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Partitioning of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans between the Atmosphere and Corn

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Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are lipophilic atmospheric contaminants that accumulate in vegetation, a process which may lead to the contamination of food. Thus, knowledge of PCDD/F accumulation in vegetation is crucial to evaluating human exposure. In an effort to determine this accumulation mechanism, we analyzed matched atmosphere, corn kernel, and corn leaf samples from a private farm in Felicity, OH. Corn is an important feed crop in the United States; both corn kernels and corn leaves (silage) are widely used. PCDD/F concentrations were below the detection limits (0.5−1 pg/g lipids) in the corn kernels. However, we found PCDD/F concentrations of 510 ± 75 fg/m^3, 1300 ± 300 fg/m^3, and 4.2 ± 1.2 ng/g lipids in the atmospheric gas phase, atmospheric particle phase, and corn leaves, respectively. For each set of air and corn leaf samples, we calculated corn leaf-atmosphere partition coefficients for both the atmospheric gas and particle phases, $K_{v,g}$ and $K_{v,p}$, respectively. On the basis of plots of the natural logarithm of these partition coefficients versus the reciprocal of the average, atmospheric temperature, we conclude that the partitioning of PCDD/F between the atmosphere and corn leaves is dependent on temperature. We calculated the enthalpies of phase change between the vegetation and air for all PCDD/F homologues; our values are comparable to literature values for polycyclic aromatic hydrocarbons and polychlorinated biphenyls. The ratio of $K_{v,p}$ to $K_{v,g}$ is a log−log function of the average vapor pressure for each PCDD/F homologue, indicating that vapor pressure plays an important role in the partitioning of both the gas and particle phases to corn leaves.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) are toxic and persistent pollutants that move long distances through the atmosphere and eventually accumulate in human tissue (*1*, *2*). Presumably, these compounds bioaccumulate in people via the human food supply; fatty foods, such as beef and dairy products, are particularly suspect (*3*). Detailed analyses of these foods have shown the presence of PCDD/F at levels ranging from 0.02 to 1.5 pg of toxic equiv/g of food (*4*−*6*). Since animals are unlikely to biosynthesize PCDD/F, it seems clear that these animals are exposed to PCDD/F through their food, which consists almost exclusively of vegetation (*7*−*9*). Thus, to fully understand human exposure to these compounds, knowledge of PCDD/F accumulation in vegetation is crucial.

There are two possible pathways for the accumulation of PCDD/F in vegetation: uptake from soil and direct deposition from the atmosphere. Apparently, accumulation from the soil is a minor pathway (*9*−*15*). Therefore, direct deposition from the atmosphere is the predominant source of PCDD/F to vegetation (*9*, *15*−*19*). Both gas- and particle-phase deposition are important pathways by which PCDD/F are accumulated in vegetation (*9*, *15*−*19*, *21*); however, the relative importance of these two pathways is not yet known. In addition, the lipid content of the plant, the roughness of the leaves, and the orientation of the vegetation to the atmosphere (i.e., horizontal or vertical) may influence the ability of vegetation to collect and retain PCDD/F from both the gas and particle phases (*9*, *19*−*21*).

The impact of atmospheric temperature on the concentrations of PCDD/F in vegetation is also not clear. McLachlan and co-workers argue that compounds with low vapor pressures such as PCDD/F do not have time to reach equilibrium between the atmosphere and vegetation; therefore, changes in atmospheric temperature, resulting in changes in the partition coefficients, will not affect the concentrations of PCDD/F in vegetation (*16*−*18*, *22*). These researchers suggest that other factors, such as length of exposure, may explain the apparent temperature-concentration correlation observed by others (*23*). Alternatively, other researchers have found that polychlorinated biphenyls do reach equilibrium with grass and that all PCDD/F congeners are transferred with the same efficiency to grass (*21*, *24*). Because several models for predicting the atmosphere-to-vegetation transfer of PCDD/F have been developed (*25*−*29*), many using these previous results, it is important to understand the effect of temperature, particularly during the growing season.

To address this issue, we collected atmosphere and corn plant samples from a private farm in Felicity, OH. The atmosphere and corn samples were paired in time; that is, whenever an atmospheric sample was collected, a corn plant sample was also collected. We selected corn because of its importance as a feed crop in the United States. At least, 10^7 t/year of corn kernels and corn silage (made by fermenting whole corn plants) are fed to cattle, chickens, and pigs (*30*). Because of its overwhelming importance as an animal feed crop, the accumulation of PCDD/F on corn may be an important, but indirect, route of human exposure to these compounds, particularly through our consumption of beef and diary products.

