

The particle-formation process has been examined by a number of investigators in detail. Particle formation at high pressures has been observed in the photochemical deposition of metal atoms such as Fe, Cr, Mo, and W<sup>27,42,43</sup> and can result in poor adhesion of films to the substrate.<sup>42</sup> Particle formation has also been observed during deposition of hydrogenated amorphous silicon from SiH<sub>4</sub> under a wide variety of conditions.<sup>28-40</sup> A study of the formation of UF<sub>6</sub> particles using a dye laser showed that a critical minimum pressure of the reactant was required to obtain particle formation,<sup>44</sup> a process that can be used as the basis for isotope separation.<sup>45</sup> Particle formation,<sup>46</sup> nucleation kinetics,<sup>47</sup> aerosol dynamics,<sup>48</sup> and film generation<sup>49</sup> have been examined for a variety of processes, and the studies generally show

(43) Draper, C. *Metall. Trans.* 1980, 11A, 349.

(44) Borsella, E.; Catoni, F.; Freddi, G. *J. Chem. Phys.* 1980, 73, 316.

(45) Ronn, A.; Earl, B. *Chem. Phys. Lett.* 1977, 45, 556.

(46) Yabuzaki, T.; Sato, T.; Ogawa, T. *J. Chem. Phys.* 1980, 73, 2780.

(47) Lin, S.; Ronn, A. *Chem. Phys. Lett.* 1978, 56, 414.

(48) Sato, T.; Yabuzaki, T.; Ogawa, T. *Jpn. J. Appl. Phys.* 1982, 21, 1599.

(49) Jervis, T.; Menon, S.; Joyce, E.; Carrol, D. *Mater. Res. Soc. Symp. Proc.* 1987, 75, 159.

that the conditions required for generation of adherent films, without cluster formation, are low pressures, low reaction rates, and a small laser-beam diameter.

### Concluding Remarks

We have attempted to provide a framework for understanding the effects of mass transport on the rates of physical and chemical processes occurring in laser-induced surface and gas-phase reactions. The fundamental interest in this area is related to the rate at which a focused laser can drive a localized chemical reaction, either in the gas phase or on a surface, and the physical limitations to this rate. The relationship between the size of the reaction zone, the mean free path in the gas phase, and the rate of gas-phase and surface reactions provides the key to the understanding of the rate phenomena. Both thermally driven reactions and photochemical reactions are influenced by these size effects. Many of the consequences of mass transport in laser-induced reactions, such as control of deposit growth rate, deposit shape, crystal morphology, and other material properties, are just now beginning to be understood.

## Environmental Behavior of Chlorinated Dioxins and Furans

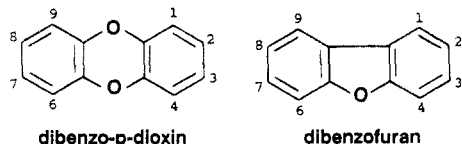
RONALD A. HITES

*School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, Indiana 47405*

*Received January 18, 1990 (Revised Manuscript Received March 26, 1990)*

### Introduction

Chlorinated dibenzo-*p*-dioxins (called dioxins in this Account) and dibenzofurans (furans) are well-known environmental contaminants. The United States has spent billions of dollars studying these compounds. They have received public attention at the highest levels from several governments. It would be hard to name another class of compounds with a similar reputation.



Most of this public scrutiny has been caused by one member of this class: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-D). This compound is known as "the most toxic man-made chemical". It takes only 0.6 µg of 2378-D/kg of body mass to kill 50% of a population of guinea pigs.<sup>1</sup> 2,3,7,8-Tetrachlorodibenzofuran (2378-F) is almost as toxic.<sup>2</sup> Clearly, the dioxins and furans are

hazardous compounds that warrant concern. Luckily, things are not as bad as they might seem. The toxicity of 2378-D to guinea pigs is not typical. There is a wide range of sensitivities among various animal species; for example, most hamsters will not die until the dose of 2378-D reaches 5000 µg kg<sup>-1</sup>, a dose 10<sup>4</sup> times higher than for guinea pigs.<sup>3</sup> Furthermore, dioxins and furans in which the chlorine atoms are at different positions on the rings are not nearly as toxic; for example, 1368-D is >10<sup>6</sup> times less toxic than 2378-D.<sup>4</sup>

These compounds came to the widespread attention of chemists (and to some extent the public) in 1973 when Baughman and Meselson pointed out that 2378-D was a contaminant in Agent Orange, a material used to kill vegetation in South Vietnam as part of a strategy by the U.S. Army to deny the Vietcong hiding places in the jungle.<sup>5</sup> Agent Orange consisted of a mixture of (2,4-dichlorophenoxy)- and (2,4,5-trichlorophenoxy)acetates; the latter was made from 2,4,5-trichlorophenol that contained low concentrations of 2378-D. This impurity was carried over into the Agent Orange, and as a result, 2378-D was delivered into the ecosystem of Vietnam. Baughman and Meselson raised questions,

(1) Sparschu, G. L.; Dunn, F. L.; Rowe, V. K. *Food Cosmet. Toxicol.* 1971, 9, 405.

(2) Moore, J. A.; McConnell, E. E.; Dalgard, D. W.; Harris, M. W. *Ann. N.Y. Acad. Sci.* 1979, 320, 151-163.

(3) Kociba, R. J.; Schwertz, B. A. *Drug Metab. Rev.* 1982, 13, 387-406.

(4) Kociba, R. J.; Cabey, O. *Chemosphere* 1985, 14, 649-660.

(5) Baughman, R.; Meselson, M. *Environ. Health Perspect.* 1973, *Experimental Issue No. 5*, 27-35.

Ron Hites was born in Michigan in 1942. He received a B.A. in Chemistry from Oakland University (near Detroit) in 1964 and a Ph.D. in Analytical Chemistry with Klaus Biemann from the Massachusetts Institute of Technology (MIT) in 1968. He remained on the staff and faculty of MIT until 1979, when he became a Professor of Public and Environmental Affairs at Indiana University; he is also a Professor of Chemistry. Last year he was elevated to the rank of Distinguished Professor. His research focuses on the behavior of potentially toxic organic compounds in the environment. He is currently President of the American Society for Mass Spectrometry.

