits. The most recent sample (1991–1993) contained 38 ng/kg, a value typical for contemporary U.K. vegetation (35), with

the OCDD, HpCDD, TCDF, and PeCDF homologues dominating. The full range of tetra- through octa-CDD/Fs were consistently present in all the samples from the mid-1800s.

Kjeller *et al.* (33) inferred that the changes in concentrations and mixtures of PCDD/Fs reflect changes in atmospheric deposition and, if interpreted cautiously, changes in PCDD/F sources to the atmosphere. They interpret the results in herbage as indicating that combustion-derived sources have provided a 'baseline' input to the air throughout the study period (i.e., since 1860), an input that will have presumably changed in intensity and composition over time as combustion sources, types, and strengths have altered. Inputs from chloroaromatics production and use are then invoked as supplementing the combustion-derived inputs post-1946.

**Soils.** Stored samples of vegetation, soils, bird eggs, and human tissues have all been used for retrospective PCDD/F analysis. If the set of samples extends over long periods and they have been collected and stored in the same manner over time, this approach can potentially provide a good, reliably dated record of PCDD/F change. However, several post-collection factors could devalue or even invalidate the use of a given set of archived samples. These are obviously contamination during collection, their method of preservation, and method of storage. Contamination associated with the deposition of both particulate and vapor-phase PCBs from the atmosphere has been shown to be a major problem when handling soils that were collected and stored prior to their industrial manufacture (36). The same problems could potentially arise when 'old' samples (either sediment cores or archived samples) are brought into contact with laboratory air during preparation for PCDD/F analysis, although the problems are unlikely to be so severe. Insufficient thought appears to have been given to this issue in the past, which is discussed further below. Although PCDD/Fs are rather involatile at ambient temperatures, volatilization (i.e., loss from the sample) may be important for these compounds in certain situations. Relatively contaminated samples could theoretically lose PCDD/Fs to the atmosphere if there is an imbalance thermodynamically between the PCDD/F content of the sample and that of the gas phase in the air.

The bulk of the environmental burden of PCDD/Fs resides in soils (37). U.K. rural and urban soils typically contain ca. 300 and 1400 ng of  $\Sigma$ PCDD/F/kg and ca. 1–5 and 10–50 ng of  $\Sigma$ TEQ/kg, respectively (33, 38–41), while industrialized sites can contain higher concentrations.

Atmospheric deposition has been the primary means of the supply of PCDD/Fs into surface soils, explaining why urban soils typically contain higher concentrations (41), with half-lives of the order of 10 years or more. Various potential loss processes apply to organic contaminants introduced into surface soils. They are (a) volatilization from the soil to air; (b) leaching from surface soil to groundwater; (c) biodegradation; (d) photolysis and chemical reactions; (e) physical transport processes; (f) apparent loss through the formation of irreversibly bound, non-extractable residues. These processes and their significance (or otherwise) with respect to PCDD/Fs have been discussed elsewhere (41). However, the persistence of PCDD/Fs in soils testifies to the fact that the combined effect of these loss processes is 'slow' and that reductions to the terrestrial burden of PCDD/Fs may lag behind reductions in air and deposition.

Kjeller *et al.* (33) analyzed archived soils collected from the control plot of the Broadbalk continuous wheat experiment at Rothamsted Experimental Station between 1846 and 1986. The control plot does not receive any additions of fertilizers or soil amendments, so changes in the composition of soils from this plot should reflect the net effect of atmospheric deposition minus any loss of PCDD/Fs, provided that post-collection changes to the archived samples have been negligible (33). As noted above, the key step of concern would be the possibility of changes during soil drying, sieving, etc.; the potential for a change in sample composition during storage in the sealed jars is believed to be negligible.

The increase in soil concentrations at Broadbalk between 1846 and 1986 is consistent with an increase in atmospheric deposition inputs to the plot through this century. Concentrations started to increase around the turn of the century and rose from 31 to 92 ng of  $\Sigma$ PCDD/Fs/kg of soil between 1893 and 1986; TCDD concentrations increased from 0.34 to 1.7 ng/kg over the same time period. The net average accumulation rate between 1893 and 1986 was 190 ng m<sup>-2</sup> year<sup>-1</sup>. Concentrations of the individual isomers and the congener groups increased steadily over the last century, by factors of between 1.7 and 18 (33).

