

DIOXINS IN THE ENVIRONMENT

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Chapter 7

DIOXINS AND DIBENZOFURANS IN AIR, SOIL AND WATER

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INTRODUCTION

Polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) are generated by combustion sources (Olie et al., 1982; Bumb et al., 1980), and the effluents from these sources, carrying particulates containing PCDD and PCDF, enter the atmosphere. The particulates will sooner or later leave the atmosphere, depositing the PCDD and PCDF on soil or in water. Thus, combustion may be an important source of PCDD and PCDF found in the environment. This paper is a review of combustion-generated dioxins and furans and their fate in air, soil, and the aquatic environment.

We begin this review by characterizing the dioxin and furan congener profiles produced in combustion sources including municipal waste incineration, chemical waste incineration, coal burning and wood burning. We will then predict the most important combustion sources of dioxins and furans. We will also calculate an "average combustion" congener profile and use this to compare the PCDD and PCDF generated in combustion sources to those found in environmental samples. Air and soil samples will be discussed to show that combustion is a source of dioxins and furans found in the environment, and that PCDD and PCDF are dispersed by airborne transport through the atmosphere.

The analysis of sediments is the main focus of our work. Surficial sediments from locations in the Great Lakes and Lake Zurich will be used to show that atmospheric transport is the major mechanism bringing dioxins and furans to remote locations. Dated sediment cores yield information on the historical input of dioxins and furans to the environment. We find a post-1940 increase in sedimentary PCDD and PCDF which is related to the production and subsequent incineration of chlorinated aromatic chemicals.

It is useful to briefly explain how we generated the figures in this paper. We used published work which reported quantitative data for dioxins and furans. In each figure, the data are presented as total concentration for each congener class (tetra- to octachlorofurans, then dioxins). If a congener class was not measured, it is not labeled on the lower axis. When a number of observations were reported by an investigator, the arithmetic average is presented; when a range was given (particularly Bumb et al., 1980) the geometric average of the high and low values was calculated. In all cases, the concentration given on the figure is that of octachlorodioxin. Finally, only work from the refereed literature was used.

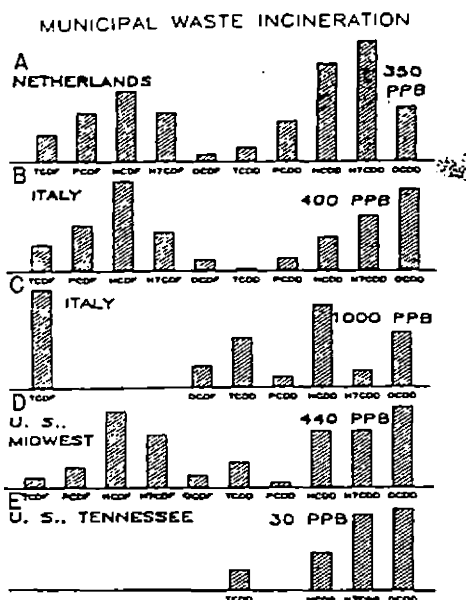


Figure 1. Dioxin and furan congener profiles found on fly ash from municipal incinerators. Reported concentrations are for octachlorodioxin in all cases. (Adapted from the following: A, Olie et al., 1982, Table 7; B, Liberti et al., 1982, Table II, Liberti and Brocco, 1982, Table II; C, Cavallaro et al., 1982; D, Czuczwa and Hites, 1984; E, Bumb et al., 1980.)

AIR

Combustion Effluents Released to Air

Municipal waste incineration. Measurements now exist of dioxins and furans in particulate matter from several combustion sources. Figure 1 contains a summary of analyses of effluents of municipal waste incinerators. No consistent trends in the congener profiles are observed. It is apparent that these sources are highly variable. Octachlorodioxin (OCDD) concentrations averaged as high as 1000 ppb (Cavallaro et al., 1982). Since typically 2% of the particles formed in municipal incinerators are released to the atmosphere (Lustenhower et al., 1980) and since incineration is currently used to dispose of 10% of all solid wastes, combustion of municipal wastes may be an important source of dioxins and furans in the environment.