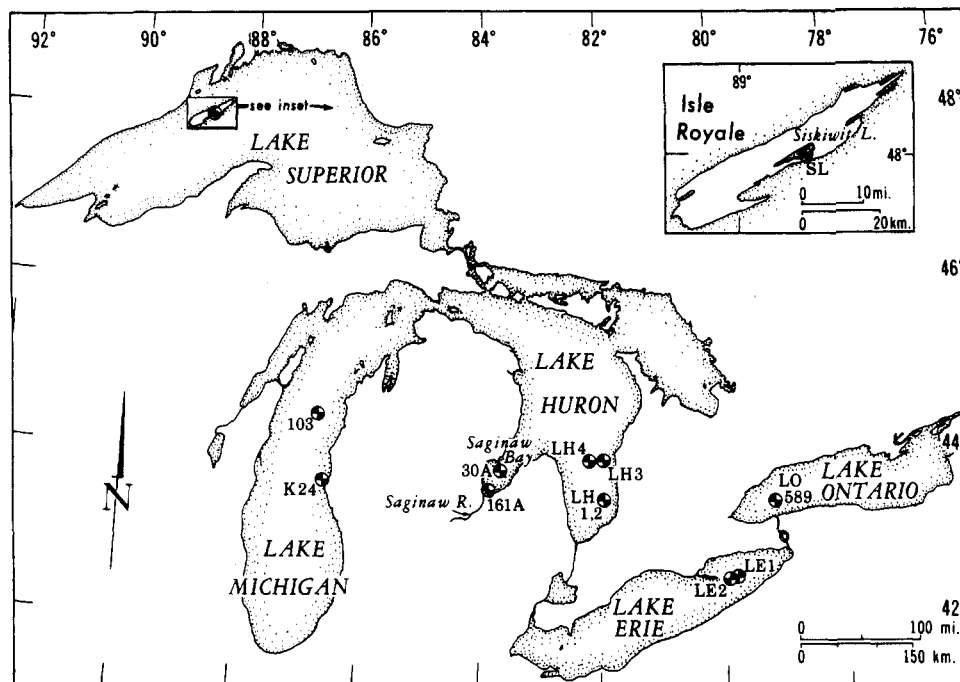


Figure 1. Map of the Great Lakes showing the locations of the sediment sampling sites. Reprinted with permission from ref 12. Copyright 1986 American Chemical Society.

still unanswered, about the effects of this 2378-D on the Vietnamese people and on U.S. military personnel.<sup>5</sup>

Although there are 75 different chlorinated dioxins and 135 different chlorinated dibenzofurans, early research focused almost exclusively on 2378-D (and to some extent 2378-F). Analytical methods were developed for measuring these compounds in commercial products (particularly in chlorinated phenols) and in environmental samples. This was not an easy task; it was necessary to measure just one or two compounds in the presence of dozens of related compounds. Via these methods, a body of knowledge was accumulated on the levels of 2378-D (and 2378-F) contamination in chemical products and in selected environmental matrices.

Research gradually expanded to include all the dioxins and furans with four or more chlorine atoms, and by 1978 it was clear that there were two major sources of these compounds: They were present as byproducts in chlorinated aromatic compounds,<sup>6</sup> and they were emitted from the combustion of municipal and chemical wastes.<sup>7</sup> The latter was an important discovery. No longer could the simple presence of dioxins in a sample indict a chemical production facility. Indeed, it was suggested that "dioxins have been with us since the advent of fire."<sup>8</sup> It was at this point that our laboratory began work on this issue. We started by developing the following operational hypothesis:

Chlorinated dioxins and furans are formed during combustion and are emitted into the atmosphere. Depending on the ambient temperature, some of these compounds are adsorbed to particles and some are in the vapor state. In either case, these compounds travel

through the atmosphere for considerable distances. While in the atmosphere, several things happen to these compounds. First, they reequilibrate between the particle and vapor phases; this is a temperature-dependent process. Second, they degrade by photo-oxidative or other chemical processes; the extent of this degradation depends on the physical state of the reactant. Eventually, the dioxins and furans leave the atmosphere by several routes. Particles with their load of adsorbed compounds settle out of the air; precipitation scavenges both particle-bound and vapor-phase compounds. Dioxins and furans from industrial sources also enter the atmosphere; however, except for sporadic and localized events, these sources are minor.

### Historical Aspects

We tested our hypothesis by making measurements of dioxins and furans in the ambient environment. Our first step was to look at historical aspects. What was the history of dioxin and furan concentrations in the atmosphere? Were these compounds really present in the environment since the "advent of fire"?

Since it was not possible retroactively to sample the atmosphere, we resorted to an indirect strategy; we used lake sediments.<sup>9-12</sup> This technique is based on the rapid transport of material deposited on the top of a lake to its bottom and on the regular accumulation of sediment at the bottom of the lake. Thus, the sediment preserves a record of atmospheric deposition. Experimentally, we punched out a cylinder of sediment (called a "core") from the bottom of a lake, sliced it into 0.5-1-cm layers, and analyzed each layer for the tetrachloro- through octachlorodioxins and -furans with

(6) Pollock, T. *Dioxins and Furans: Questions and Answers*; Academy of Natural Sciences: Philadelphia, PA, 1989.

(7) Olie, K.; Vermuelen, P. L.; Hutzinger, O. *Chemosphere* 1977, 6, 455-459.

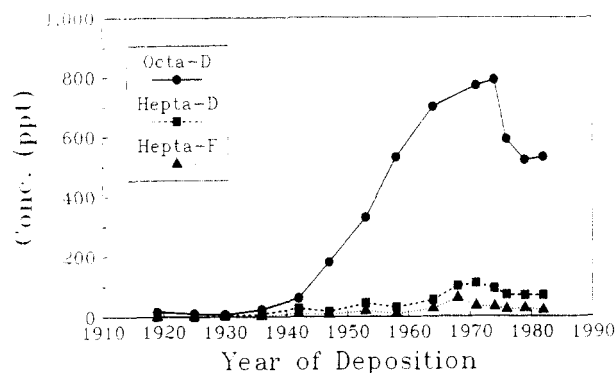
(8) Rawls, R. L. *Chem. Eng. News* 1979, Feb 12, 23-29. Bumb, R. R.; Crummett, W. B.; Cutie, S. S.; Gledhill, J. R.; Hummel, R. H.; Kagel, R. O.; Lamparski, L. L.; Luoma, E. V.; Miller, D. I.; Nestrick, J. J.; Shadoff, L. A.; Stehl, R. H.; Woods, J. S. *Science* 1980, 210, 385-390.