In summary, there is evidence that U.K. soils have increased in PCDD/F concentration through this century, as a result of cumulative atmospheric deposition. PCDD/Fs are persistent in soils, such that declines in atmospheric emissions may not result in a decline in the U.K. PCDD/F burden for some time. Indeed, it may be that even with the anticipated declines in the primary emissions of PCDD/Fs over the next decade, the rate of deposition may still exceed the rate of loss from soils. However, the significance of the soil PCDD/F burden really depends on whether soil-bound PCDD/Fs remain likely to enter food chains or whether they effectively become or remain 'occluded'. Further research is required to address this issue (42–44).

**Sewage Sludge.** Sludge composition reflects a combination of depositional inputs and wastewater discharges to the wastewater treatment plants' catchment. Consequently, it provides a useful 'index' of regional and long-term temporal PCDD/Fs environmental trends. However, (a) sewage sludge is a challenging medium for the analyst to deal with, (b) it may vary in composition over the short-term (e.g., days); (c) some PCDD/Fs have been shown to form during wastewater treatment processes (45, 46); however, this is considered minimal and insignificant compared with inputs via the sludge itself.

There is limited information available for PCDD/Fs from which to infer temporal trends. The first is circumstantial evidence from Germany, where one group has analyzed samples collected for different surveys in different places at different times. Hagenmaier and co-workers first reported PCDD/Fs in 15 sewage sludge samples from municipal wastewater treatment plants (WWTPs) in southwest Germany in 1986, detecting PCDDs in all samples ( $\Sigma$ PCDDs 4000–65 000 ng/kg) and PCDFs in most ( $\Sigma$ PCDFs 1000–7000 ng/kg) (19). These samples primarily represented urban/industrialized catchments, although no details are given of the sample locations. Hagenmaier (19) subsequently extended his analysis of sludges to 28 samples collected in the mid-1980s from all over Germany. Samples from two provinces (Waldshut and Lorach) suspected of having high concentrations were included. The  $\Sigma$ TEQ values ranged between 28 and 1560 ng/kg, with a median

and mean of 90 and 202, respectively. These data were derived using the German TEQ system, not the I-TEQ scale. However, the two systems are unlikely to give data that differ by more than 10%. The median value gives a better indication of 'typical' levels, since it is not biased by the highly contaminated samples. Later Hagenmaier *et al.* (47) reported the I-TEQ value of sludges from 13 German WWTPs, which go to agricultural soils. They ranged between 20 and 177 ng/kg, with a median of 37 and mean of 47. Gahr *et al.* (48) reported on an extensive survey of 72 German sewage sludges collected in 1989. The mean  $\Sigma$ PCDD/F content was  $\sim 20\,000$  ng/kg, ranging between 1700 and 150 000 ng/kg. Hagenmaier's mid-1980s study of German sludges had reported a mean of 50 000 ng/kg (19). These studies may therefore collectively provide some evidence that German sludges have declined in PCDD/F content through the 1980s.

There is good evidence from German studies that the use of PCP and chloranil-based dyes and pigments by the textile industry has been an important and possibly dominant source of  $\Sigma$ PCDD/Fs to German sewage sludges (19, 41, 48–50). This would have been a more important source in the 1980s than now, since PCP usage has been prohibited in Germany in recent years. However, imported fabrics may still be an important source of PCDD/Fs, although the predominance of the Hp- and octa-CDD/Fs in PCP means that  $\Sigma$ TEQs of sludge may be more influenced by other sources, notably combustion.

Lamparski *et al.* (51) present data from an interesting study in which they analyzed a sample of municipal sewage sludge, collected and sealed in 1933. It contained a broad range of PCDDs, similar to that in samples collected by the authors in 1981.

**Livestock Tissue and Milk.** The composition of meat and milk can be considered to give a broad 'integration' of PCDD/F recent atmospheric inputs over large areas. Milk provides a particularly valuable indication of regional deposition, since dairy cattle effectively bioaccumulate PCDD/Fs (30) and can 'process' PCDD/Fs recently deposited onto vegetation into a homogenous, readily sampled and analyzed matrix.

The Ministry of Agriculture, Fisheries and Foods Total Diet Study in the U.K. provides extremely useful data on the PCDD/F content of milk, milk products, carcass meat, and offals collected in 1982, 1988, and 1992 (39, 52). The 1982, 1988, and 1992 samples have all been analyzed by the same laboratory that regularly participates in interlaboratory comparison exercises. The data for milk and milk products are summarized in Figure 4. These data provide good evidence that there has been an underlying decline in the PCDD/F emissions in the U.K. since the early 1980s. Clearly, this study has important implications for human exposure since the vast majority (>95%) of human exposure to PCDD/Fs comes from the diet (53). Average U.K. dietary intakes were estimated to be 250 pg of TEQ person<sup>-1</sup> day<sup>-1</sup> in 1982, 145 pg/day in 1988, and 88 pg of TEQ person<sup>-1</sup> day<sup>-1</sup> in 1992. Clearly, the estimated human exposure in the U.K. has declined substantially over this time period. However, this may be due to several factors, not only changing concentrations of PCDD/Fs in food items. Notably (i) The composition of some of the food group samples will have been changed between 1982 and 1992 to reflect changes in household consumption. (ii) Analysis of the composite food groups shows that the average fat content of many foods

