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the uptake times of hydrophobic contaminants may be very long; thus, equilibrium may not be reached. An example is the recent study of chlorobenzene (CB) congener uptake by Oliver and Niimi (*14*). In this case, the half-times for uptake were approximately the following: tetra-CB, 15 days; penta-CB, 50 days; in which the hexa-CB congener had not reached equilibrium after 120 days. This is the trend predicted by the equation. These authors correctly identified that the experimental BCF of HCB after 120 days was not an equilibrium value and showed that this could lead to erroneous prediction of fish concentrations in Lake Ontario.

It should be emphasized that although the narcotic effect of PAB esters is well described by this equation, not all toxic effects are likely to be amenable to such simple analysis.

It is apparent that by formulating the equations in the fugacity format, it becomes easier to manipulate the variables and new insights are obtained into the pharmacokinetic processes. It is relatively easy to formulate and test equations describing uptake from food, to include metabolic degrading reactions, and thus to build up more comprehensive equations describing these pharmacokinetic processes.

Registry No. 2,5-Dichlorobiphenyl, 34883-39-1; 2,2',5-trichlorobiphenyl, 37680-65-2; 2,4',5-trichlorobiphenyl, 16606-02-3; 2,2',5,5'-tetrachlorobiphenyl, 35693-99-3; 2,3',4',5-tetrachlorobiphenyl, 32598-11-1; methyl *p*-aminobenzoate, 619-45-4; ethyl

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Environmental Fate of Combustion-Generated Polychlorinated Dioxins and Furans

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■ Polychlorinated dioxins and furans were found in sediments from the Saginaw River and Bay and from Lake Huron. The congener distributions of the dioxins and furans indicate that combustion may be the major source of these compounds. The depth vs. concentration profiles in dated sediment cores showed that emission of dioxins and furans has increased greatly since 1940. This historical increase is similar to trends for the production, use, and disposal of chlorinated organic compounds and suggests that chlorinated precursors of dioxins and furans, present in incinerator combustion fuels, may be the main source of the dioxins and furans found in these sediments.

Introduction

Polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) are the subject of a recent, often heated debate because some of these compounds are very toxic. For example, 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) has been found to be acnegenic to humans (*1*), teratogenic to mice (*2*), carcinogenic to rats (*3*); and acutely toxic to guinea pigs (*4*). Other isomers of PCDD (75 total) show differing degrees of toxicity; isomers of PCDF (135 total) are generally as toxic as the corresponding PCDD.

Initially, PCDD and PCDF were discovered as trace impurities in various chlorinated aromatic compounds. We will call these "industrially generated" dioxins and furans. PCDD and PCDF were found in chlorophenols (*5–7*), herbicides (*8–10*), and PCB's (*11*). Industrially generated PCDD and PCDF have entered the environment through accidental release during chlorophenol production (*12*), aerial application of phenoxy herbicides (*13*), and improper disposal of wastes (*14*). These events tend to be sporadic and localized.

More recently, PCDD and PCDF have been identified in effluents from combustion processes. In particular, dioxins and furans have been found in the fly ash and flue gas of municipal incinerators (*15–18*). The PCDD and PCDF may be associated with small particulates, which have long residence times in the atmosphere, and in this manner, combustion-generated dioxins and furans could become distributed over large areas. Thus, combustion may have made PCDD and PCDF ubiquitous in the environment.

The initial reports of PCDD and PCDF in municipal incinerator fly ash led to an investigation of a variety of combustion processes each of which was a possible source of PCDD and PCDF (*19*). PCDD and PCDF were measured in particulates from the combustion of municipal and chemical wastes and fossil fuels, and in some unusual samples such as cigarette smoke and charcoal-broiled steak. The researchers concluded that PCDD and PCDF are ubiquitous products of the combustion of organic materials. In an interview (*20*), an author of this paper stated,

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suggested that there may be fewer sources of combustion-generated dioxins than initially thought.

A fundamental point in this debate centers on the mechanism of formation of dioxins and furans in combustion sources. PCDD and PCDF may be formed by the cyclization of chlorinated precursors present in the fuel or by the reaction of organic compounds with inorganic chlorine both present in the fuel. It is likely that the first mechanism is operative; model pyrolysis experiments have shown that PCDD and/or PCDF are formed by pyrolyzing chlorinated precursors such as chlorobenzenes (*23*), chlorophenols (*24*), and PCB's (*25*). There is little experimental evidence for the second mechanism, but it cannot yet be excluded. In any case, the first mechanism is likely to form PCDD and PCDF in higher yields than the second mechanism.

Because of the toxicity of these compounds, it is important to know their environmental fate. We propose the following paradigm: Once emitted from a combustion source, the particulates (carrying their load of dioxins and furans) can travel some distance, which is a strong function of the size of the particle. Larger particles will settle close to the source while small particles may have sufficient residence times in the atmosphere to be transported to remote locations. Thus, PCDD and PCDF may be carried by direct airborne transport to ultimate environmental sinks such as the oceans or lakes. After deposition in these aquatic systems, the dioxins and furans will settle to the bottom sediments. As earlier sediments become buried by materials deposited in subsequent years, an historical record to dioxin and furan inputs to the environment will be preserved.