(9) Czuczwa, J. M.; Hites, R. A. *Environ. Sci. Technol.* 1984, 18, 444-450.

(10) Czuczwa, J. M.; McVeety, B. D.; Hites, R. A. *Science* 1984, 226, 568-569.

(11) Czuczwa, J. M.; Niessen, F.; Hites, R. A. *Chemosphere* 1985, 14, 1175-1179.

(12) Czuczwa, J. M.; Hites, R. A. *Environ. Sci. Technol.* 1986, 20, 195-200.



**Figure 2.** Concentrations of octa- and heptachlorodioxins and of heptachlorofurans (in parts per trillion) versus year of deposition into Siskiwit Lake on Isle Royale.

isotope dilution, electron capture, negative ion, gas chromatographic mass spectrometry. Using radioisotopic methods, we determined when the sediment was last in contact (through the water column) with the atmosphere.

We decided to begin these sediment-core studies with samples from the Great Lakes. Figure 1 is a map of the sampling sites. The site that we consider to be the most significant is the one on Isle Royale.<sup>10</sup> This island is in northern Lake Superior; it is a poorly visited national park; it lacks roads and other development; it is a wilderness area and a biome preserve. Siskiwit Lake is the largest lake on Isle Royale; its water level is 17 m higher than that of Lake Superior. Clearly, the only way for dioxins and furans to get into this lake is through the atmosphere. Siskiwit Lake is a collector of atmospheric deposition.

Figure 2 gives the concentrations of the dioxins and furans in the sediment core taken from Siskiwit Lake as a function of year of deposition. These data are typical of those for all the sediment cores we studied.<sup>9-12</sup> We note two things: First, octachlorodioxin is always the most abundant of these compounds; the heptachlorodioxins and -furans are next in abundance. The other chlorinated dioxins and furans are present, but their concentrations are small. This pattern is considerably different from those observed for combustion sources; more on this latter. Second, we notice that the concentrations of dioxins and furans have not been constant over the last century. The concentrations maximized in about 1970 and dropped to unmeasurable levels before 1930. From these data we concluded that atmospheric dioxin and furan levels increased slowly starting in about 1935 and have decreased since about 1970.

We also obtained sediment cores from three high-altitude lakes in Switzerland; the dioxin and furan concentration profiles in these cores were similar to those in the Great Lakes.<sup>11</sup> Table I summarizes all our sediment-core data. In every case, we noted that dioxins and furans were not present in the sediments before 1930–1940, and by implication, they were not present in the atmosphere before this time. This is true despite large differences in the rate of sediment accumulation and in the locations of the lakes. The overall average horizon date is 1938, a date well after the “advent of fire”.

What happened in the mid to late 1930s that led to the emission of dioxins? We suggest that it was the

**Table I**  
Date at Which Dioxins and Furans First Appeared in Significant Amounts (“Horizon Date”) and the Current Flux of These Compounds to 13 Lake Sediments

core location	sedimentation rate, cm yr <sup>-1</sup>	horizon date	current flux, pg cm <sup>-2</sup> yr <sup>-1</sup>
Huron 1	0.15	1925	64
Huron 2	0.15	1935	110
Huron 3	0.21	1940	190
Huron 4	0.41	1950	350
Michigan 103	0.14	mixed <sup>a</sup>	35
Michigan K24	0.04	mixed <sup>a</sup>	5
Erie 1	1.6	1935	400 <sup>b</sup>
Erie 2	2.5	1935	560 <sup>b</sup>
Siskiwit	0.24	1940	23
Ontario 589	0.16		530
Zurich	varved <sup>c</sup>	1940	140
Baldegg	varved <sup>c</sup>	1950	210
Lugano	varved <sup>c</sup>	1930	300

<sup>a</sup> The mixing processes taking place in the sediment were so large that we could not determine a horizon date. <sup>b</sup> We corrected these values by a factor of 5 to account for sediment focusing. <sup>c</sup> The annual sediment layers were visually distinct, and thus, dates were assigned by simply counting the layers.

change in the chemical industry that took place at about that time. Before World War II (1939–1945), the chemical industry was commodity based, selling large amounts of inorganic products. During the War, organic products were introduced: plastics became an important part of the chemical industry. Some of these products were organochlorine based; poly(vinyl chloride) is but one example. As waste materials containing these chemicals were burned, dioxins and furans were produced and released into the atmosphere. These compounds eventually ended up in lake sediments.

Incidentally, coal combustion cannot account for the historical record that we have observed. Coal combustion has been almost constant since 1910; there was no major shift either in amount burned or in combustion technology around 1935.<sup>13</sup> We observed the 1970 maximum in most of the sediment cores. To us this suggests that emission control devices, which were beginning to be widely installed at about this time, were effective in removing dioxins and furans as well as the more conventional air pollutants.<sup>14</sup>

Subsequent work in other laboratories has confirmed our data. Hagenmaier et al. measured dioxins and furans in a sediment core from Lake Constance in Germany and observed a profile similar to those we have seen in the Great Lakes and in Switzerland.<sup>15</sup> Other authors have looked for dioxins and furans in prehistoric samples of human tissue and have found none.<sup>16</sup> Modern human tissue samples, on the other hand, have an average of 1 ppb dioxins and furans (mostly octachlorodioxin).<sup>17</sup> This difference confirms our historical measurements.

The last column of Table I gives the total flux of the dioxins and furans to the sediment and thus, by implication, the flux of these compounds from the atmo-

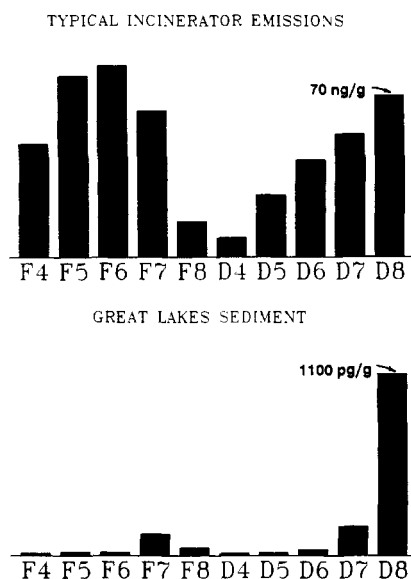
(13) *Minerals Yearbook*; U.S. Bureau of Mines: 1870–1980.