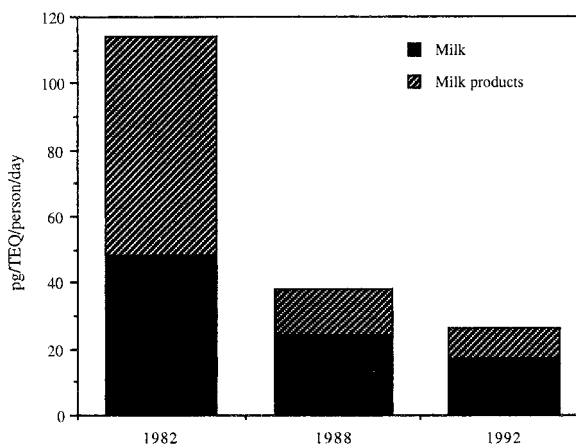


FIGURE 4. Estimated dietary intakes of dioxins by average U.K. consumers of milk and milk products (calculated using U.K. National Food Survey consumption data).

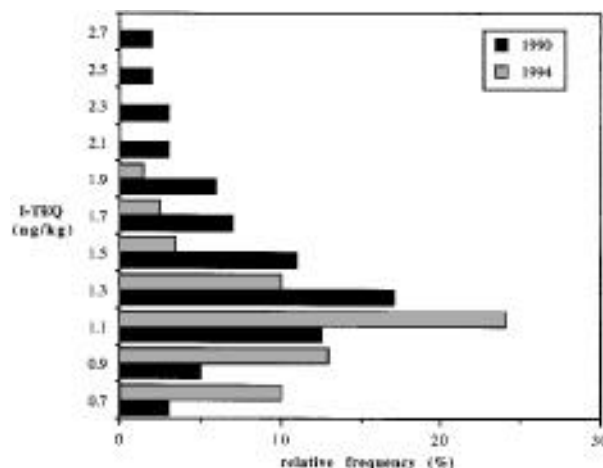


FIGURE 5. Declining relative frequency of I-TEQ concentrations in German cows' milk from 1990 to 1994.

fell between 1982 and 1992. The total amount of fat in the part of the average U.K. daily diet made up of the 11 food group categories used in the survey fell from 92 g in 1982 to 72 g in 1992 (52). As PCDD/Fs are primarily found in fat, the fall in the fat content of the diet will have contributed to the observed decrease in average dietary intakes. (iii) Other changes in dietary habits, for example, the increase in the proportion of dietary fat that is of vegetable rather than animal origin, may also have contributed to the observed decrease (52).

In another important paper, Fürst and Wilmers (54) compared the  $\Sigma$ TEQ content of German dairy products collected in 1990 and 1994. Milk and milk products were collected from 30 dairies (sampling each quarter) in North Rhine-Westphalia, thereby matching the air data obtained by Heister *et al.* (25) from the same region. Comparing the results in 1990 and 1994, the average  $\Sigma$ TEQ of cow's milk and dairy products decreased by almost 25%. Milk fat contained an average 1.35 (range 0.76–2.62) and 1.02 (0.61–1.75) pg of  $\Sigma$ TEQ/g in 1990 and 1994, respectively. Figure 5 presents a summary of the data and shows that the range of concentrations was narrower in 1994. They also considered the significance of these declines in the PCDD/F content of dairy products on human exposure in North Rhine-Westphalia (55). In summary, good quality PCDD/F time trend data from dairy products and grazing animals in the U.K. and Germany both provide clear evidence of

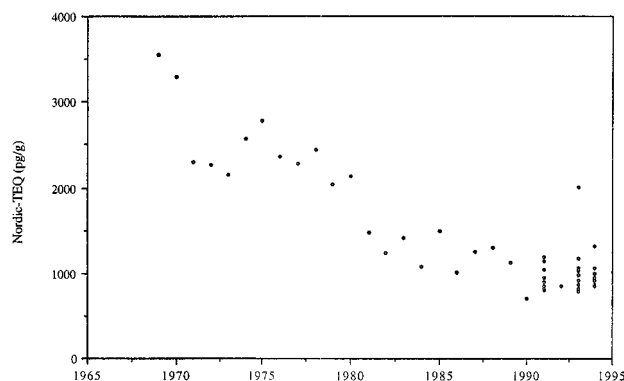


FIGURE 6. Nordic-TEQ trends (1969–1994) in guillemots from Stora Karlsö, Sweden.

declines in atmospheric concentrations through the 1980/1990s.