Some caveats should be stated regarding this general model for the environmental fate of PCDD and PCDF. First, the sources are highly variable. The quantity and isomeric distribution of PCDD and PCDF emitted will depend on combustor design, operating conditions, composition of the fuel, and degree of emission control. Second, environmental alterations in the air or water column due to photodecomposition, biodegradation, volatilization, or bioaccumulation may occur. Third, we have assumed that these compounds are not subject to degradation once they are in the sediments. This is probably a good assumption; a recent summary of the environmental chemistry of PCDD suggests that microbial degradation is negligible (*26*). Fourth, sediment mixing processes introduce some, usually minor, uncertainty in interpreting the historical trends of compounds deposited in sediments.

The goal of our study is to approach two of the present questions concerning PCDD and PCDF: (a) Are the PCDD and PCDF which are present in the environment the result of industrial production or combustion? (b) Is there evidence regarding the historical input of these materials into the environment which could more clearly define the mechanism of their formation? To address these questions, we measured PCDD and PCDF in samples from combustion sources and from lacustrine sediments.

Fly ashes from a municipal incinerator and from coal-fired power plants were analyzed to study the dioxin and furan congener distributions typical of combustion samples. These distributions can be used to determine if sources. Another was PCDD and PCDF concentrations as a function of distance from anthropogenic activity. The most valuable information came from the analysis of sediment cores. Sections of cores were analyzed for PCDD and PCDF and dated by radioisotopic techniques. Thus, the historical input of dioxins and furans was obtained. We used these data to distinguish between anthropogenic and natural inputs of PCDD and PCDF.

Experimental Section

Fly Ash. Four fly ash samples were obtained from B. J. Kimble (Laboratory of Energy-Related Health Research, Davis, CA). Samples 1 and 2 were collected from the cyclone stage (cyclone ash) and electrostatic precipitator (ESP hopper ash), respectively, of a midwestern municipal incinerator. Samples 3 and 4 were from two coal-fired power plants burning western (low sulfur, low chlorine) coal.

Approximately 10 g of fly ash was spiked with 100 ng of $^{37}Cl_8$-OCDD (KOR Isotopes, Cambridge, MA), allowed to dry, and Soxhlet extracted with 200 mL of "distilled in glass" grade benzene (MCB Reagents, Cincinnati, OH) for 24 h. The resulting extract was concentrated by rotary evaporation to less than 1 mL and the solvent exchanged to hexane for alumina fractionation.

Preextracted neutral alumina (Brockman Activity I, Fisher Scientific) was activated at 250 °C for 2 h. It was then deactivated with 1% by weight distilled water and allowed to equilibrate for 16 h. A 0.5 × 6.5 cm microcolumn was packed and washed with hexane. The sample was introduced and eluted with 8 mL each of hexane, 2% methylene chloride in hexane, and 40% methylene chloride in hexane. Dioxins and furans eluted in the 40% fraction, which was concentrated to 100 μL by slowly passing a stream of purified N_2 over the sample. The sample was then ready for analysis by methane negative chemical ionization gas chromatographic mass spectrometry (NCI-GC/MS).

Sediments. The sampling sites are shown in Figure 1. A sediment grab sample, nominal depth of 8 cm, was collected in 1981 from the Saginaw River (station 161) by C. P. Rice (Great Lakes Research Division, University of Michigan, Ann Arbor, MI). The location was close to the mouth of the Saginaw River (43° 39′N, 83° 51′W). A sediment core from Saginaw Bay (station 30A) (43° 52′N, 83° 40′W) and two companion sediment cores from Southern Lake Huron (SLH-75-46L, and H, 43° 30′N, 81° 55′W, further referred to as cores 1 and 2, respectively) were collected by J. A. Robbins (National Ocean and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, MI). We used only the top 1-cm section of the Saginaw Bay core. Two cores from southern Lake Huron were collected by S. J. Eisenreich (Department of Civil and Mineral Engineering, University of Minnesota, Minneapolis, MN) and J. A. Robbins. These samples were collected in 1981 by using a box corer at coordinates 43° 59′N, 81° 59′W (core 3) and 43° 59′N, 82° 10′W (core 4). All cores were sectioned into intervals of 1 cm to a depth of 10 cm and then into 2–5-cm segments, depending on depth.

