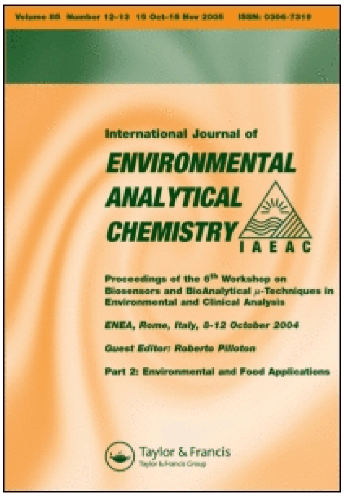

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# Concentrations of Dioxins and Dibenzofurans in the Atmosphere†

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Polychlorinated dibenzo-*p*-dioxins and dibenzofurans have been found in environmental sinks such as lake sediments and human fat. We have previously shown that the most likely source of these compounds is municipal or chemical incineration of chloroaromatic compounds and that there is a transformation of the congener class profile for these compounds as they move from source to sink. This report examines the transportation and depositional media of these compounds by analyzing ambient air and rain samples. Air was sampled with a high volume sampler and split into operationally defined particulate and vapor phases with a glass fiber filter and a polyurethane foam plug. Rain was sampled with a one square meter wet-only collector. The analytical methodology is based on a two step chromatographic clean-up followed by negative ion gas chromatographic mass spectrometry. Concentrations of the different congeners in the samples were 1 to 750 femtograms per cubic meter of ambient air for the vapor and particulate samples. Concentrations of the rain samples were in the picogram per liter range. These are the first measurements of these compounds in ambient air and rain samples. The concentrations in these samples were used to determine vapor/particulate ratios and to compare vapor and particulate scavenging by rain.

KEY WORDS: Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, environmental sinks, municipal incineration, chemical incineration, negative ion GC/MS.

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## INTRODUCTION

When a toxic compound is found in an evironmental sample, several questions arise. These questions include: (1) Where did the compound come from originally? (2) How did it get transported from its source to its current location? (3) What changes took place during the transport process? (4) What impact will this compound have at this site at this concentration? (5) Where else have the compounds emitted from the same source gone? Answers to these and other questions are necessary if we are to mitigate the impact of the compound on the environment. Two related groups of toxic compounds, for whom these questions have been raised, are the polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).

It has previously been shown that a major source of PCDD and PCDF to the environment is the combustion of municipal or chemical waste.[1] This source produces a complex mixture of the various isomers of these compounds. When these compounds are quantified by congener class (level of chlorination), it is seen that combustion generally produces a broad range of congener classes with no class predominating in the sample.[2-9] In contrast, when environmental samples such as sediment[7,10,11] or human fat[12] are analyzed for these compounds, we see a vastly different situation. Octachlorodioxin is the major component; the heptachlorodioxins and furans are minor components; and the other congener classes are present at much smaller concentrations. Thus, a major change in the congener profile has occurred between the source (combustion) and sink (sediments or human fat).

We have undertaken a project to study this change in congener profile by examining the environmental compartments between the sources and sinks. This report will focus on the physical characteristics of dioxins and furans in environmental samples. This will be done by analyzing ambient air for the presence of these compounds; dioxins and furans in both particle bound and vapor phase forms will be measured. This will allow us to examine how these compounds partition between these phases which is important because the vapor phase is more likely to undergo photochemical degradation. A second aspect of this project will be to examine rain for dioxins and furans. This will allow us to directly measure the deposition of these compounds from their dispersal medium (the atmosphere) to the environment. This report will cover the analytical methodology we have chosen to undertake this study and present some preliminary data.

## EXPERIMENTAL

### Materials

All glassware used was washed with detergent (Alconox, Fisher Scientific), rinsed with distilled water, acid washed for 24 hr, rinsed with distilled water, dried at 180°C, and rinsed several times with solvent just prior to use. All solvents were "Omni-Solv" quality (distilled in glass grade, MCB Reagents, Cincinnati, OH); glass wool, sodium sulfate, silica gel, and alumina (Brockman Activity 1) were obtained from Fisher Scientific. These were soxhlet extracted with methylene chloride for 24 hr and oven dried prior to use. Glass fiber filters (Type A/E, Gelman Sciences, Inc., Ann Arbor, MI) were rinsed in methylene chloride, wrapped in solvent rinsed aluminum foil, and put in a muffle furnace for 24 hr at 450°C. Polyurethane foam (Olympic Products Company) was cut into plugs, washed with detergent, rinsed with acetone, put into glass thimbles, soxhlet extracted for 72 hr (24 hr each with acetone, methylene chloride, and petroleum ether) and dried in a vacuum for 24 hr.