**Wildlife.** There is particular interest in PCDD/Fs in biota, given the bioaccumulatory potential of these compounds in both terrestrial and aquatic food chains. There can be practical difficulties in obtaining good, continuous long-term sample sets, particularly given the inherent variability in body/organ residue concentrations. Age, sampling location, time of year, and sex are all potentially important variables that can affect the residue concentrations of organochlorine compounds in wildlife and provide potential confounding factors in time trend studies.

**Fish.** Samples of pike collected from a lake in a remote part of Lapland, northern Sweden have been analyzed by de Wit and colleagues (56; further unpublished data have been kindly supplied by Dr. C. de Wit, University of Stockholm). Homogenates from 1969–1991 were analyzed, along with individual samples obtained in 1992. Only 2,3,7,8-TeCDF was detected in all samples and showed no obvious temporal trend. Pike are at the top of freshwater ecosystems and have a life span of many years. One important confounding factor with this particular data set could be the age of the pike. Previous studies on organochlorine compounds in fish in the Great Lakes have shown that residue concentrations vary markedly with age, generally bioaccumulating through life.

**Birds.** Birds, particularly those species that occupy positions near the top of food chains, have frequently been used as bioindicator species for bioaccumulatory organochlorine compounds (57). Two such studies have used egg samples to investigate temporal trends of PCDD/Fs. A comprehensive set of guillemot egg samples from one colony that inhabits St. Karlsö in the Baltic Proper, northern Sweden, have been analyzed for PCDD/Fs by de Wit and colleagues (56; further unpublished data have been kindly supplied by Dr. C. de Wit, University of Stockholm). Homogenates of archived eggs from 1969–1992 were analyzed, together with 10 individual samples collected in 1991, 1993, and 1994. The latter were intended to provide information on variability within the population. The  $\Sigma$ TEQ data are shown in Figure 6 and provide evidence for a decline over time, from ~3500 pg/g in 1969 to ~900 in 1994.

Concentrations of PCDD/Fs were measured in pooled herring gull eggs collected from colonies in the Great Lakes and the St. Lawrence River between 1981 and 1991 by Herbert *et al.* (58). Levels of TCDD, PeCDD, and HxCDD declined in most colonies between 1981 and 1991, with no obvious trends after 1984.

**Human Tissues.** Estimations of the human body burden can be obtained by measurements of PCDD/Fs in body fat and body fluids such as blood and milk. PCDD/Fs accumulate in fatty tissues, so adipose tissue is an appropriate index of exposure. Only the 2,3,7,8-substituted compounds accumulate in the human body, with concentrations of the higher chlorinated homologues predominating.

**Adipose.** PCDD/Fs accumulated in human adipose tissue and levels reflect the history of intake by the individual. Several factors have been shown to affect adipose tissue concentrations/body burdens, notably age, the number of children and the period of breast feeding in females, and dietary habits (59). U.K. concentrations (60) are within the range of the most recent samples from other industrialized nations, including Japan (61), Canada (62), and Spain (63).  $\Sigma$ TEQ concentrations in contemporary adipose are of the order of 0.03 ng/g;  $\Sigma$ PCDD/Fs are of the order of 1 ng/g (64, 65).

Generally, the studies published to date on adipose concentrations provide less statistically rigorous information on human tissue trends than that reviewed below for milk. Three studies are available. Stanley *et al.* (66) reported data for 2,3,7,8-TCDD for U.S. samples from 15–44-year-olds collected from 1971–1987. The mean value for tissue collected in 1971–1973 was ca. 18 pg/g of lipid; by 1977–1979, this had declined to ca. 10 pg/g, and by 1987, it was ca. 4 pg/g. Ryan *et al.* (67) reported levels of  $\Sigma$ PCDD/F in North American adipose tissue collected from different locations between 1972 and 1983–1984. Based on limited sample numbers, they noted that 'samples from New York State residents collected in 1983–1984 contain somewhat lower levels of higher chlorinated PCDDs than samples from across Canada in 1976 and from Ontario in 1980'. Higher concentrations of all 2,3,7,8-substituted congeners except OCDD were found in samples from 1972 than those from 1983–1984, but no statistically significant difference was found. Time trends in human adipose tissue have been reported for Japan from 1959 to 1993 (61). Lowest levels were found in the earliest samples with concentrations rising to an early maximum in 1970 with OCDD dominating the congeners composition. Maximum concentrations were found in 1991 when HxCDD (particularly 1,2,3,6,7,8-HxCDD) dominated the congener composition, after which a decline in 1992 and 1993 was observed. Since the number of samples analyzed during this study was small (11 samples during 1990–1993) and full congener-specific data are unavailable, it is very difficult to relate the changes to changing sources of PCDD/Fs.