(14) Furlong, E. T.; Cessar, L. R.; Hites, R. A. *Geochim. Cosmochim. Acta* 1987, 51, 2965–2975.

(15) Hagenmaier, H.; Brunner, H.; Haag, R. Berchtold, A. *Chemosphere* 1986, 15, 1421–1428.

(16) Ligon, W. V., Jr.; Dorn, S. B.; May, R. J.; Allison, M. J. *Environ. Sci. Technol.* 1989, 23, 1286–1290. Schecter, A.; Dekin, A.; Weerasinghe, N. C. A.; Arghestani, S.; Gross, M. L. *Chemosphere* 1988, 17, 627–631.

(17) Data reviewed in the following: Eitzer, B. D.; Hites, R. A. *Environ. Sci. Technol.* 1986, 20, 1185–1186.



**Figure 3.** Top: Typical concentrations of the tetra-, penta-, hexa-, hepta-, and octachlorofurans (F4, F5, F6, F7, and F8, respectively) and tetra-, penta-, hexa-, hepta-, and octachlorodioxins (D4, D5, D6, D7, and D8, respectively) being emitted from municipal waste incinerators.<sup>15</sup> Bottom: Geometric average concentrations of the dioxins and furans in sediments from the Great Lakes. The total concentrations of octachlorodioxin are given as scaling factors.

sphere. We calculated these fluxes from three measured sediment-core parameters: the total dioxin and furan concentration, the sediment rate, and the in situ sediment density. Except for three sites, these fluxes lie between 100 and 500  $\text{pg cm}^{-2} \text{yr}^{-1}$ . The exceptions are those sites that are remote from combustion sources (Siskiwit Lake, for example); at these locations, the flux is about 10 times lower. Using a low overall flux estimate of 20  $\text{pg cm}^{-2} \text{yr}^{-1}$  and an area of North America of  $2.4 \times 10^{13} \text{ m}^2$ , we calculate an annual dioxin and furan deposition rate of 5000 kg. This is a substantial amount of these compounds, and it far exceeds the load from noncombustion sources (fugitive emissions from pentachlorophenol production and use, for example). We estimate that these sources release only 1–10% of that from combustion sources.<sup>10</sup> We will return to these flux estimates when we discuss atmospheric concentrations later.

### Environmental Transformations

On the basis of this historical argument and these fluxes, we concluded that most of the dioxins and furans present in the environment come from combustion emissions as opposed to industrial leakage. Unfortunately, there was a big problem: The relative distribution of the various dioxins and furans from combustion sources did not resemble the pattern that we observed in the sediments. Combustion sources are highly variable; the emissions depend on the fuel, the combustion temperature, the residence time at temperature, and many other factors. Nevertheless, if one takes an average of the relative concentrations of dioxins and furans emitted from combustion systems, one finds that all the compounds have a similar likelihood of being present (except for the octachlorofuran and the tetrachlorodioxins). Figure 3 (top) shows these data as a chloro-homologue profile. In this figure, we have plotted one bar for each level of chlorination. The first five bars represent the tetra- through octachlorofurans,

and the last five bars represent the tetra- through octachlorodioxins. Figure 3 (bottom) gives the relative concentrations of dioxins and furans in the Great Lakes sediments in the same format. Octachlorodioxin dominates, the heptachlorofurans and -dioxins are significant, and the other homologues are much less abundant. Clearly this distribution is nothing like that from the sources, and understanding this discrepancy became a major focus of our research.

There are several possible explanations for this difference: The less chlorinated dioxins and furans could degrade, perhaps biologically, after deposition in the sediments. We can rule this out for two reasons. First, the composition of the dioxins and furans is constant all down the sediment core; it is unlikely that these compounds would all be degrading at the same rate. Second, in most cores there is a concentration maximum at a depth corresponding to about 1970; it is unlikely that a degradation process would first create these compounds before consuming them.

A second explanation for this discrepancy: Perhaps the less chlorinated dioxins and furans are lost preferentially from the atmosphere by photochemical processes. At the time we began this work, there were no data to support or refute this idea; however, dioxins and furans have significant UV absorption bands at 310–320 nm, wavelengths that are available at the surface of the Earth. Thus, this was a reasonable hypothesis. Because dioxins and furans are likely to be present in the atmosphere in both the vapor and the particle phases, the photochemical behavior of these compounds in both phases must be understood to test this idea.

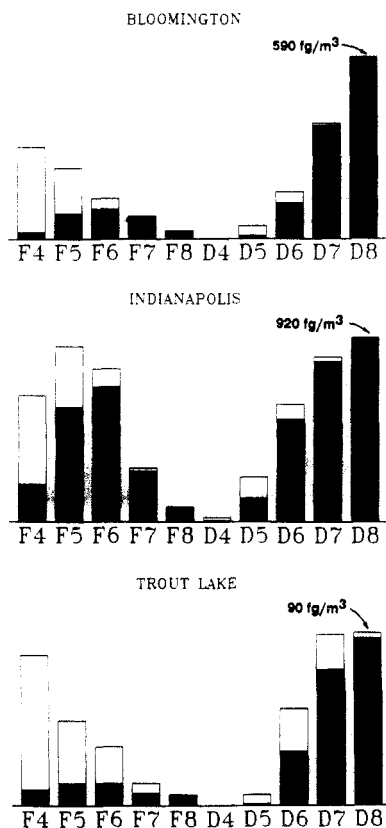
A third explanation: Perhaps only the more highly chlorinated dioxins and furans are deposited from the atmosphere. For example, precipitation scavenging processes could favor the removal of only the more highly chlorinated (and less volatile) compounds. Again these processes would be dependent on the atmospheric phase in which the dioxins and furans found themselves.

To find out if any of these explanations were correct, it became necessary to understand the atmospheric behavior of dioxins and furans. There was, however, no data on the atmospheric concentrations and phase distribution of dioxins and furans. Therefore, our next step was to make these measurements.