Standards used for this study were 1,2,3,4-TCDD; OCDD; OCDF (Foxboro/Analabs, North Haven, CT); 1,2,3,7,8-P5CDD; 1,2,3,4,7,8-HCDD; $^{13}$C-OCDD (KOR Isotopes, Cambridge, MA); 1,2,3,4,6,7,8-H7CDF; 1,2,3,4,6,7,8-H7CDD (Cambridge Isotope Laboratories, Woburn, MA); 2,3,7,8-TCDF; 1,2,4,7,8-P5CDF; 2,3,4,6,7,8-HCDF (gifts of R. Thompson, Canada Centre for Inland Waters, Hamilton, Ontario); see Figure 1 caption for abbreviations.

### Samples

Air and rain samples were obtained using samplers located on a third floor terrace of the SPEA Building of Indiana University, Bloomington, Indiana. This site was inaccessible to the general public, thus assuring the integrity of the samples. The sample location was not ideal because it was located next to a road and near the Indiana University Power Plant, but it was suitable for our preliminary work.

Air was sampled with a high volume air sampler (Sierra-Misco, Inc., Berkeley, CA) operating in a constant flow mode. A pressure gauge on the sampler was claibrated with a Venturi calibrator (Sierra-Misco, Inc.). The gauge was then used to set the flow rate at $0.5\,m^3/min$. Sampled air first passed through a precleaned $0.1\,\mu m$ glass fiber filter to remove the particulate matter and then passed through a precleaned polyurethane foam plug to absorbe the vapor phase dioxins and furans. This has been shown to be an effective technique for sampling pesticides, polycyclic aromatic hydrocarbons, and polychlorinated organics in ambient air.[13–20] The air sample was thus split into operationally defined particulate and vapor phases.

It is important to note that this sampling technique could overestimate the vapor phase and underestimate the particulate phase by two processes. In the first, very fine particulate matter could pass through the filter and be absorbed by the plug. The second is blow-off, in which dioxins absorbed to particulate matter are carried off the particulates by the constant flow of air past the particulate; the "blown-off" material is then adsorbed by the polyurethane foam plug. Air samples were taken over 2–3 day periods (1500–2000 $m^3$ air). This introduces the additional error of temperature variation over the sampling period. A high and low range thermometer was used so that the average temperature during the sampling period could be estimated.

Rain was sampled with a one square meter wet-only collector (Aerochem Metrics, Miami, FL). The sampler was composed of a stainless steel funnel which drains into a precleaned 20 liter bottle. The sampler was equipped with a heated rain sensor so that the funnel's cover opened only when the sensor was wetted at the start of a rain event and closed within two minutes of the end of the event. This ensured that the sampler was not receiving dioxin and furan inputs from dry deposited matter. This sampling strategy was in accordance with the National Academy of Science's view that a wet-only collector is the only accurate way of sampling precipitation.[21]

## Methods

Prior to extraction, all samples were spiked with carbon-13 labeled OCDD. This compound was used as an internal standard, and it was assumed that any losses that occur during the sample extraction and clean-up procedure are the same for the internal standard and for the analytes.

Air particulate samples were soxhlet extracted with 300 mL benzene for 24 hr. Foam plugs were soxhlet extracted with 2 L petroleum ether for 24 hr. Rain samples were extracted with 1 L of methylene chloride by using a stir bar to thoroughly mix the sample for 24 hr. The organic fraction was then siphoned off and transferred to a separatory funnel to fully separate the layers. The methylene chloride was passed through a funnel containing 60 g of anhydrous sodium sulfate to remove water. All samples were solvent exchanged to hexane and concentrated to 5 mL with a rotary evaporator prior to the clean-up procedure.