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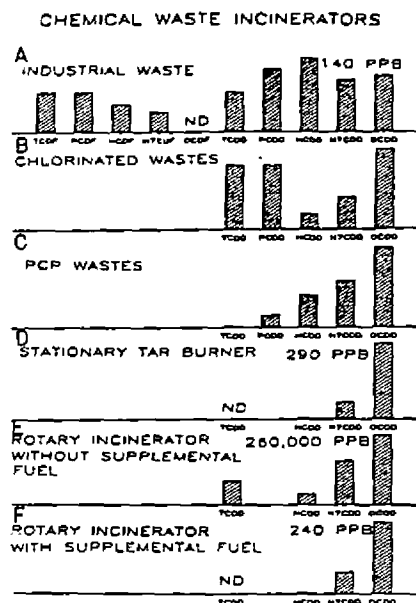


Figure 2. Dioxin and furan congener profiles found on fly ash from chemical waste incineration. (Adapted from: A, Buser and Bosshardt, 1978; B, C, Tiernan *et al.*, 1983; D-F, Bumb *et al.*, 1980.)

Chemical waste incineration. Analyses of effluents from the incineration of chemical wastes are shown in Figure 2. Variation in the congener profiles is again seen. The OCDD concentration ranged from 140 to 260,000 ppb, significantly higher than municipal waste incineration. The effect of combustion conditions on the formation of PCDD and PCDF is clearly seen (Figure 2E and 2F) in a rotary incinerator operated with and without supplemental fuel (Bumb *et al.*, 1980).

The importance of elevated temperatures for the destruction of PCDD and PCDF has only recently been appreciated. Incinerators which were not operated under the most stringent conditions could have released large amounts of PCDD and PCDF to the environment. Thus, we conclude that chemical waste incineration is an important source of dioxins and furans.

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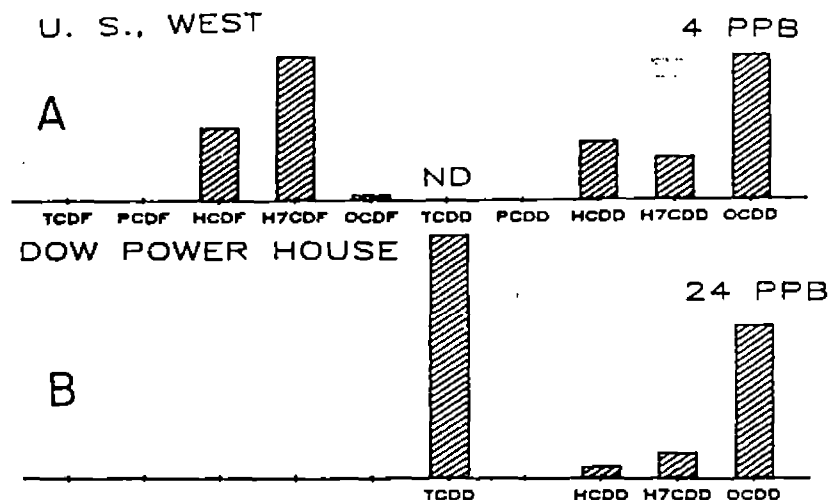


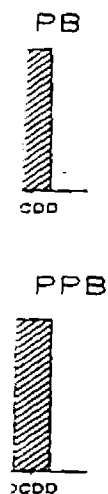
Figure 3. Dioxin and furan congener profiles found on fly ash from coal burning. (Adapted from A, Czuczwa and Hites, 1984; B, Bumb *et al.*, 1980.)

Coal burning. Coal fly ash is another possible source of combustion-generated dioxins and furans (see Figure 3). The analysis of two coal fly ash samples from a western coal-fired power plant (Figure 3A), analyzed by our laboratory, showed a predominance of OCDD. The average concentration of OCDD was 4-24 ppb, and is low in comparison to municipal incinerator fly ash.

Wood burning. Some studies of the combustion of wood and pentachlorophenol (PCP) treated wood are shown in Figure 4. Particulates from residential wood burning units (Nestrick and Lamparski, 1983) contain low levels of dioxins, primarily the hexa-, hepta- and octachlorinated isomers, while the combustion of PCP treated wood produced higher concentrations of dioxins. Again, significant variation is noted.

Average combustion congener profiles. In Figure 5, we show the calculated average congener profiles for each type of combustion. It is interesting to note the relative amounts of dioxins and furans produced in each type of combustion. The combustion of chemical wastes and municipal wastes (which may contain synthetic chemicals) produce the greatest amount of PCDD and PCDF, while the combustion of wood and coal produced smaller amounts. Thus, we conclude that chemical and municipal waste incineration are the major combustion sources of dioxins and furans. Combustion of coal and wood (presumably including natural combustion such as forest fires) is a minor source of PCDD and PCDF. We will test these conclusions below.