Approximately 50 g (wet weight) of sediment was placed in glass Soxhlet thimbles and spiked with between 2 ng

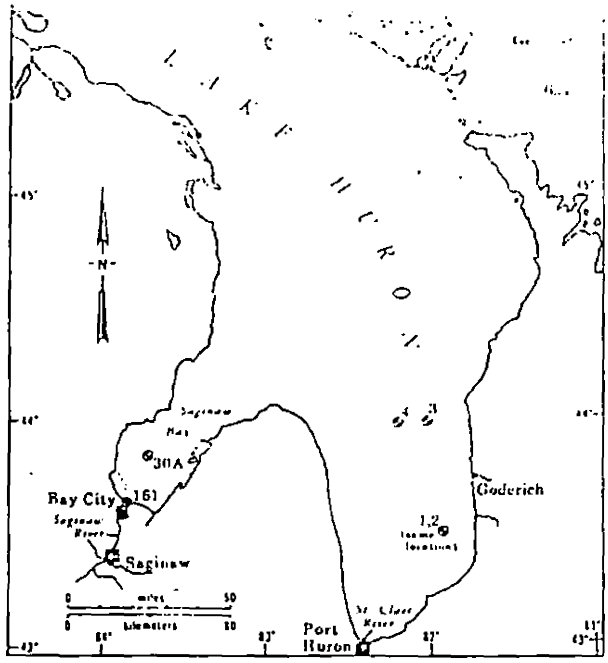

Figure 1. Map showing the Lake Huron sample sites.

and 200 pg of the $^{37}Cl_8$-OCDD standard, depending on the expected dioxin and furan levels. The samples were extracted for the first 24 h with 200 mL of 2-propanol to remove water, followed by extraction with 200 mL of methylene chloride for an additional 24 h. The methylene chloride and 2-propanol extracts were combined, then reduced to 2 mL by rotary evaporation, and subjected to a three-step chromatographic cleanup.

Natural sediments sometimes contain significant amounts of elemental sulfur which can interfere in the analysis. Thus, sulfur was removed by an activated copper column. Fifty grams of copper (purified electrolytic dust; Fisher Scientific) was activated with concentrated HCl. A glass column (1 × 25 cm) was filled with the copper slurry. The sediment extract was passed through the column and eluted with 150 mL of methylene chloride. The eluent was concentrated to 2 mL, and the solvent was exchanged to hexane for fractionation on silica.

Preextracted silica gel (Davidson Chemical, Baltimore, MD) was activated at 160 °C for 16 h, deactivated with 1% water, and loaded into a 1.5 × 25 cm column with hexane. The sample was introduced and eluted with 75 mL each of hexane, 15% methylene chloride in hexane, and methylene chloride. Dioxins and furans eluted in the second fraction. The solvent was again reduced and exchanged to hexane. The final step was alumina chromatography as described above.

NCI-GC/MS Analysis. Negative chemical ionization (NCI) mass spectrometry is particularly sensitive to molecules that have a high electron capture cross section due to electrophilic atoms such as chlorine (27). Thus, NCI is an ideal technique for the analysis of PCDD and PCDF. The enhancement of sensitivity is especially pronounced for the more highly chlorinated dioxins and furans. In our laboratory, OCDD showed a 100-fold increase in sensitivity over that of electron impact (EI).

All the analyses were obtained on a Hewlett-Packard 5985B GC/MS system. Chromatographic separation was

this work	0.2	1.0	1.2	25	170
ref 19	0.2		2	34	210

achieved on a 30 m × 0.25 mm DB-5 fused silica column (J & W Scientific, Rancho Cordova, CA) with helium carrier gas (splitless injection at 30 °C, isothermal for 4 min, 4 °C/min to 280 °C, isothermal for 20 min). The ion source temperature was 250 °C, and the pressure of methane was typically maintained at 0.7 torr in the ion source. To further increase sensitivity, selected ion monitoring was used. Ions were monitored for tetrachloro- through octachlorodioxins and furans, including a confirming ion [M^- or $(M - Cl)^-$, depending on the isomer]. The ions used for quantitation were the following: tetrachlorodioxins (TCDD), *m/e* 322; pentachlorodioxins (PnCDD), *m/e* 356; hexachlorodioxins (HxCDD), *m/e* 355; heptachlorodioxins (HpCDD), *m/e* 389; octachlorodioxin (OCDD), *m/e* 423; tetrachlorofurans (TCDF), *m/e* 306; pentachlorofurans (PnCDF), *m/e* 340; hexachlorofurans (HxCDF), *m/e* 374; heptachlorofurans (HpCDF), *m/e* 408; octachlorofuran (OCDF), *m/e* 444. In addition, *m/e* 435 was monitored, representing the M – Cl ion of the internal standard. Dioxins and furans were quantitated by ratioing the appropriate peak area to that of the internal standard and correcting for relative response factors which were obtained from a standard mixture of PCDD and PCDF (one isomer per congener class). Concentrations are reported in parts per billion (ppb = 10^{-9}) or in parts per trillion (ppt = 10^{-12}).

Dating of Sediment Cores. Sedimentation rates for the cores were determined by J. A. Robbins and K. A. Johansen (NOAA, Ann Arbor, MI) by using the ^{137}Cs and ^{210}Pb techniques of Robbins and Edgington (28). Sedimentation rates varied from 0.15 to 0.41 cm/year and will be discussed below.