### Atmospheric Measurements

If our hypothesis were correct, dioxins and furans must be moving through the atmosphere from combustion sources, depositing on lakes, and becoming incorporated in lake sediments. If this were true, we should be able to find these compounds in the air, although perhaps at very low concentrations. We began and eventually focused our atmospheric sampling in Bloomington, IN. This is a city of approximately 50 000 people, and it is the home of Indiana University. Besides convenience, we choose Bloomington because it might be the site of an incinerator that would burn polychlorinated biphenyl (PCB) contaminated soil with the town's municipal waste. Given previous evidence on the production of dioxins and furans in municipal incinerators<sup>18</sup> and in PCB fires,<sup>19</sup> this incinerator could

(18) Yashuhara, A.; Ito, H.; Morita, M. *Environ. Sci. Technol.* 1987, 21, 971–979.



**Figure 4.** Geometric average concentrations of the dioxins and furans in ambient air from Bloomington, IN; Indianapolis, IN; and Trout Lake, WI. See Figure 3 caption for an explanation of the code. The solid portion of the bar is particle bound while the blank portion is vapor phase. The total concentrations (vapor plus particle) of octachlorodioxin are given as scaling factors.

have a significant impact on Bloomington's air quality. Thus, besides our more fundamental goals, we undertook this study to provide base-line data against which the impact of this incinerator on the local dioxin and furan concentrations could be judged.

We put atmospheric samplers on the roofs of four buildings in Bloomington.<sup>20</sup> Two of these sites corresponded to areas of high human habitation, and the other two corresponded to sites of high potential incinerator impact. We collected monthly samples at each site with high-volume air samplers modified to collect both vapor and particle-bound phases separately. As with the sediment samples, we analyzed these atmospheric samples by negative ion, gas chromatographic mass spectrometry.

The four sites that we sampled showed few differences, and thus, we have composited the data. The average total dioxin and furan concentration was  $2.5 \text{ pg m}^{-3}$ , and the individual total dioxin and furan concentrations ranged from  $0.74$  to  $12 \text{ pg m}^{-3}$ . None of the concentrations were affected by season (as measured by atmospheric temperature). This suggests that heating fuels are not a major source of these compounds to the ambient atmosphere, at least in Bloomington. We cannot rule out other sources that do not have a

seasonal component, such as waste incineration or automobile exhaust.<sup>21</sup> Figure 4 (top) shows the geometric average dioxin and furan concentration chloro-homologue profiles for both phases. The total (vapor plus particle-bound) concentrations of the furans decrease with increasing level of chlorination, while the dioxin concentrations increase with level of chlorination. This pattern looks similar to the average pattern coming from combustion sources; see Figure 3 (top).

To get an idea of geographic variability and its causes, we briefly sampled two sites outside Bloomington, one with a higher and one with a lower degree of urbanization. These sites were Indianapolis, IN, a city with a population of about 800 000, and Trout Lake, WI, a forested area about 100 km south of Lake Superior. Figure 4 (middle and bottom) shows the average dioxin and furan chloro-homologue profiles for air samples at these two locations; clearly there are some significant differences between the locations. The primary difference is in absolute concentrations, which are 1.6–6 times higher in Indianapolis than in Bloomington and 7–30 times higher in Indianapolis than at Trout Lake. That urban sites such as Indianapolis have more dioxins and furans in their air is not surprising; for example, all of the municipal waste in Indianapolis is incinerated while none is incinerated in Bloomington. As air masses move away from urban areas, they are diluted with cleaner air, lowering the dioxin and furan concentrations. Note that, for both sites, the chloro-homologue patterns are very similar to that in Bloomington and that from combustion sources.

Because we have a larger data set, let us focus on the Bloomington measurements. Although we did not observe a seasonal effect on the total concentrations, there is an effect on the proportion of the total atmospheric burden present in the vapor phase. During the warm summer months, the total vapor to particle-bound ratio ( $V/P$ ) can be as great as 2, while in the winter, it can be less than 0.5. To examine this effect in more detail, it is necessary to understand the effects of temperature and vapor pressure on the process of vapor-particle partitioning. Bidelman and Foreman have shown that, at constant temperature and total suspended particulate (TSP) concentrations,  $\log(V/P) = \log P^\circ + a_0$ , where  $P^\circ$  is the subcooled liquid vapor pressure of the compound and  $a_0$  is a constant.<sup>22</sup> ("Subcooled liquid" refers to a physical state that is a liquid at a temperature below the compound's melting point.) The slope of 1 in this equation indicates that  $V/P$  is directly proportional to vapor pressure.

To use this equation, we measured the vapor pressures of the dioxins and furans using a gas chromatographic retention time correlation method.<sup>23</sup> We then calculated an average  $V/P$  ratio for each measured dioxin and furan isomer. This averaging eliminated the effects of varying atmospheric temperatures and TSP concentrations, which we will discuss later. Figure 5 is a plot of this  $V/P$  ratio versus vapor pressure. The strong effect of vapor pressure on vapor-particle partitioning is apparent. The regression is excellent, and

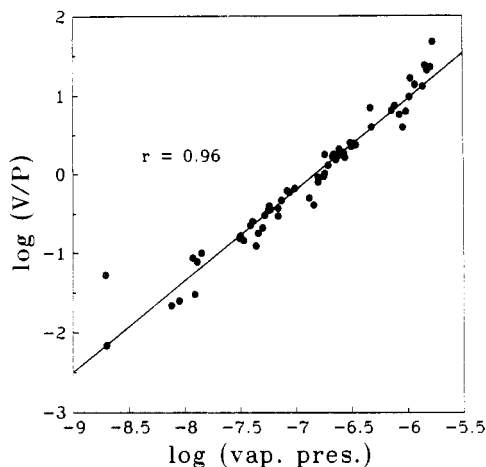
(19) Rappe, C.; Marklund, S.; Kjeller, L.-O.; Begqvist, P.-A.; Hansson, M. In *Chlorinated Dioxins and Dibenzofurans in the Total Environment II*; Choudhry, G., Keith, L. H., Rappe, C., Eds.; Butterworth: Stoneham, MA, 1985; pp 401–424.

(20) Eitzer, B. D.; Hites, R. A. *Int. J. Environ. Anal. Chem.* **1986**, *27*, 215–230. Eitzer, B. D.; Hites, R. A. *Environ. Sci. Technol.* **1989**, *23*, 1389–1395.