**Blood.** Very few trend studies of non-occupationally exposed individuals are available in the literature. Background PCDD/F levels in human blood have been reported to have declined in Germany (68). Concentrations ranged from 11.6–93.5 (median = 37.8;  $n = 102$ ) pg of TEQ/g of lipid in 1989 to 10.3–48.8 (19.4;  $n = 70$ ) pg of TEQ/g of lipid in 1993, an average decline of ~50%. This is generally consistent with the declines in breast milk concentrations discussed below.

**Milk.** Several factors affect the PCDD/F content of human breast milk, but most notably the mother's age, the lifetime duration of breast-feeding, and the fat content of the milk (69). Concentrations can also vary during a lactation period (70). Trend studies should therefore ideally be performed on samples from a large number of mothers and take these variables into account (71, 72).



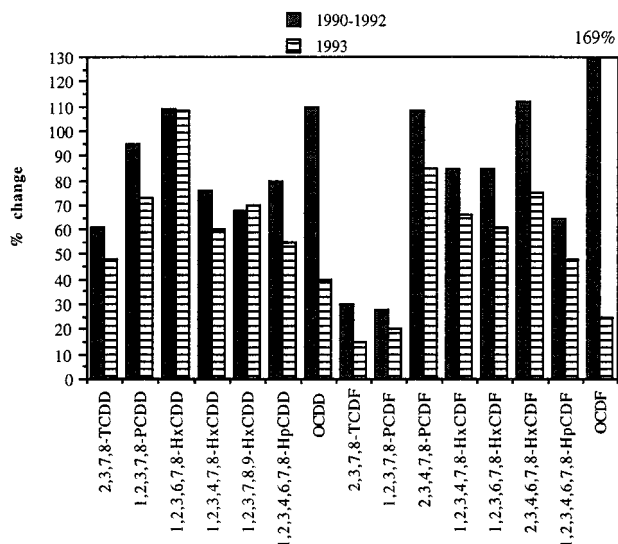


FIGURE 7. Change in mean concentrations of PCDD/Fs (in pg/g of fat) in Dutch human milk between 1988, 1990–1992, and 1993. The figures show mean concentrations in 1990–1992 (74) and 1993 (73) expressed as a percentage of the concentrations found in 1988.

**Germany.** A large amount of milk data has been generated in Germany over the last 10 years. For example, more than 600 individual human milk samples have been analyzed for PCDD/Fs from mothers living in North Rhine Westphalia, providing evidence that concentrations in human milk have declined somewhat, from annual average  $\Sigma$ TEQs in 1987, 1988, and 1989 of 32.5, 32.1, and 33.9 pg of  $\Sigma$ TEQ/g, respectively, to 29.4 and 23.0 pg/g in 1990 and 1991 (55). This decline is mainly due to lower levels of 2,3,4,7,8-PeCDF, HxCDDs, and 2,3,7,8-TCDF, prompting Fürst *et al.* (55) to comment that 'it seems that efforts to reduce emissions are already effective to a certain extent', although it may be more appropriate to see these declines in human tissue in the context of longer-term declines in PCDD/F emissions. This trend has been confirmed by the extremely comprehensive data set of over 2000 samples reported by Alder *et al.* (71). On the basis of an averaged mean of all the German data, these workers reported a 40% decline in TEQ between 1985–1989 and 1993 (71, 72).

**The Netherlands.** In The Netherlands, human milk surveys of PCDD/Fs have been performed in 1988 and 1993. In the 1988 survey, a mean TEQ of  $34.3 \pm 3.4$  pg/g fat was found for 10 pooled samples of milk. Each of these samples was composed of milk from 9–13 individuals. The 1993 survey, in which all samples were analyzed individually, had an average  $\Sigma$ TEQ concentration of  $23.5 \pm 8.9$  pg of TEQ/g of fat, a decrease of about 30% as compared to 1988 (73). No drift in the analytical data produced for 2,3,7,8-TCDD and TEQ over the period 1988 to 1993–1994 has been observed, and various checks give confidence that a comparison of individual congener concentrations between 1988 and 1993–1994 is valid (A. K. D. Liem, National Institute of Public Health and Environmental Protection, Bilthoven, personal communication). This is done in Figure 7, where the 1988 data for individual congeners has been normalized to 100% and compared with the 1993 study (73) and 1990/1992 levels reported by Koopman-Essenboom *et al.* (74). A preliminary statistical evaluation of the data suggests that the decline is statistically significant when levels in 1988 and 1993 are expressed as TEQs, but not when individual congeners are considered (Liem, personal communication). Pronounced differences between the