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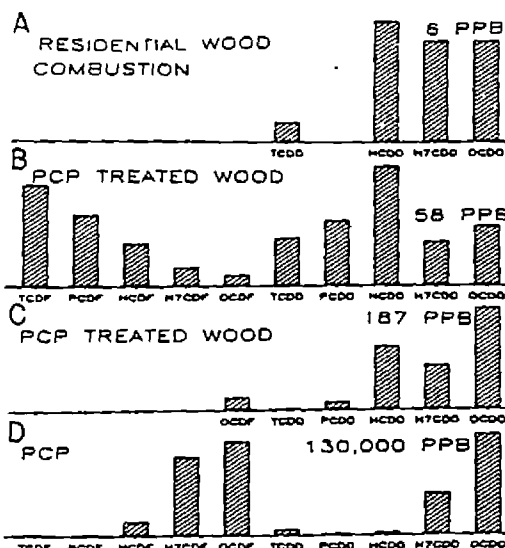


Figure 4. Dioxin and furan congener profiles found on fly ash from wood and PCP treated wood burning. (Adapted from: A, Nestrick and Lamparski, 1983; B, Olie *et al.*, 1983; C, Chui *et al.*, 1983; D, Buser and Bosshardt, 1976.)

From Figure 5 it is obvious that there is great variability in combustion congener profiles. In fact, when we calculated an "average" combustion profile (Figure 5, bottom), we see no specific congener classes are preferred. All classes are present in about equal amounts with the exception of OCDF, which is consistently low. In addition, combustion samples characteristically contain many isomers within each congener class. How do these trends compare to those found in environmental samples?

Air Particulates

Analyses of air particulates are shown in Figure 6. We see that dioxins and furans are associated with air particulates. One notes that environmental samples are enriched in OCDD compared to combustion source samples. The most abundant furans are the heptachlorofurans (H7CDF). The highest level of OCDD (2000 ppb) is found in Midland, Michigan (Bumb *et al.*, 1980), which suggests that combustion of chemical wastes is an important local source of PCDD and PCDF.

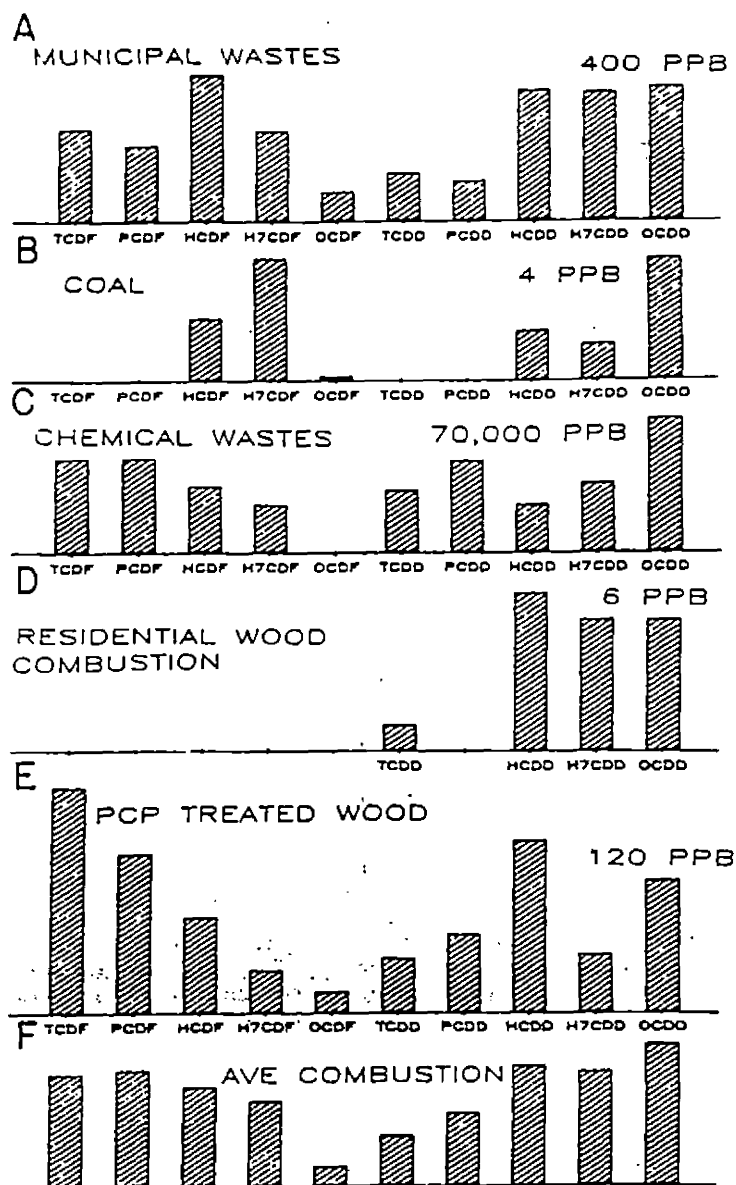
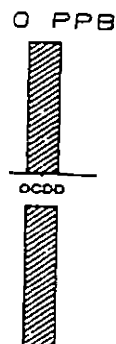
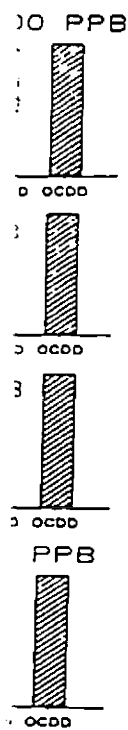