Quality Assurance. The analytical work followed the guidelines suggested by the ACS Committee on Environmental Improvement (29). Experiments included replicates, procedural blanks, and recovery measurements. The recovery averaged 75% even for the lowest level samples. The average reproducibility was better than ±30%, the least reproducible being the tetrachloro- and pentachloro-PCDD and -PCDF. The limit of detection was 20 pg for 1,2,3,4-TCDD and 0.2 pg for OCDD. Subsequently, it was found that lowering the GC/MS ion source temperature to 150 °C resulted in increased sensitivity, lowering the limits of detection to 0.05 pg for 1,2,3,4-TCDD and 0.1 pg for OCDD.

Method validation included an interlaboratory calibration experiment. In Table I, dioxin concentrations measured by the above procedure in a sample of St. Louis air particulates (National Bureau of Standards, Standard Reference Material 1648) are compared with those reported by Bumb et al. (19). Although the extraction, cleanup, and mass spectrometric techniques are different, the results agree within the measurement error of the procedures.

Results and Discussion

Combustion Sources. Figure 2 shows the results of the fly ash analyses; note that four different concentration scales are used in this figure. Sample 1, collected at the

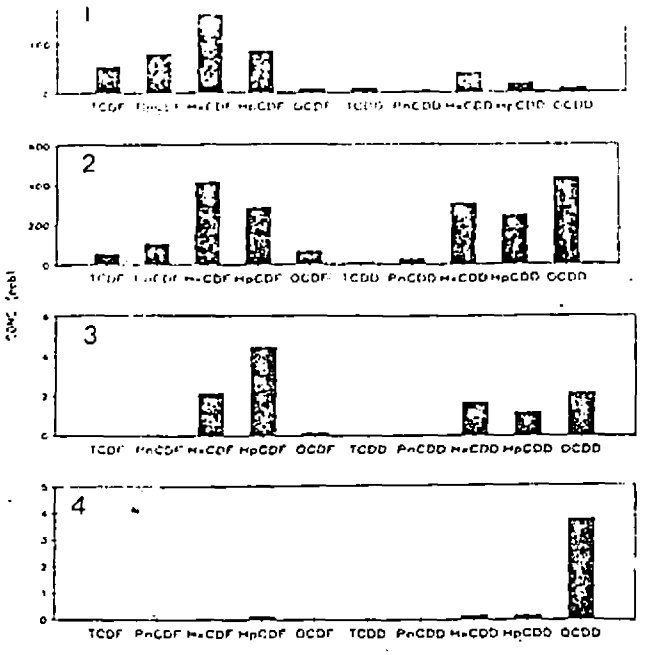

Figure 2. Concentration profiles of PCDD and PCDF congeners in combustion particulate samples from the following: 1, a midwestern municipal incinerator cyclone; 2, the electrostatic precipitator from the same incinerator; 3 and 4, two coal-fired power plants burning western coal.

cyclone stage of a municipal incinerator, contained lower concentrations of PCDD and PCDF than the electrostatic precipitator (ESP) hopper ash (sample 2) from the same plant. This can be explained by the following mechanism: At the cyclone stage, materials are close to the combustion chamber and are collected at a higher temperature than at the ESP. In the cyclone, the dioxins and furans could be primarily in the vapor phase and, therefore, not associated with the particulates. As the effluents reach the ESP, the temperature has decreased, and PCDD and PCDF are now condensed on the particulate phase and, thus, are collected.

It is useful to note some trends in the PCDD and PCDF congener distributions in the fly ash samples (see Figure 2, samples 2–4). First, a large number of isomers were detected for each PCDD and PCDF congener. Second, OCDD is the most abundant dioxin, and OCDF is present in much lower concentrations than OCDD. And third, the hexa- or heptachlorodibenzofurans are the most abundant furans. Similar dioxin congener profiles were also measured in fly ash samples from a powerhouse, a rotary kiln, and waste incinerating facilities in a recent study (*19*) and in municipal incinerator fly ash (*15–18*). These general trends will be compared in the profiles found in environmental samples to distinguish among possible sources.

It is important, however, to recognize that these samples represent only a few sampling occasions and, therefore, may not be representative of combustion processes in general. Furthermore, an extrapolation of these trends to those found in environmental samples does not take into account the probability that fly ash collected in an electrostatic precipitator may not accurately reflect the PCDD and PCDF that are emitted. These data will simply be used to compare combustion processes with environmental samples.

The coal fly ash samples (Figure 2, samples 3 and 4) differ significantly from the municipal incinerator ash samples. Although some PCDD and PCDF were detected, no tetrachloro- or pentachlorodioxins or -furans were detected, with limits of detection of 100 ppt (tetra) and 10