Liem data and Koopman-Essenboom data are noted for some congeners. These congener differences may be due to changes in exposure patterns (i.e., levels in food) and toxicokinetic factors (i.e., biological half-lives). Levels of congener 1,2,3,6,7,8-HxCDD have not declined from 1988 to 1993. Interestingly, this stable congener has not declined in German cows milk either (54) over a similar period. The general trend, however, is clearly one of declines over time, particularly for the 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 1,2,3,7,8-PeCDF compounds (Figure 7).

**Norway and Sweden.** Milk from mothers in Stockholm has been collected in different time periods since 1967 for organochlorine contaminant analysis (75, 76). PCDD/F concentrations were already declining between 1972 and 1985 and then stabilized between 1985 and 1989. Becher *et al.* (77) have recently reported results of part of a WHO/EURO-coordinated study of PCDD/Fs in human milk in Norway. These have provided geographical and temporal differences in levels in Norway and Lithuania. Sampling was carried out in the same locations, using the same protocol as a corresponding study in 1985/1986, but using a different laboratory for analysis. In Norway, concentrations of almost all individual PCDD/F congeners have decreased in the 7-year time interval between the two studies, the exception being 1,2,3,4,6,7,8-HpCDF, which has increased slightly. Mean TEQ has decreased by ~37% from 1985/1986 to 1992/1993.

**The 'Pre-Industrial' Question: Is There a 'Baseline' Level of PCDD/Fs?** The presence or absence of PCDD/Fs in pre-industrial samples has attracted considerable attention from the scientific community as well as from pressure groups and government agencies. This is because it is of fundamental importance to the question of whether there are natural inputs/formation of PCDD/Fs, or whether all PCDD/Fs detected in the contemporary environment are the result of relatively recent anthropogenic activities (78). Bumb *et al.* (79) first propounded the view that natural combustion formation of PCDD/Fs occurs, with their 'trace chemistries of fire' hypothesis. It is appropriate to discuss this issue here since the use of PCDD/F historical monitoring data has the potential to provide important evidence.

As the sediment studies reviewed earlier show, fluxes of PCDD/Fs into the environment have changed substantially over recent decades as a direct result of anthropogenic activity (80, 81). What is unclear, however, is whether recent anthropogenic inputs have superimposed on a natural burden of PCDD/Fs in the environment, or whether inputs through this century have further supplemented longer-term anthropogenic influences (such as wood and coal burning, metal processing, etc.), which have operated over several centuries to introduce PCDD/Fs into the environment (81). These questions are important, for the following reasons:

(1) If PCDD/Fs have been introduced solely by anthropogenic activities, then they represent 'new' chemicals that biological systems will not have encountered until very recent time. This could have implications for the ability of biological systems to adapt to the presence of these compounds if they are exposed to them.

(2) It has been claimed that PCDD/Fs are linked exclusively to the introduction of synthetic complex chloro-aromatic compounds into the environment, leading to calls for 'chlorine-free' industries. If this is true, PCDD/Fs will only have been introduced into the environment in the last few decades.

(3) Other studies have reported the formation of PCDD/Fs from the combustion of coal and wood (78, 81). Clearly, these human activities have increased and been widespread over recent centuries and—if they represent important sources of PCDD/Fs—would presumably have resulted in a longer-term increase in the environmental burden of PCDD/Fs over several decades.

(4) As long as uncertainties remain over the significance, or otherwise, of natural and anthropogenic sources, the effectiveness of emission control and source reduction measures introduced by the regulatory authorities will remain unclear.

Unfortunately, studies often purporting to provide evidence of natural formation are ambiguous because of the way in which samples have been handled and processed, while studies purporting to show no evidence of natural formation may not be working with sufficiently sensitive procedures. Analytical constraints may relate to some of the earlier work on 'natural formation', either because of detection limit improvements that have been made over the last 10–15 years or because a greater appreciation of the need for ultra-clean handling and preparation procedures was needed. It is appropriate to briefly discuss some examples.