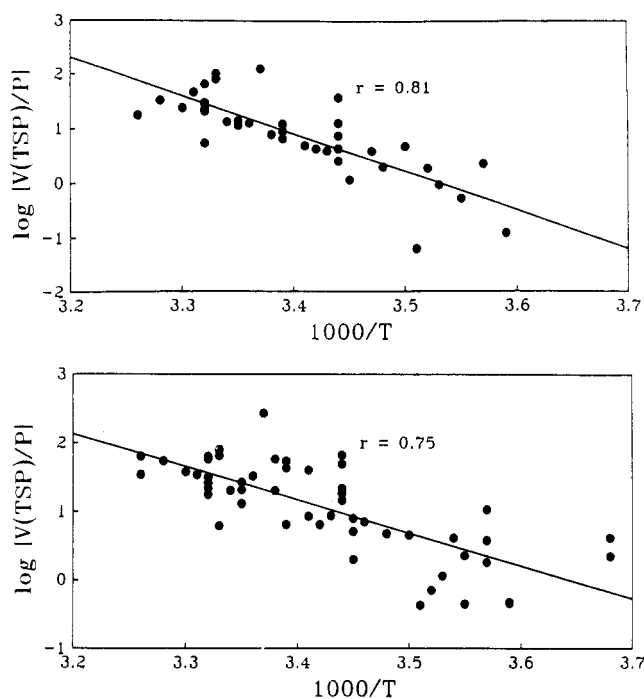
(21) Ballschmiter, K.; Buchert, H.; Niemczyk, R.; Monder, A.; Swerev, M. *Chemosphere* **1986**, *15*, 901–915.

(22) Bidleman, T. F.; Foreman, W. T. In *Sources and Fates of Aquatic Pollutants*; Hites, R. A., Eisenreich, S. J., Eds.; American Chemical Society: Washington, DC, 1987; pp 27–56.

(23) Eitzer, B. D.; Hites, R. A. *Environ. Sci. Technol.* **1988**, *22*, 1362–1364.



**Figure 5.** Average vapor to particle-bound ratio for each measured dioxin and furan vs. its sub-cooled liquid vapor pressure.



**Figure 6.** Plots of the logarithm of the vapor-phase concentration times the total suspended particle load divided by the particle-bound concentration versus the reciprocal temperature for 1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin (top) and 1,2,3,4,6,7,8-heptachlorodibenzofuran (bottom).

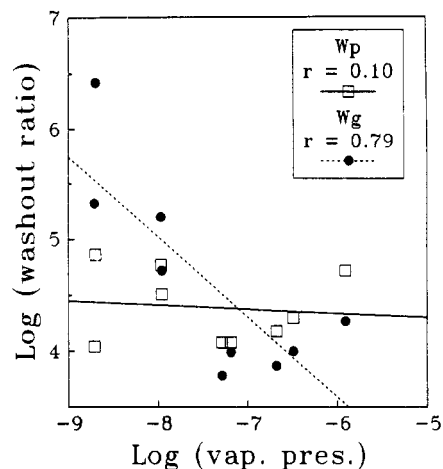
the slope is close to 1 (1.15), as predicted by the above equation. The  $V/P$  ratio ranges from 0.01 to 50, which is in good agreement with theoretical predictions of  $V/P$  ratios between 0.05 and 20 for compounds with vapor pressures equal to those given here.<sup>24</sup>

Vapor pressure is a strong function of temperature; thus, the  $V/P$  ratio also should depend on the ambient atmospheric temperature. Yamasaki et al.<sup>25</sup> and Bidleman and Foreman<sup>22,26</sup> addressed this issue, and their models say that  $\log [V(TSP)/P] = b_0 + b_1/T$ , where  $b_0$

(24) Junge, C. E. In *Fate of Pollutants in the Air and Water Environments, Part I*; Suffet, I. H., Ed.; John Wiley & Sons: New York, 1977; pp 7-25.

(25) Yamasaki, H.; Kuwata, K.; Miyamoto, H. *Environ. Sci. Technol.* **1982**, *16*, 189-194.

(26) Bidleman, T. F.; Foreman, W. T. *Environ. Sci. Technol.* **1986**, *20*, 1038-1043. Bidleman, T. F.; Foreman, W. T. *Environ. Sci. Technol.* **1987**, *21*, 869-875.



**Figure 7.** Washout ratios (except for the tetrachlorodioxins) as a function of average vapor pressure. The data have been averaged over each level of chlorination.

and  $b_1$  are determined experimentally. For each dioxin and furan, we carried out a regression analysis using this equation. Figure 6 shows examples of these regressions for 1234679-D (top) and for 1234678-F (bottom). Given the very low concentrations we were dealing with, the scatter around the regression lines is acceptable. In fact, except for the seven least abundant dioxins and furans, all correlations were significant at the 98% confidence level or better.

To summarize, we now know that dioxins and furans are present in the atmosphere albeit at very low concentrations. The chloro-homologue distributions closely resemble the average distribution from sources when the vapor and particle phases are added together. A substantial fraction of the atmospheric burden of these compounds is present as the particle phase. The fraction in each phase is controlled by the ambient temperature and by the compound's vapor pressure. Since the less chlorinated dioxins and furans have higher vapor pressures, they are found to a greater extent in the vapor phase (see Figure 4). Obviously, this has implications on the atmospheric transport process and on the ultimate environmental fate of these compounds. Depositional and degradational processes will proceed at different rates for the different phases.

### Depositional Processes

In general, there are two types of processes by which the dioxins and furans can be removed from the atmosphere: dry and wet. "Dry" refers to the simple settling of particles and the dissolution of vapor-phase compounds onto surficial materials (such as water or vegetation). "Wet" refers to the removal of atmospheric components by rain, fog, or snow. Dry deposition is almost impossible to measure directly, but wet deposition (at least rain) can be collected and analyzed. We made these measurements<sup>27</sup> and compared the air and rain concentrations to one another using the concept of washout.<sup>28</sup> This is expressed as the ratio between the concentration in rain and the concentration in air on a volume to volume basis. This ratio, usually given

(27) Eitzer, B. D.; Hites, R. A. *Environ. Sci. Technol.* **1989**, *23*, 1396-1401.