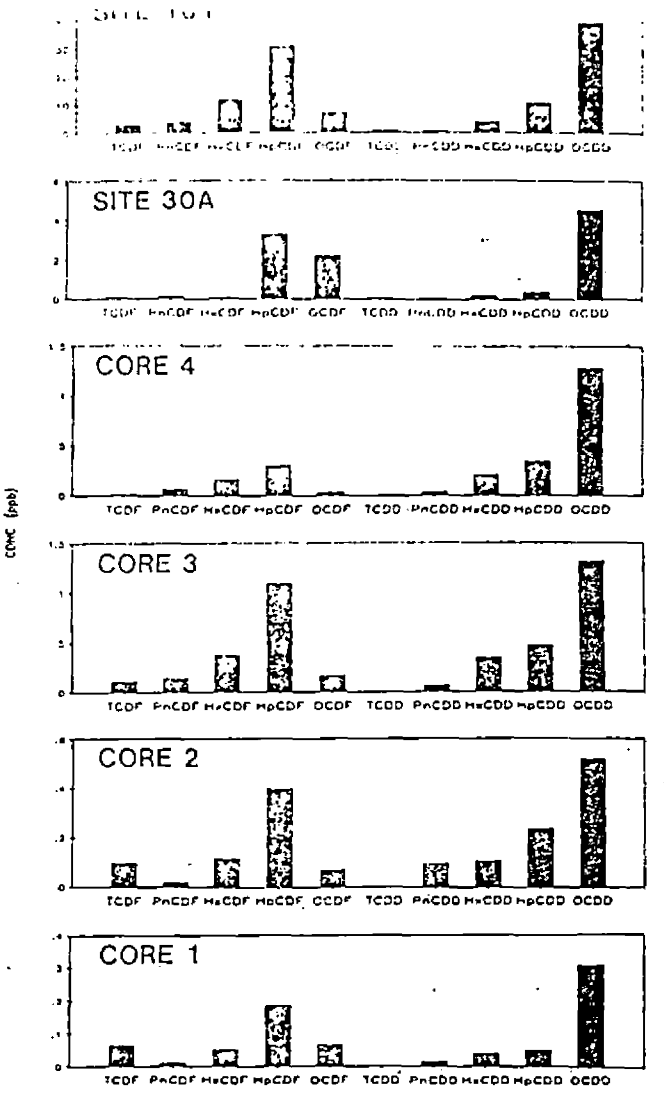

Figure 3. PCDD and PCDF congener profiles in six surficial sediments (see Figure 1 for site locations).

ppt (penta). Dioxins and furans, when present, were in much lower concentrations than in the municipal incinerator ash. For example, the levels of OCDD in the coal fly ash samples (2.2 and 3.8 ppb in samples 3 and 4, respectively) were at least 100 times lower than those found in the municipal incinerator ash (440 ppb).

Although coal fly ash clearly contains less OCDD then municipal incinerator ash, it still could be a significant source of OCDD to the environment, since coal combustion is so prevalent. In 1974, the amount of particulates emitted from coal combustion was estimated to be 2.4×10^9 kg (*30*). The amount of particulates emitted from solid waste incineration in 1971 was estimated at 7×10^8 kg (*31*). Thus, approximately 3 times more particulates are emitted from coal combustion than from solid waste combustion. If the OCDD concentration on coal particulates is 100 times lower, then total emission of OCDD from coal combustion would still be approximately 30 times lower than that from municipal waste incineration.

Finally, we should address the ongoing debate regarding 2,3,7,8-TCDD in coal fly ash. No isomer of TCDD was detected in these samples with a limit of detection of about 100 ppt. This reaffirms similar findings (*21*, *22*) and suggests that coal combustion is not a significant source of 2,3,7,8-TCDD to the environment.

Surface Sediments. Figure 3 shows that the dioxin and furan congener profiles obtained from surficial sedi-

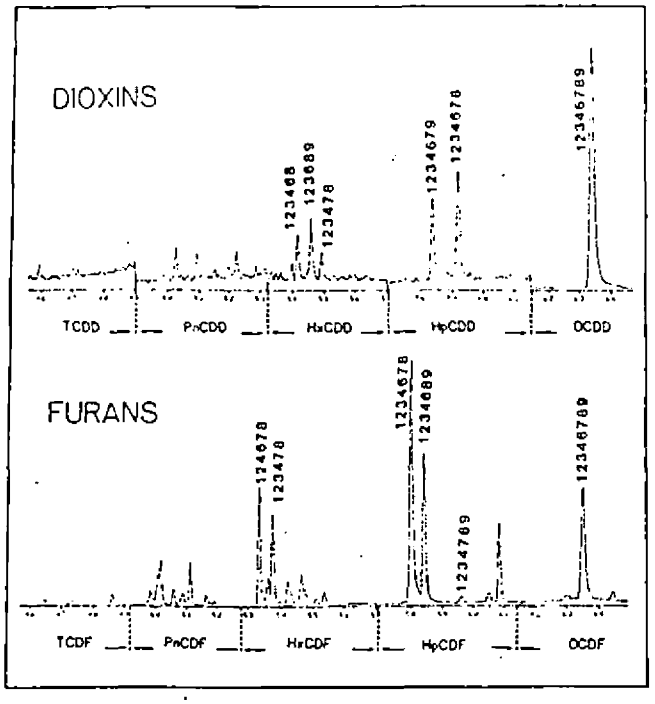

Figure 4. Mass chromatograms showing PCDD and PCDF in the surficial segment from core 1. These data have not been corrected for response factors.

ments from the Saginaw River and Bay and from southern Lake Huron. PCDD and PCDF are ubiquitous in the samples studied, including the most remote locations. The profiles are similar to those shown in Figure 2. The concentrations of PCDD and PCDF are highest in those sediments collected closest to urban areas (161 and 30A) and lowest in the open lake cores. This indicates that the PCDD and PCDF found in these samples are anthropogenic in origin.