Sample extracts were then taken through a two step chromatographic clean-up procedure to remove interfering compounds such as polychlorinated biphenyls. This was necessary because these compounds would be present at concentrations much higher than the dioxins and furans, and they could compete with the analytes for electrons in the negative ion mode of the mass spectrometer, thus reducing sensitivity. The extracts (in hexane) were passed through a 1.5 × 20 cm column packed with silica gel, activitated at 160°C for 16 hr then deactivated with 1% by weight of water and equilibrated for 16 hr. The sample was eluted with 75 mL each of hexane, 15% methylene chloride in hexane, and methylene chloride. The dioxins and furans were collected in the second fraction. The solvent of this fraction was exchanged to hexane and reduced to less than 1 mL. This sample was then passed over a 0.5 × 6.5 cm micropipet packed with alumina, activated at 250°C for 2 hr then deactivated with 1% by weight of water and equilibrated for 16 hr. The sample was eluted with 8 mL each of hexane, 2% methylene chloride in hexane, and 40% methylene chloride in hexane. The dioxins and furans were present in the third fraction which was collected in an 8 mL sample vial and concentrated to 100 $\mu$L by slowly passing purified $N_2$ over the sample. The sample was then ready for gas chromatographic mass spectrometry (GC/MS).

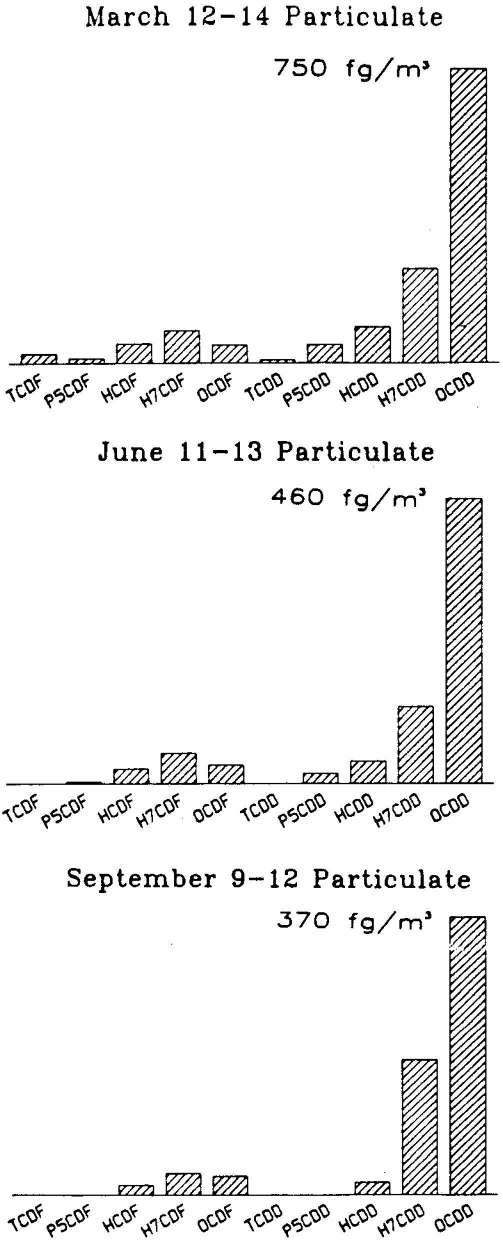
The samples were analyzed on a Hewlett-Packard 5985B GC/MS system. A 30 m × 0.25 mm DB-5 fused silica column (J&W Scientific, Rancho Cordova, CA), with helium as the carrier gas, was temperature programmed (splitless injection at 40°C, isothermal for 4 min, 4°C/min to 280°C, isothermal for 20 min) to separate the dioxins and furans. The mass spectometer was operated in the electron capture negative ionization mode with methane as the reagent gas. The ion source pressure was 0.4 torr, and the ion source temperature was 150°C. To enhance sensitivity, selected ion monitoring was used. Two ions from the most intense cluster of each congener group were monitored for each of the dioxins and furans. If these ions were not present in the proper ratio, as predicted by the isotopic abundances, it was assumed that the peak was that of an interferent and was not quantified.