(28) Bidleman, T. F. *Environ. Sci. Technol.* **1988**, *22*, 361-367. Ligocki, M. P.; Leuenberger, C.; Pankow, J. F. *Atmos. Environ.* **1985**, *19*, 1609-1617. Ligocki, M. P.; Leuenberger, C.; Pankow, J. F. *Atmos. Environ.* **1985**, *19*, 1619-1626.

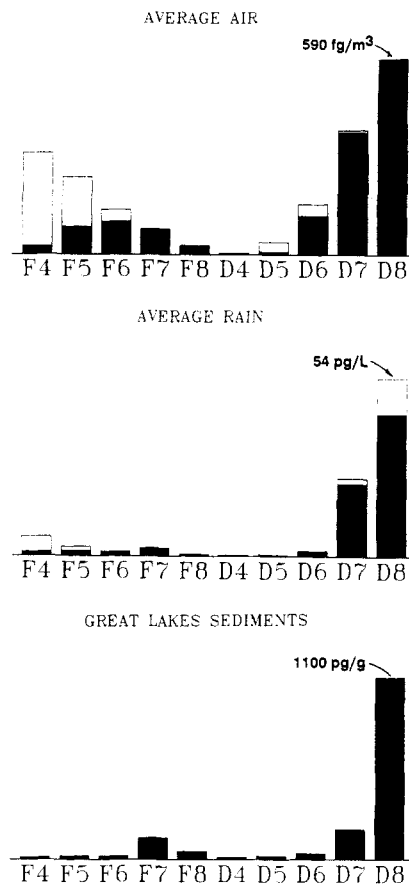
the symbol  $W$ , is a measure of scavenging efficiency. There are two distinct and separate phenomena to be examined. Gas scavenging is the equilibrium process in which a compound partitions between vapor and aqueous phases; its measure is  $W_g$ , which is the ratio of the rain dissolved phase to the air vapor phase concentrations. Particle scavenging is the process by which rainfall removes particles and the compounds bound to those particles from the atmosphere; its measure is  $W_p$ , which is the ratio of the rain particle phase to the air particle phase concentrations. Figure 7 shows the differences between these two processes. This figure is a plot of the washout ratios as a function of the vapor pressure averaged for each level of chlorination. Note the strong correlation for  $W_g$  (significant at the 1% level) and the lack of correlation for  $W_p$  with vapor pressure. This suggests that particle washout is a physical process that affects all the compounds bound to particles similarly. Conversely, vapor washout is highly dependent on the compound's vapor pressure, and therefore, it must involve a different process than particle washout.

Total washout is given by  $W = W_g(1 - \phi) + W_p\phi$ , where  $\phi$  is the fraction of the total air concentration that is bound to particles.<sup>28</sup> Dividing  $W_p\phi$  by  $W$  allows us to determine which type of scavenging is the dominant process for a given compound. For the tetra- and pentachloro homologues, about 40% is removed by particle scavenging; for the hexa- through octachloro homologues, about 80% is removed this way. Particle scavenging is generally a more important process than gas scavenging, and total scavenging efficiency of dioxins and furans generally increases with level of chlorination. These observations suggest that the more chlorinated dioxins and furans have a greater tendency to be scavenged and to reach sedimentary sinks than the less chlorinated dioxins and furans. In other words, wet depositional processes favor a sedimentary profile that shows higher concentrations of the more chlorinated dioxins and furans. This is what we see.

### Depositional Fluxes

It is now possible to compare the observed air and rain concentration data with flux data from sediments. This can be done qualitatively by comparing the profiles and quantitatively by comparing depositional fluxes. The qualitative comparison is shown in Figure 8, which plots the chloro-homologue profiles of Bloomington air and rain and of average Great Lakes sediments. Note that all three profiles show octachlorodioxin to be the highest in concentration. There is a strong similarity between the particle-bound portion of air, total rain, and sediment. Thus, it appears that the deposition of particles is a very important process.

Deposition is best measured in terms of flux. For rain, the flux can be calculated by multiplying the average rain concentration by the yearly rainfall. Particle deposition is dependent on the deposition velocity of the particle, which, for particles produced by combustion, we have estimated to be  $1 \text{ cm s}^{-1}$ .<sup>29</sup> Table II gives depositional flux estimates for Bloomington rain, for air particles from all three locations, and for average Great Lakes and Siskiwit Lake sediments. Given the errors in the analysis of each compartment, the inherent



**Figure 8.** Average concentrations of dioxins and furans in air and rain taken in Bloomington, IN, and in surface sediments from the Great Lakes. See Figure 3 for the code. The solid portion of the bars represents the particle bound for the air and rain samples, and the blank portions represent the vapor and dissolved phases in air and rain, respectively.

**Table II**  
Comparison of Fluxes Calculated from Atmospheric Measurements versus Those from Lake Sediments

location	sample type	flux, $\text{pg cm}^{-2} \text{ yr}^{-1}$
Trout Lake	dry	7.4
Bloomington	wet	9.2
Bloomington	dry	44
Bloomington	dry and wet	53
Indianapolis	dry	130
Great Lakes	sediment	110 <sup>a</sup>
Siskiwit Lake	sediment	23

<sup>a</sup> Geometric average of the fluxes to the 10 Great Lakes sites (see Table I).

approximations necessary to make the calculations, and the difference in geographic locations, we were pleased at the similarity of the dry and wet fluxes as compared to those measured in the sediments. For example, the Siskiwit Lake fluxes are similar to those calculated at Trout Lake, the rural location. The Great Lakes flux is similar to the total Bloomington and the Indianapolis particle values. This agreement, rough though it is, tells us that the atmospheric dioxin and furan concentrations are compatible with those measured in the sediments.

We also can use the Bloomington fluxes to estimate the relative importance of the wet and dry pathways. The average dry to wet deposition ratio was 5:1. These data are similar to the 9:1 ratio we reported for polycyclic aromatic hydrocarbons<sup>29</sup> and to the 10:1 ratio reported for other chloroorganics.<sup>30</sup> Clearly, the dry



deposition of particles is the more important of the two depositional pathways.