Figure 4 shows the mass chromatograms for the dioxins and furans in the surficial segment of core 1. These data illustrate the typical combustion "fingerprint" discussed earlier. A number of isomers for each dioxin and furan congener class are detected. One finds a predominance of OCDD and HpCDF and greater levels of TCDF and PnCDF than the corresponding dioxins. In general, the PCDD and PCDF isomer distributions, even in the most remote samples, are similar to each other and are indicative of combustion. We, therefore, conclude that combustion is probably the major source of PCDD and PCDF to these locations. These data emphasize the importance of determining the entire PCDD/PCDF profile rather than just the 2,3,7,8-TCDD content. Future work will include isomer-specific quantitation of all tetra- through octachlorodioxins and -furans, thus increasing our ability to distinguish among sources.

Sediment Cores. As outlined above, we have obtained data on sediment cores to determine the historical input of PCDD and PCDF. Obviously, the amount and the composition of fuels have changed with time. The effect of these changes on the input of dioxins and furans to the environment should be reflected in the sedimentary record. Similar work by Hites et al. (*32*) showed that sedimentary polycyclic aromatic hydrocarbons reflected the changing use of fossil fuels.

The most abundant PCDD and PCDF in cores 1–4 were HpCDD, HpCDF, and OCDD. The depth vs. concentration profiles for these species are shown in Figure 5. The sedimentation rate for cores 1 and 2 (companion cores from the same location) was calculated from the radioisotopic data and was found to be 0.15 cm/year. This was used to

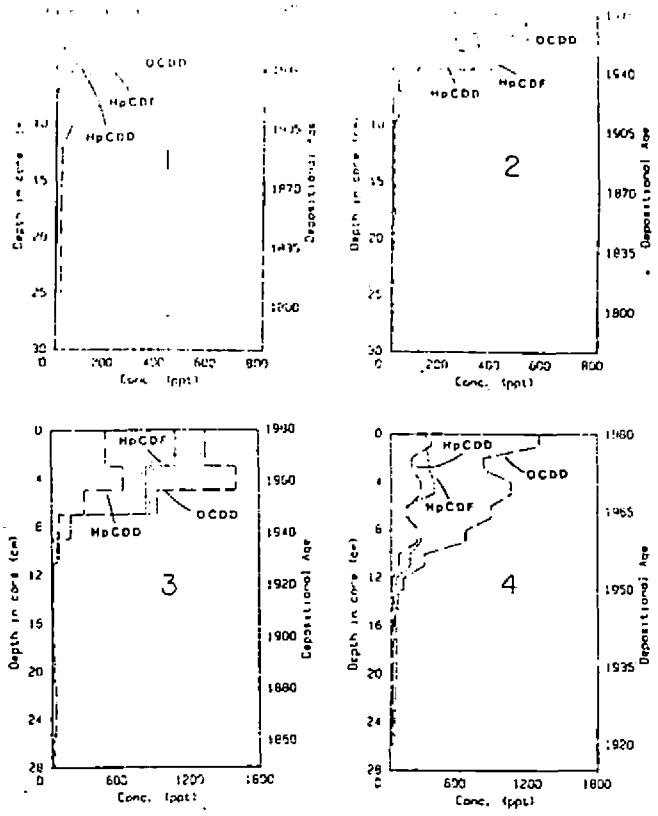

Figure 5. HpCDF, HpCDD, and OCDD concentrations in four Lake Huron cores vs. depth (left axis) and depositional age (right axis).

estimate the year of deposition corresponding to each depth, and these data are also plotted in Figure 5 (top). The mixing depth was 2.8 cm and is an indicator of the degree of movement of materials after deposition. This indicates that there may be an averaging of inputs over as much as a 15-year interval. In both cores 1 and 2, there is an abrupt increase in PCDD and PCDF concentrations around 1940. Lake Huron core 3 had a sedimentation rate of 0.21 cm/year and a mixing depth of 6.4 cm. This core also showed that PCDD and PCDF inputs increased around 1940 (see Figure 5, bottom left). Core 4 had a substantially higher sedimentation rate (0.41 cm/year, mixing depth of 5.9 cm) and thus offered greater time resolution for this trend. From this core, it is apparent that PCDD and PCDF inputs increased slowly during the 1940s and early 1950s to the present levels (see Figure 5, bottom, right). In general, the concentrations of PCDD and PCDF in core sections corresponding to deposition before 1940 are low, representing a much lower input of these materials before this time.