Figure 5. Average dioxin and furan congener profiles from various combustion processes. Averaged from the information in Figures 1-4.

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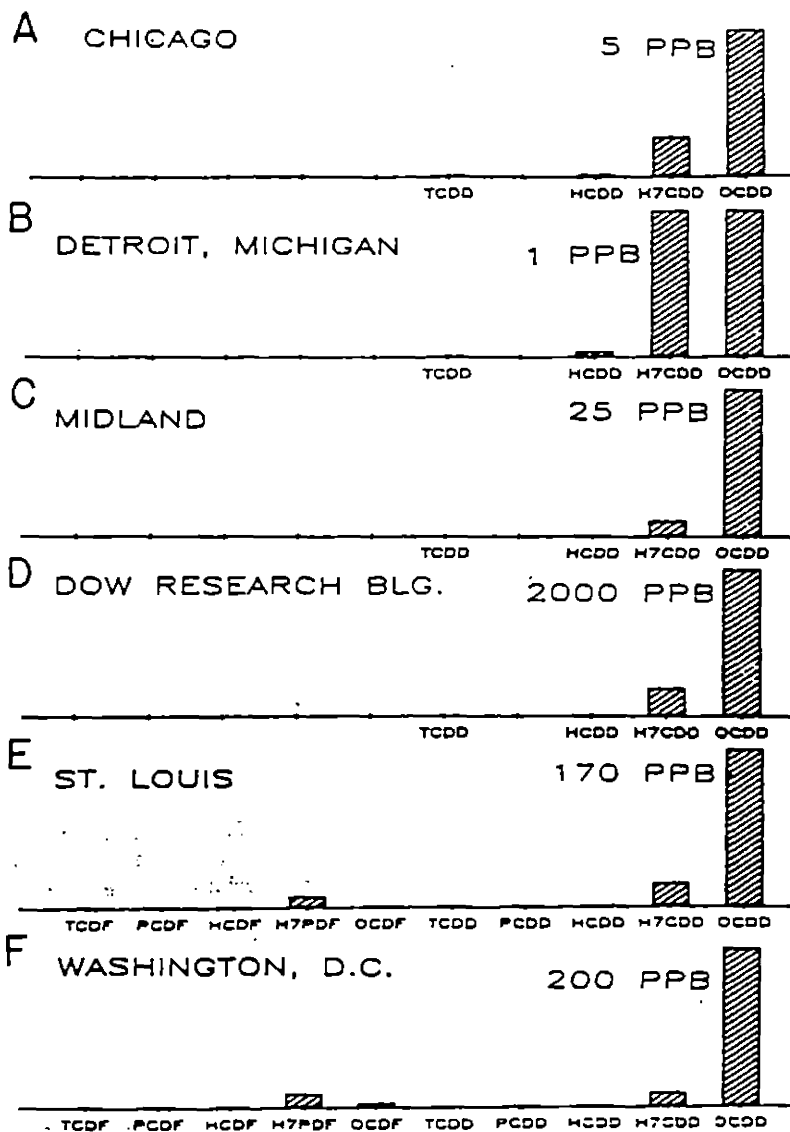


Figure 6. Dioxin and furan congener profiles found in air particulate samples. (Adapted from: A-D, Bumb *et al.*, 1980; E-F, this work.)