### Concluding Remarks

Let us review our operating hypothesis: A broad range of dioxins and furans, which are injected into the atmosphere by many combustion sources, form a uniform, ambient air mixture. As the air mass moves away from the (primarily) urban sources, it is diluted with cleaner air and starts to "age". Less chlorinated dioxins and furans partition into the vapor phase; this process is highly temperature dependent. The particles with their enhanced load of the more chlorinated dioxins and furans are deposited by both wet and dry processes. Although the dry process dominates, the efficiency of the wet process improves for the more chlorinated dioxins and furans. Every process that occurs favors a deposited profile enriched in the more chlorinated dioxins and furans. It is, therefore, not surprising that the sediment profiles are enriched in octachlorodioxin and that the next most abundant are the heptachlorodioxins and -furans. Our data suggest that only the

(30) Villeneuve, J.-P.; Cattini, C. *Chemosphere* 1986, 15, 115-120.

most chlorinated dioxins and furans are persistent in the atmosphere. This finding may be of interest to policy makers because these dioxins and furans tend to be the least toxic.

The one part of our hypothesis that we have not yet addressed well is the issue of photochemical degradation in the atmosphere. We suspect that such a mechanism is operative; Orth and co-workers, for example, have shown that 2378-D in the vapor phase degrades photochemically with a half-life of about 2 min.<sup>31</sup> There are too few data, however, on which to generalize. Furthermore, there are no data at all on the degradation of dioxins and furans in the particle phase. We are busily correcting these lapses.

*Dr. Jean M. Czuczwa, Dr. Brian D. Eitzer, and Carolyn J. Koester have done all the work on this project. It was not easy to quantitate a few picograms of material, but they did it routinely. They also made major contributions to the development of the concepts discussed above. The U.S. Department of Energy, the U.S. Environmental Protection Agency, and the Westinghouse Corporation supported this research.*

(31) Orth, R. G.; Ritchie, C.; Hileman, F. *Chemosphere* 1989, 18, 1275-1282.

## C-Glycoside Synthesis by Palladium-Mediated Glycal-Aglycon Coupling Reactions

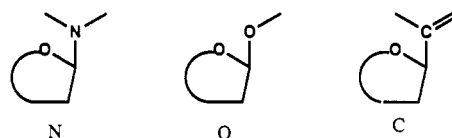
G. DOYLE DAVES, JR.

*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180*

*Received November 29, 1989 (Revised Manuscript Received March 15, 1990)*

Living systems utilize numerous, structurally diverse *N*- and *O*-glycosides in metabolically functional roles. These glycosides possess reactive aminal (*N*) and acetal (*O*) glycosidic linkages between their glycon (carbohydrate) and aglycon (noncarbohydrate) structural units. Also present in nature are *C*-glycosides (*C*-nucleosides)<sup>1</sup> in which a glycon (usually furanosyl or pyranosyl) and an aglycon (heterocyclic or anthracyclic) are linked via a hydrolytically stable carbon-carbon bond (*C*).<sup>2</sup> It is noteworthy that, with the single exception of pseudouridine, which is a constituent nucleoside of transfer RNA, and closely related naturally occurring derivatives,<sup>3</sup> all other naturally occurring *C*-glycosides appear to be antibiotics.<sup>1</sup> Many microbial<sup>1</sup> and plant species<sup>4</sup> elaborate and deploy *C*-glycosides; presumably they derive significant competitive advantage from this ability. It is interesting to speculate<sup>5</sup> that the impressive biological effects exhibited by "natural stable analogue" *C*-glycosides depend importantly on the re-

sistance of the carbon-carbon glycosidic linkage to hydrolytic or enzymatic cleavage.<sup>2</sup>



The discovery of the antibiotic formycin<sup>6</sup> and the recognition<sup>7</sup> that it was a *C*-nucleoside isomer of adenosine created great interest in the mid 1960s and fo-

(1) For reviews of the chemistry and biology of *C*-glycosides, see: (a) Hacksell, U.; Daves, G. D., Jr. *Prog. Med. Chem.* 1985, 22, 1-65; (b) Buchanan, J. G. *Prog. Chem. Org. Nat. Prod.* 1983, 44, 243-299. Goodchild, J. *Top. Antibiot. Chem.* 1982, 6, 99-227.

(2) Carbocyclic nucleosides, in which the carbohydrate ring oxygen is replaced by carbon, are a second class of naturally occurring, hydrolytically stable nucleoside analogues; see: Marquez, V. E.; Lim, M. I. *Med. Res. Rev.* 1986, 6, 1-40.

(3) Daves, G. D., Jr.; Cheng, C. C. *Prog. Med. Chem.* 1976, 13, 303-349.

(4) For reviews of plant *C*-glycosides, see: Franz, G.; Gruen, M. *Planta* 1983, 47, 131-140. Bandyukova, V. A.; Yugin, V. A. *Khim. Prir. Soedin.* 1981, 5-24. Chopin, J.; Bouillant, M. L. In *The Flavonoids*; Harborne, J. B.; Mabry, T. J., Mabry, H., Eds.; Academic Press: New York, 1975; pp 631-691.

(5) Daves, G. D., Jr. *Acta Pharm. Suec.* 1987, 24, 275-288.

(6) Hori, M.; Ito, E.; Takita, T.; Koyama, Y.; Takeuchi, T.; Umezawa, H. *J. Antibiot.* 1964, 17A, 96-99. Aizawa, S.; Hidaka, T.; Otake, N.; Yonehara, H.; Inose, K.; Igarashi, N.; Suzuki, S. *Agric. Biol. Chem.* 1965, 29, 375-376.

(7) Robins, R. K.; Townsend, L. B.; Cassidy, F.; Gerster, J. F.; Lewis, A. F.; Miller, R. L. *J. Heterocycl. Chem.* 1966, 3, 110-114. Koyama, G.; Maeda, K.; Umezawa, H.; *Tetrahedron Lett.* 1966, 597-602.

G. Doyle Daves, Jr., a native of Clayton, NM, studied at New Mexico Highlands University, Arizona State University (B.S., 1959) and Massachusetts Institute of Technology (Ph.D., 1964). After postdoctoral research (Karl Folkers, Stanford Research Institute), he joined the faculty of the Oregon Graduate Center in 1967. In 1981 he moved to Lehigh University and in 1989 to Rensselaer Polytechnic Institute. His research involves isolation, structure elucidation, and synthesis of biologically potent molecules and emphasizes applications of mass and nuclear magnetic resonance spectrometry.