These changes cannot be accounted for by in situ degradation of PCDD and PCDF in the sediment. The congener profiles in all cores were similar to each other and were consistent along the depth of the core. This is best illustrated in Figure 6 which shows the congener distributions for core 4 as a function of depth. Note the similarity of the pattern with depth. Furthermore, isomer ratios were calculated at each depth in core 4 and were found to be constant. For example, the ratio of 1,2,3,4,6,7,8-HpCDF to 1,2,3,4,6,8,9-HpCDF was 0.71 ± 0.27, the ratio of 1,2,3,4,6,7,9-HpCDD to 1,2,3,4,6,7,8-HpCDD was 0.72 ± 0.06, and the ratio of OCDD to 1,2,3,4,6,7,8-HpCDD was 2.8 ± 0.36. There were no trends in the ratios with increasing depth for any of the hepta- or octachlorodioxins or -furans. Thus, there is no evidence of degradation of these PCDD or PCDF in these Lake Huron cores.

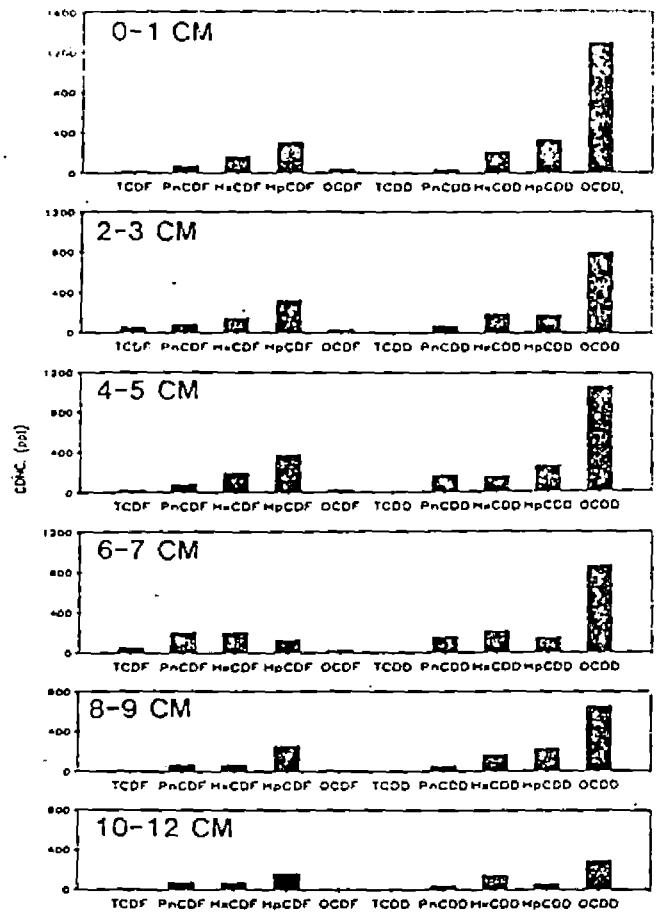

Figure 6. PCDD and PCDF congener profiles in core 4 as a function of depth.

Clearly, the dioxin and furan inputs have changed considerably over time; much more were deposited since 1940. It seems likely that a major source began in the 1940s and increased until the present time. What is such a source?

The burning of coal has been a major combustion process since the last century, and coal fly ash, as shown earlier, contains some PCDD and PCDF. The trend for U.S. coal consumption for the last century is shown in Figure 7 (top) (*33*). Coal use in the Great Lakes area parallels that of the nation. For example, in 1930, Illinois, Indiana, Ohio, Michigan, and Wisconsin accounted for 40% of the nation's coal consumption, in 1957, 30%, and in 1970, 30% (*33*). Therefore, we may safely compare U.S. coal consumption to sedimentary dioxins and furans in the Great Lakes. Figure 7 compares coal consumption with the total HpCDD, HpCDF, OCDD, and OCDF found in the four Lake Huron cores (see Figure 7, bottom). It is obvious that coal use cannot account for the increase in dioxin and furan concentration since 1940. Indeed, coal use has been relatively constant since 1910.

The U.S. Tarriff Commission Reports of Production and Sales of Synthetic Organic Chemicals (*34*), published since 1918, reveal that the chemical industry grew greatly beginning in 1940. Starting at this time, the production of chlorinated organic compounds such as chlorobenzenes and chlorophenols increased substantially (see Figure 7, middle). These compounds are used in a variety of products, including building supplies, herbicides, and packaging. Much of these materials eventually become incorporated in solid wastes. The trend for the production of chloro organic compounds is very similar to the sedimentary PCDD and PCDF profiles (compare Figure 7, middle and bottom). The agreement between these two trends is convincing despite the uncertainties introduced by sedi-