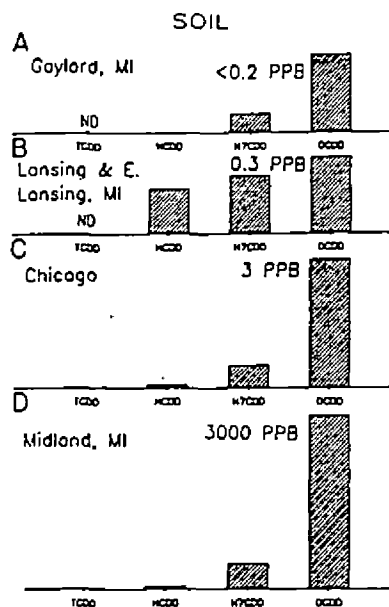


Figure 7. Dioxin and furan congener profiles found in soil. (Adapted from Bumb *et al.*, 1980.)

SOIL

As seen in the analyses of air particulates above, the analysis of soil (Figure 7) also shows a predominance of OCDD. Again, we find high levels of OCDD in Midland, Michigan close to chemical waste combustion sources. Dioxins are also found in rural locations such as Gaylord, Michigan suggesting that atmospheric transport may carry combustion particulates (with their load of PCDD and PCDF) to remote areas.

THE AQUATIC ENVIRONMENT

Water

No data have been published on PCDD and PCDF in natural waters. Although PCDD and PCDF were found in Great Lakes fish (Stalling *et al.*, 1983), we lack information on the concentration and congener profiles of PCDD and PCDF in water itself. There is an obvious need for research in this area.

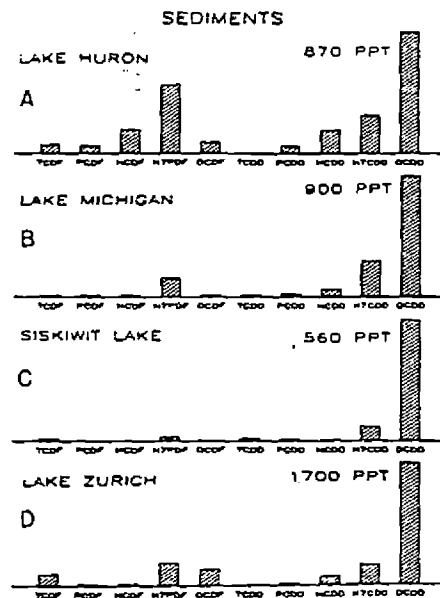


Figure 8. Dioxin and furan congener profiles found in surficial lake sediments (ppt).

Aquatic Sediments

Surficial sediments. Sediments are the ultimate sink of many anthropogenic compounds. We report in Figure 8 the analysis of surficial sediments from the Great Lakes, Siskiwit Lake and Lake Zurich for PCDD and PCDF. The coordinates for these sample sites are reported below. Analytical methods are described in Czuczwa and Hites (1984). Dioxin and furan congener profiles are similar in all sediments and are similar to those in the air and soil samples reported above. OCDD predominates, with lesser amounts of H7CDF and H7CDD. The average concentrations of OCDD found in Lake Huron (870 ppt) and Lake Michigan (900 ppt) are equal, suggesting that atmospheric transport is the common source of dioxins and furans to both areas.

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Historical record of dioxins and furans in sediment cores. We believe that dioxins and furans emitted on particulates from combustion sources travel through the atmosphere to remote locations where they are deposited in sediments. Sediments, sampled in such a way that the historical input of materials is preserved, can be analyzed for dioxins and furans. Thus, analyses of dated sediment cores provide us with the relative historical emission rates of PCDD and PCDF. Since combustion practices have changed with time, we should see similar changes in the dioxins and furans found in sediment cores.