PCDD/Fs are ubiquitous in modern air, albeit at very low concentrations. The more abundant Hp- and octa-CDD/Fs exist in the air primarily on aerosols, which could settle onto samples during air-drying or exposure to laboratory air. The tetra-, penta-, and hexa-CDD/Fs can have an important vapor-phase component in air, which would partition onto samples exposed to the air for prolonged periods, or onto laboratory glassware. Recent work with PCBs has emphasized how quickly pre-industrial samples can become contaminated with modern air (36); exposure of deep peats and archived soils to laboratory air for as little as a few hours was sufficient to result in detectable contamination. Importantly, of the studies on sediment cores, those by Czuczwa and Hites (e.g., ref 22) Soxhlet extracted the samples *wet*, avoiding the air-drying stage. The studies by some others (e.g., 10 and 17) refer to an air-drying step. Interestingly, the studies by Czuczwa and Hites (14, 22) were unable to detect PCDD/Fs in the pre-1940 samples as being significantly different from the laboratory blanks. In contrast, the study by Rappe and Kjeller (10) detected PCDD/Fs in all slices down to 1882, although they used a more sensitive HRGC-MS analytical procedure than the NICI-MS procedure used by Czuczwa and Hites (22). Kjeller *et al.* (33) reported the presence of the full range of PCDD/Fs in archived soils collected from Rothamsted Experimental Station in the 1800s. Samples collected pre-1900 contained ca. 30 ng of  $\Sigma$ PCDD/F/kg, but these samples were also air-dried for a time in modern laboratory air.

Hashimoto *et al.* (82, 83) present data from Japanese sediments, reporting the presence of PCDDs in deep samples, dated over many thousands of years old. No PCDD/Fs were found in the lake sediments, but both PCDDs and PCDFs could be found in the coastal sediments. Highest concentrations were found in sediments from the late 1960s and early 1970s. Around 1980, concentrations decreased by a factor of 2–5; the PCDFs decreasing more than the PCDDs. No PCDFs could be found in the deep sediments dated more than 8000 years old, but PCDDs, primarily octa-CDDs and hepta-CDDs (ratio 6:1), were found (82). Subsequently, Hashimoto *et al.* (83) reported

the occurrence of Hx-, Hp-, and OCDD in sediments dated as 1–10 million years old from the Yellow and East China Seas and the Pacific Ocean. However, perhaps critically, the samples were air-dried and sieved in the laboratory before analysis.

**Human Tissue Studies of the Pre-industrial PCDD/Fs.** Schecter *et al.* (84) analyzed Eskimo tissue (lung and liver) and food (meat) from Alaska that had been preserved frozen for over 400 years. These authors wanted to specifically test the 'trace chemistries of fire' hypothesis and were aware of the need for careful sample preparation. However, they noted that the opportunity to use Eskimo samples '... was only realized sometime after their discovery. As a result, sufficient care may not have been taken to prevent chemical contamination with PCDD/Fs. To minimize this problem, samples for analysis were taken from the inner portions of the human tissue and food samples whenever possible.' Although small amounts of HpCDF were detected in some of the samples, the authors suspected that these samples may have become contaminated. Subsequently Tong *et al.* (85) reported that the re-analysis of those ancient samples showed a presence of low ppt (ng/kg) levels of HpCDD and OCDD after the contamination discussed by Schecter *et al.* (84) was 'carefully eliminated'. However, the levels in Eskimo tissue (~10 ng of HpCDD/kg and ~30 ng OCDD/kg) were well below those reported for tissue from modern people living in industrialized countries (~90–230 for HpCDD; 400–1100 for OCDD).

Ligon *et al.* (86) examined the mummified tissues of Chilean Indians buried 2800 years ago in a desert environment. These specimens are interesting because they pre-date the industrial era and because this civilization is known to have cooked over wood fires. No PCDD/Fs were found at detection limits of between 0.3 and 5 ng/kg. Fatty acids in the remains were substantially intact, suggesting long-term stability of PCDD/Fs in the tissue samples and negligible chemical/biochemical degradation over time.

Contamination of pre-industrial samples is a potential problem that has often undermined attempts to assess the relative importance of possible natural, historical, and recent sources of PCDD/Fs to the environment. Extreme care is necessary when working at the ultra-trace levels required for such studies. The study of ancient Eskimo tissue provides some interesting but inconclusive evidence for pre-industrial levels of HpCDD and OCDD in the environment; nonetheless, it is clear that levels of these congeners in the modern environment and biota have been supplemented substantially by recent anthropogenic sources. Many of the lighter congeners are present at such low concentrations in the environment that it is impossible to state categorically at present whether baseline levels of these contaminants have been present in the environment prior to this century.

**Comments on the Trends and Possible Sources.** The evidence reviewed here suggests that PCDD/F emissions to the environment in Europe and North America increased post-1940, probably reaching a peak in the 1960/1970s, before declining through the late-1970s, 1980s, and early 1990s.