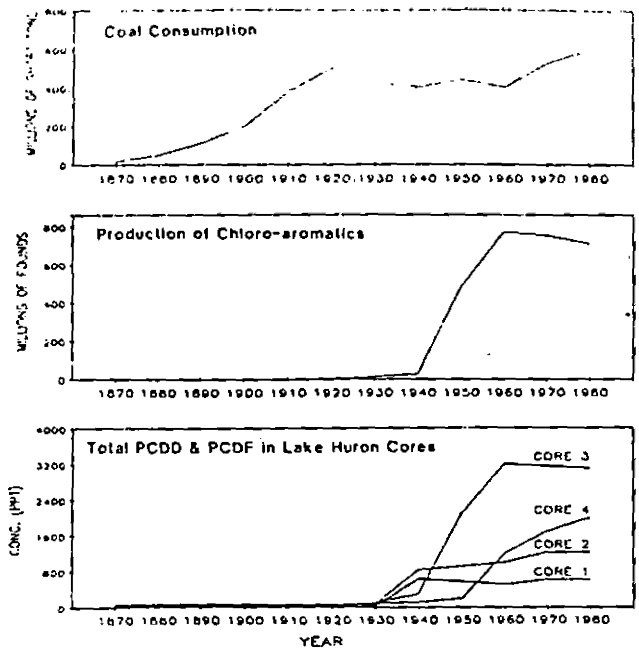

Figure 7. U.S. consumption of coal and production of synthetic chlorinated organics (includes chloro- and dichlorobenzenes, 2,4-dichloro- and 2,4,5-trichlorophenoxyacetic acid, esters and salts, and pentachlorophenol) compared to the total PCDD and PCDF in the four Lake Huron cores as a function of time (all are plotted on a decade basis).

ment mixing and the errors inherent in the dating and quantitation techniques.

From these data, we conclude that the input of dioxins and furans to the sedimentary environment is probably due to the combustion of chlorinated organic products present in various wastes. These wastes may be municipal wastes from Saginaw, Bay City, or other urban areas, or they may be industrial wastes from chemical manufacturing taking place in central Michigan. The direct dumping of chemical wastes (for example, from pentachlorophenol production) is an alternate, but unlikely, interpretation of our results. The agreement of the congener and isomer profiles of PCDD and PCDF in the sediments with those in combustion effluents and in air particulates (see Table I) and the coincidence of the production and concentration profiles (see Figure 7) are persuasive pieces of evidence that combustion is the major source. Direct dumping and coal or natural combustion may be real sources, but we believe them to be minor. In any case, it is clear that the high levels of dioxins and furans found in presently accumulating sediments are not due to the "advent of fire."

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Registry No. TCDD, 41903-57-5; PnCDD, 36088-22-9; HxCDD, 34465-46-8; HpCDD, 37871-00-4; OCDD, 3268-87-9; TCDF, 55722-27-5; PnCDF, 30402-15-4; HxCDF, 55684-94-1; HpCDF, 38998-75-3; OCDF, 39001-02-0.

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Reduction and Dissolution of Manganese(III) and Manganese(IV) Oxides by Organics. 1. Reaction with Hydroquinone

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■ The chemical processes by which manganese oxides are solubilized by reduction in anoxic waters are poorly understood. A study of the reduction and dissolution of manganese oxide suspensions by hydroquinone was undertaken to determine the rate and mechanism of the solubilization reaction. Dissolution of the manganese(III,IV) oxide suspension by hydroquinone in the pH range $6.5 < pH < 8.5$ is initially described by the following empirical rate law:

$$d[Mn^{2+}]/dt = k_1[H^+]^{0.46}[QH_2]^{1.0}([MnO_x]_0 - [Mn^{2+}])$$

where $[Mn^{2+}]$ is the dissolved manganese concentration, $[QH_2]$ is the hydroquinone concentration, and $[MnO_x]_0$ is the amount of manganese oxide added. The apparent activation energy was found to be at +37 kJ/mol. Calcium and phosphate inhibited the reaction, by adsorbing on the oxide surface. A model is proposed for the observed rate dependence, according to which complex formation between hydroquinone and manganese oxide surface sites occurs prior to electron transfer.

Introduction

Within the pH range of natural waters, Mn(III) and Mn(IV) form sparingly soluble oxide/hydroxide solid phases, while Mn(II) is soluble. For this reason, dissolution reactions 1 and 2 greatly enhance the mobility of manganese in natural systems. Although oxygenation of Mn^{2+} has been studied extensively (*1–3*), reduction and dissolution reactions are poorly understood. The purpose of this work is to systematically explore the factors that influence how quickly manganese oxides are reduced and dissolved under natural conditions.

$$MnOOH(s) + 3H^+ + e^- = Mn^{2+} + 2H_2O \quad (1)$$

$$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad (2)$$

Natural organic compounds have been found to reduce a variety of inorganic species and are the most readily available reductants in most natural systems. Soil fulvic acids have been shown to reduce Hg(II) to Hg(0), Fe(III) to Fe(II), and I_2 to I^- (*4*). A number of studies have shown that organic compounds with structures similar to natural organics reduce and dissolve manganese oxides (*5–7*).

Generation of radicals by reaction of manganese dioxide with hydroquinone was studied by Fukuzumi et al. (*8, 9*) and Ono et al. (*10*). The rate of semiquinone radical formation was found to be first order with respect to hydroquinone concentration and initial manganese dioxide loading. A mechanism was proposed that involves hydrogen atom abstraction from hydroquinone (*10*).

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