Samples were quantified by using response factors for each congener class as compared to $^{13}$C-OCDD (one isomer per congener class). Concentrations were then determined by ratioing the peak areas, multiplying by the amount of the internal standard added, dividing by the sample weight, and correcting for the response factor. Concentrations are reported as fg/m$^3$ for air samples and pg/L for rain samples for the total concentration of each congener class.

## RESULTS

As previously noted, the ambient air sampling technique chosen for this study separates the air into operationally defined, particulate and vapor phases. Figure 1 shows the PCDD and PCDF congener profiles for three typical air particulate samples. These samples represent the range of temperatures and concentrations of the entire data set. For these samples, the total concentration varies by a factor of two. While the total concentration varies, the congener profiles remain very similar from sample to sample as demonstrated by the fact that the worst correlation coefficient ($r$) for any pair of samples is 0.970.

Figure 2 shows the vapor phase congener profiles for the same three samples. Note, the maximum concentrations again fall in the hundreds of femtograms per cubic meter range, with total concentrations varying by a factor of two. However, the congener



March 12–14 Particulate

June 11–13 Particulate

September 9–12 Particulate

FIGURE 1 Congener profiles of PCDD and PCDF in three typical particulate phase air samples. Total concentrations of each congener class of the tetra-, penta-, hexa-, hepta-, and octa-chlorodibenzofurans (TCDF, P5CDF, HCDF, H7CDF, OCDF, respectively) and tetra-, penta-, hexa-, hepta-, and octa-chlorodibenzo-*p*-dioxins (TCDD, P5CDD, HCDD, H7CDD, OCDD, respectively). Concentration of OCDD is shown.

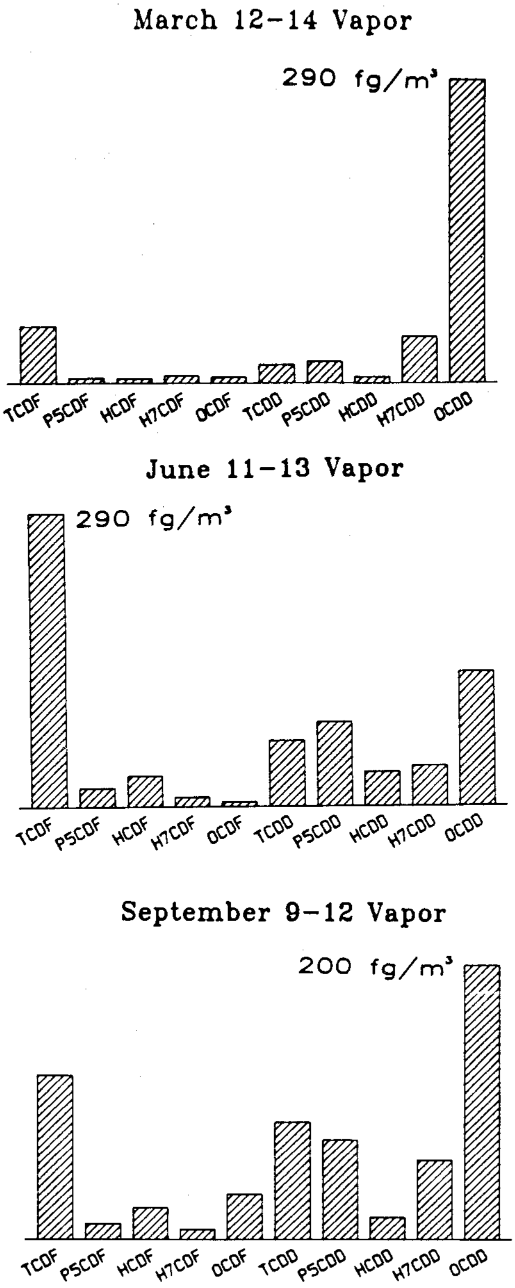


FIGURE 2 Congener profiles of PCDD and PCDF in three typical vapor phase ai samples. Average air temperatures were 287°K for March 12–14, 293°K for June 11-13 and 298°K for September 9–12. The concentration of the most abundant congener i shown.

profiles show large differences from sample to sample. A possible cause for this difference is the change in temperature between the sampling dates. The average temperatures for these three samples are 278°K for March 12–14, 293°K for June 11–13, and 298°K for September 9–12. Thus, it can be seen that the higher temperature samples have higher concentrations of the less chlorinated congeners.