We can use historical emission rates to address three questions about combustion-generated dioxins and furans. First, Bumb *et al.*, (1980) use data on emissions from a variety of combustion sources to suggest that dioxins and furans have been formed since the advent of fire. Is there any evidence for this in the sediment record? Second, is coal a major source of PCDD and PCDF? Coal combustion has been extensive since 1900. If this source is significant it should be apparent in sediment core studies. Third, can we find any evidence to suggest that PCDD and PCDF are formed in significant amounts only when combustion fuels contain chlorinated precursor compounds present in chemical and municipal wastes?

In Figure 10A to C, we show the analyses of sediment cores from 3 locations in Lake Huron (Core 1, 43° 30'N, 81° 55'W; Core 3, 43° 50'N, 82° 0'W; Core 4, 44° 0'N, 82° 10'W). We show the most abundant species, OCDD, H7CDD, H7CDF and OCDF. The concentrations are plotted against the average year of deposition. The congener ratios remain relatively constant with depth suggesting that these compounds are stable after burial. In all cases, we see significant increases in PCDD and PCDF after the 1940's. The small background amounts of dioxins, (predominantly OCDD) reported before 1940 are not significantly greater than our laboratory background; and therefore, they may not be indicative of inputs due to natural or coal combustion sources.

In Figure 10D, we find the same trend for a location from northern Lake Michigan (43° 43'N, 86° 38'W). Again, significant amounts of dioxins and furans occur after 1940. We have not yet determined sedimentation rates for the Siskiwit Lake core (48° 02'N, 88° 48'W). However, based on previous work, we estimate a sedimentation rate of 0.1 cm/yr, and use this to calculate depositional ages. Therefore, the results from this core (see Figure 10E) must be considered preliminary, but it is apparent that PCDD and PCDF increased with time.

The core from Lake Zurich, shown in Figure 10F, had yearly carbonate laminae or varves (Kelts and Hsu, 1978). The dating of this sediment core is, therefore, done in a straightforward manner by counting yearly lamina. Mixing effects between layers are minimal. Thus, this core is ideal for studying the historical input of dioxins and furans. We again see an increase in PCDD and PCDF after 1940. Congener ratios are again constant with depth.

Figure 11, bottom, shows the historical trends for the cores from the Great Lakes, Siskiwit Lake and Lake Zurich. The agreement is remarkable despite the uncertainties inherent in environmental measurements. If we compare these trends with that for the use of coal (shown in Figure 11, top) we would have expected dioxins and furans to increase around 1900. Thus, coal is clearly not a major source of PCDD and PCDF found in these sediments.

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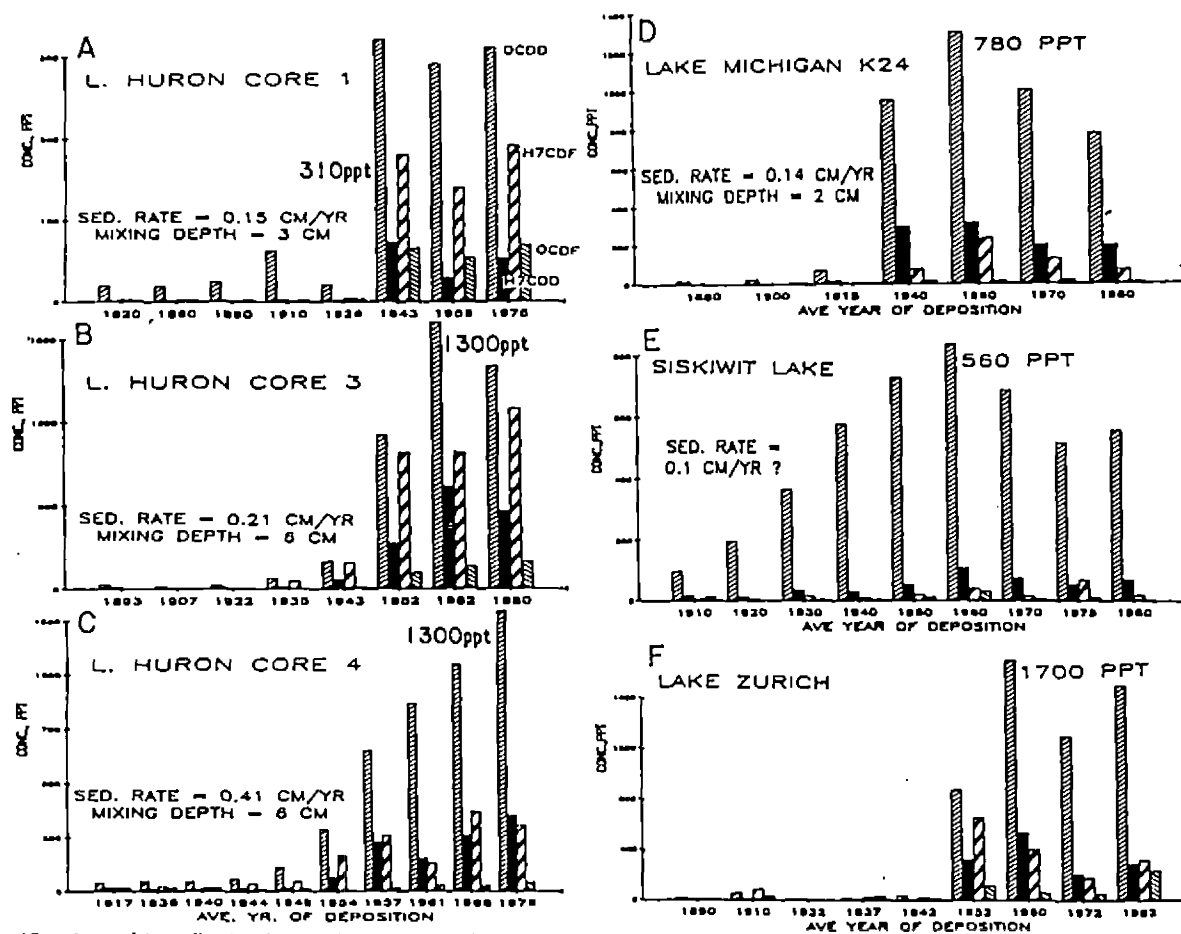