The major contemporary sources of PCDD/Fs to the U.K. environment have been reviewed, with municipal solid waste incineration (MSWI) estimated to be responsible for 70% of total emissions from industrial sources. Emissions from metal industries, combustion of coal, and clinical waste were listed as other important contemporary primary

sources (87). It is appropriate to briefly consider how the timing and magnitude of potentially important sources of PCDD/Fs has varied, to assess possible contributors to past emissions, and to assess their possible relationship to the environmental PCDD/F input profile.

Very little data appear to exist in the public domain over the history of MSWI in the U.K. It is believed that some crude MSWI were in operation early in this century, but most of the current stock of ~30 incinerators were built in the late 1960s/early 1970s, with a collective current throughput of ~3 million/year. Obviously, general improvements in combustion technology have been achieved over the years, while the volume of waste burnt has increased. In addition, municipal waste composition has changed; about 30% of modern MSW is paper, 20% putrescible matter and ~10% glass, with plastic constituting ~6%, ferrous metal ~7%, and textiles 4%.

This century has seen substantial changes in the use of fossil fuels. Total coal consumption peaked in the 1950/1960s but was already high in the early 1900s. Perhaps more importantly, there has been a dramatic shift away from the use of coal domestically—which involves generally inefficient, diffuse combustion conditions—to a situation today where almost 80% of coal consumption is for electricity generation. This is reflected in the demand for house coal in the U.K. In the 1950s, ~40 million t was supplied annually. In 1970, this figure had fallen to ~18 million t, and in the 1990s declined to <3 million t/year. Practice in the home would often have been to burn some domestic refuse (perhaps containing plastics) and wood (which may have been treated with PCP) in the domestic grate under rather poor combustion conditions. These practices may have been particularly important in contributing to past emissions.

PCDD/F emissions from vehicles have been related to the use of leaded petrol. For example, the use of Pb in petrol in the U.K. increased from ca. 3400 t in 1955 to a peak of ca. 8700 t in 1973, followed by a steady decline to ca. 6700 t in 1985, and a sharper drop to ca. 3000 t in 1986 and thereafter (88). The consumption of unleaded petrol has correspondingly increased and is projected to increase further over the next decade.

The use of PCP is likely to have been an important direct source of PCDD/Fs to the environment. Production and use of PCP started worldwide in the 1940s, increased through the 1950s and 1960s, and peaked in the 1970s (89). Some countries (e.g., Japan) had stopped manufacturing PCP by the early 1970s (89), while U.K. production ceased in 1980. Nonetheless, it has continued to be used for timber preservation, with an estimated 320 t/year used in 1980, 290 t in 1988, and 200 t in 1990 in the U.K. The diffuse burning of PCP-treated wood is another potentially important source that may have been more important in the past than it is today. PCB production started worldwide in 1929, but did not commence in the U.K. until 1954. Between 1954 and 1977, an estimated 40 000 t of PCBs was manufactured (90).

The formation of PCDD/Fs as a result of the production, use, and disposal of chlorine-containing plastics, notably polyvinyl chloride (PVC) polymers, has been the subject to much controversy over the last decade or so. However, the case for PVC being an important direct or indirect source of PCDD/Fs to the environment is far from clear-cut. It has been estimated that plastics make up about 6% of municipal solid waste, with PVC constituting 10% of the

plastic disposed of (91). PVC production and use started in the late 1950s, and consumption in western Europe has risen from the early 1960s to about 600 000 t in the early 1990s. However as PVC use continues to rise, PCDD/F concentrations in a wide range of environmental media are on the decline.

The question of whether PCDD/Fs existed in the environment before industrialization is one still under review. Analytical constraints from operating near the limits of detection and uncertainties over the possibility of post-collection contamination have presented practical problems to obtaining definitive information on this issue. However, the evidence for the occurrence of some heavier homologues of PCDDs is quite good. Nonetheless, the weight of evidence suggests that even if there were PCDD/Fs formed pre-industrially, the PCDD/F burden of the contemporary environment exceeds any historical burden. As long as uncertainties remain over the significance, or otherwise, of natural and anthropogenic sources, the effectiveness of emission control and source reduction measures introduced by the regulatory authorities will remain unclear. Some of the studies presenting relatively long-term time trend data provide only limited evidence for a change in PCDD/F homologue/congener mixtures emitted to the environment. Several changes to the range, intensity, and relative importance of sources are likely to have been influential, as has the introduction and subsequent widespread production, use, and dispersal of various chlorinated aromatic chemicals from the middle of this century.

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