Figure 3 combines the data for these three dates. We see a changing vapor phase profile added to a relatively constant particulate profile. It is important to note that the vapor phase contains a significant portion of the total atmospheric burden of these compounds. Although octachlorodioxin is the major congener, the concentration of all the other congeners are significant. It is, therefore, possible that some of the differences between combustion and sediment profiles could be caused by the combustion effluent partitioning into the vapor phase (more prevalent for the less chlorinated congeners) which is not deposited as readily as the particulate bound dioxins and furans. Thus, it is important to focus on the partitioning between the vapor and particulate phases.

This partitioning can be examined in more detail by determining a vapor/particulate (V/P) ratio for each congener in each sample. This ratio will be dependent on the vapor pressure for a congener as well as the ambient temperature. Since the level of chlorination acts as a surrogate for the vapor pressure, we see from Figure 3 that the less chlorinated congeners (higher vapor pressures) have a larger fraction of the PCDD and PCDF in the vapor phase.

The V/P ratio should also be dependent on temperature. If the V/P ratio is proportional to vapor pressure, then the Clausius–Clapeyron equation (which relates log vapor pressure to inverse temperature) indicates that a plot of log V/P *vs.* inverse temperature should be linear. This functional relationship has been demonstrated by other workers for polycyclic aromatic hydrocarbons and for other polychlorinated organics.[20,22] These workers included a total suspended particulate factor in their equation (a factor we plan to measure in future work). Figure 4 illustrates the temperature effect by showing plots of the log V/P *vs.* inverse temperature for a typical pair of congeners. As expected, an increase in temperature results in a larger V/P ratio.

The data from three typical rain samples are shown in Figure 5. Note that the concentrations are in picograms per liter. Also, note

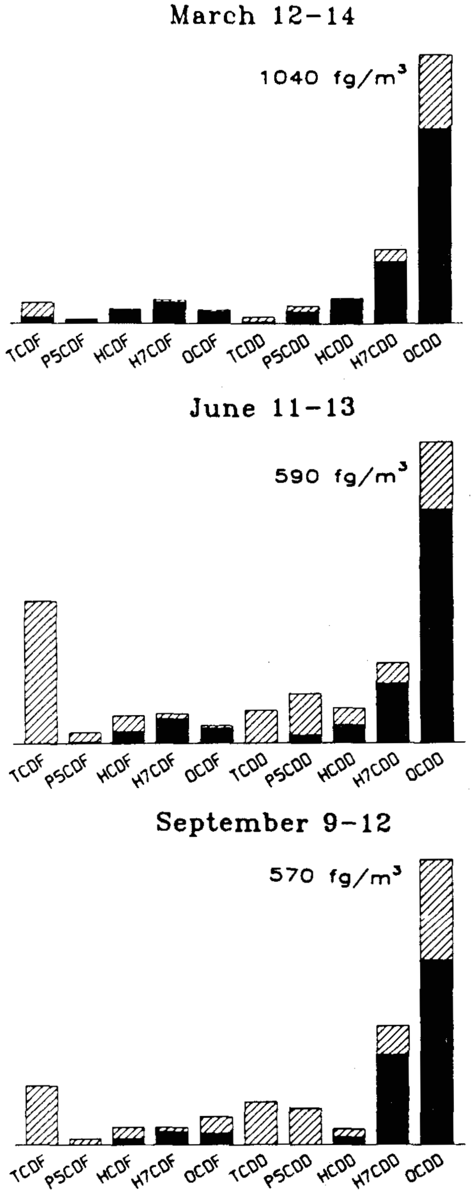


FIGURE 3 Congener profiles of PCDD and PCDF in three typical total air samples showing the contribution of the particulate bound (solid shading) and vapor phase (cross hatched) forms. The concentration of OCDD is shown.