Figure 10. Octachlorodioxin, heptachlorodioxin, heptachlorofuran and octachlorofuran concentrations, in ppt, as a function of average year of deposition in several sediment cores. A-C, Lake Huron Sediment cores; D, Lake Michigan sediment core; E, Siskiwit Lake sediment core (depositional ages preliminary); F, Lake Zurich sediment core. Concentration given is OCDD.

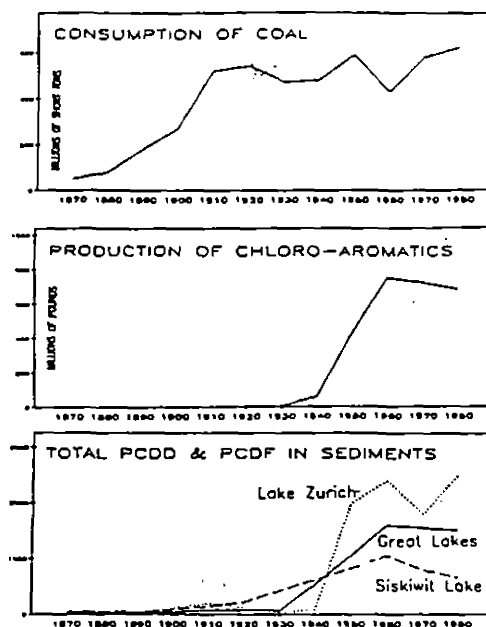


Figure 11. U.S. consumption of coal (top) and production of synthetic chlorinated organics (taken from Czuczwa and Hites, 1984) compared to the total PCDD and PCDF in sediment cores from the Great Lakes, Siskiwit Lake and Lake Zurich (bottom).

Records for the production of chlorinated aromatics are shown in Figure 11, middle. Production has increased steadily since 1940, and this trend agrees well with the dioxin and furan profiles for the sediment cores. Some portion of the chemical wastes produced in the synthesis of chloro-aromatics are incinerated. As we noted above, the emission of dioxins and furans from such incineration is one source of PCDD and PCDF. Chlorinated aromatic compounds produced by the chemical industry are used in a variety of products, some of which enter solid wastes, with a portion eventually being disposed of by incineration. This is a second source of airborne PCDD and PCDF.

Thus, we believe that the observed historical increase in PCDD and PCDF found in the sedimentary record is the result of the combustion of chlorinated compounds present in combustion fuels. We see no evidence of inputs from coal or natural combustion sources. The high levels of dioxins and furans presently accumulating in the sedimentary environment are not due to the advent of fire, but are indirectly due to the chemical industry.

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