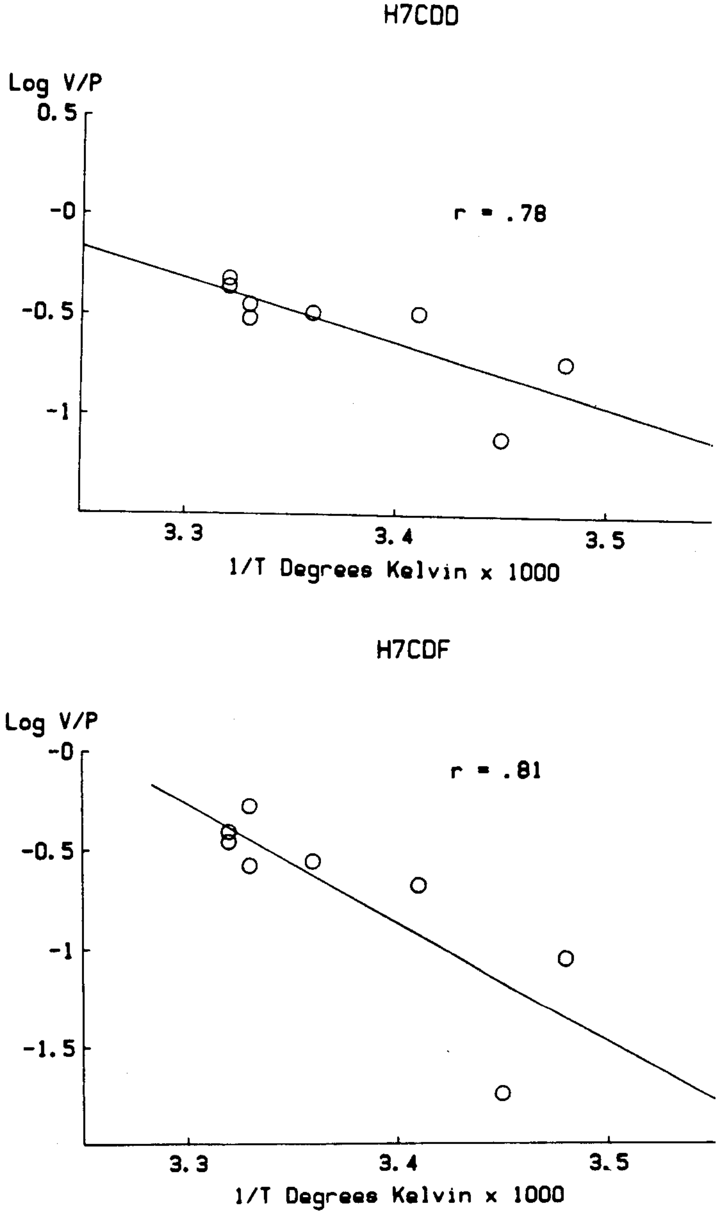
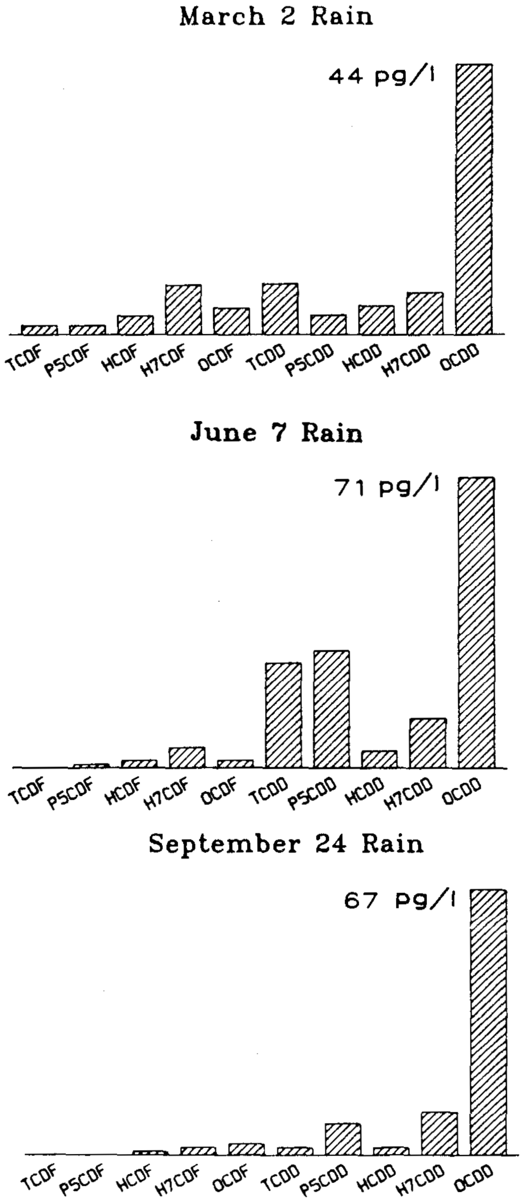


FIGURE 4 Log vapor/particulate ratio *vs.* inverse temperature for H7CDD and H7CDF. The correlation coefficient (*r*) is given. This is significant at the 5% level.



March 2 Rain

June 7 Rain

September 24 Rain

FIGURE 5 Congener profiles of PCDD and PCDF in three typical rain samples. The concentration of OCDD is shown.

the similarities between the samples with the OCDD being the most abundant congener. The OCDD concentration varied over a factor of six over the entire data set.

Four samples were taken such that rain was sampled either during or shortly after an air sample was taken. Data averaged over these four sets of samples are shown in Figure 6. Note how the data from the rain samples are more similar to the particulate than to the vapor. This would suggest that the rain is a more efficient scavenger of the particulate phase. This idea will be examined more closely in future work.

## CONCLUSIONS

It has been shown that transformations take place between the environmental source of PCDD and PCDF (combustion) and their sinks (sediment or human fat). We have developed and tested methods by which the physical characteristics of dioxins and furans, ones that control the transformations, can be determined. The methods are based on the measurement of concentrations of dioxins and furans in air and rain samples.

The results obtained to date demonstrate that the chosen methods work well at low concentrations (fg/m$^3$ in air and pg/L in rainwater). These results are also the first measurements of the PCDD and PCDF concentrations in ambient air and rainwater. Analysis of the current data shows some scatter due to limited quantity and temperature range, but the vapor/particulate ratio has been shown to be inversely proportional to both the level of chlorination (a surrogate for vapor pressure) and the average temperature of the sampling period. Rain appears to be a more efficient scavenger of particulate bound PCDD and PCDF than of the vapor phase compounds.

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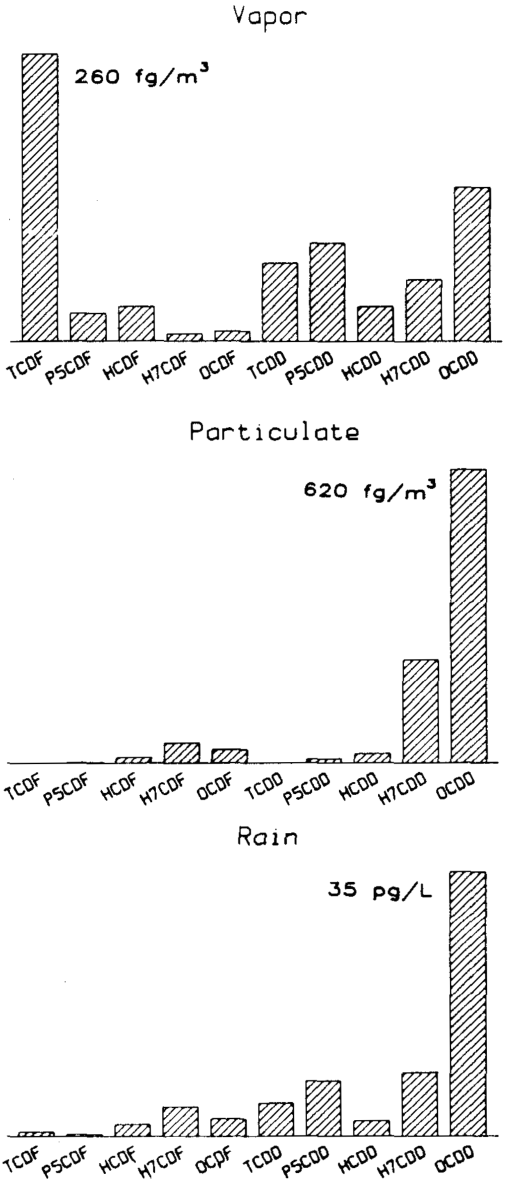

FIGURE 6 Average congener profiles of PCDD and PCDF in the vapor, particulate, and rain of corresponding samples. Concentrations represent the geometric average of each compartment over four samples.

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