Experimental Section

Sample Collection. A high-volume air sampler was used to collect samples roughly once a month from July 1996 to January 1997 on a private farm in Felicity, OH, near Cincinnati. The sampler was located 1 km southwest of a corn field. Prior to sampling, a 10 cm high, 10 cm diameter, polyurethane foam plug (PUF) was Soxhlet extracted with a 50% mixture of acetone in hexane (EM Science, Gibbstown, NJ) for 24 h, and a 20 cm by 25 cm glass fiber filter (GFF) was cleaned by heating it at 450 °C for 12 h. Prior to use, the sampler flow rate was calibrated with a venturi calibrator (Sierra-Misco, Model 1080). The flow rate was set to 0.6 m^3/min and then checked at the conclusion of sampling. The PUF and GFF were placed into the air sampler, and samples were collected for 2−3 days, resulting in 1700−2600 m^3 of sampled air. The GFF collected particulates, while the

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PUF collected gas-phase constituents. At the end of each of the seven atmospheric sampling periods, whole corn plants (*Zea mays L.*) were collected from the cornfield near the sampler. The plants were placed into large plastic bags and frozen whole after arrival at the laboratory. All samples were stored at −20 °C until extraction.

Moisture and Lipid Determination. Between 2 and 5 g of intact leaves from each plant were weighed into a small beaker, dried at 95 °C for 24 h, and reweighed to obtain the percent moisture. A 50% mixture of hexane in acetone was added to cover the vegetation, and the samples were sonicated once for 2 h. The solvent was filtered, decanted into a preweighed drying pan, and allowed to evaporate. The pans were reweighed, and the percent lipids was calculated (*31*).

Sample Extraction and Cleanup. The GFF and PUF were placed into separate Soxhlet extractors, directly spiked with an internal standard solution consisting of [$^{13}C_{12}$]1,2,3,4-TCDF, [$^{13}C_{12}$]1,2,3,7,8-PCDF, [$^{13}C_{12}$]1,2,3,6,7,8-HxCDD, [$^{13}C_{12}$]1,2,3,4,6,7,8-HpCDD, and [$^{13}C_{12}$]OCDD (Cambridge Isotope Laboratories, Inc., Andover, MA) and extracted for 24 h with 350 and 800 mL of petroleum ether (EM Science, Gibbstown, NJ), respectively. All sample extracts were rotary evaporated to 25 mL, solvent exchanged three times with 50 mL volumes of hexane, and rotary evaporated to 1 mL.

Each leaf sample (2−10 g wet weight) was carefully removed from the container, placed into 250 mL Erlenmeyer flasks, weighed, directly spiked with the above internal standard, and then the flasks were sealed with a glass stopper. Each sample was sonicated once for 2 h in 200 mL of dichloromethane (EM Science, Gibbstown, NJ). The solution was then filtered into round-bottomed flasks. All sample extracts were rotary evaporated to 25 mL, solvent exchanged three times with 50 mL volumes of hexane, and rotary evaporated to 1 mL.

Husks were removed from the corn cobs, and the kernels were sliced off the cob with a knife, which had been cleaned with dichloromethane and hexane. A Braun coffee grinder adapted for rigorous grinding was cleaned with dichloromethane and hexane, and wiped dry. Approximately 50 g of kernels were mixed with an equal amount of clean sodium sulfate (J. T. Baker, Phillipsburg, NJ), placed into the grinder, and ground for 20 s. This mixture was then placed into a glass extraction thimble, spiked with the above internal standard solution, and Soxhlet extracted for 24 h with 350 mL of toluene. (On the basis of several recovery studies, toluene recovered the largest amount of all PCDD/F congeners.) The extracts were rotary evaporated to 25 mL, solvent exchanged three times with 50 mL of a 40% dichloromethane in cyclohexane solution (EM Science, Gibbstown, NJ), rotary evaporated to 5 mL, and transferred to graduated test tubes.

Gel permeation chromatography (GPC) was used to remove lipids from the corn kernel extracts. A 25 mm i.d. × 1000 cm long GPC column was packed with Bio-Beads (porous styrene-divinylbenzene copolymer beads; Bio-Rad Laboratories, Hercules, CA) in 40% dichloromethane in cyclohexane. Prior to use, a mixture of corn oil and PCDD/F was used to characterize the column. The flow was set at 10 mL/min, and the standard solution was injected onto the column. The elutant was collected in 25 mL aliquots and each was analyzed using gas chromatographic mass spectrometry as described below. It was determined that lipids eluted in the first 250 mL of collection, while PCDD/F eluted from 250 to 600 mL.

The maximum amount of lipids that could be injected onto the column was 100 mg/mL. On the basis of the previously determined lipid content, each kernel extract was diluted to 10 mL. The maximum injection volume was 4.8 mL; therefore, each sample required three injections. With the final injection, 2 mL of GPC solvent was injected to rinse the injection port tubing. The elutant was collected in two fractions. The first contained a majority of the lipids, while the second contained the PCDD/F. Like fractions from the three injections were combined. The lipid fractions were rotary evaporated and archived. PCDD/F fractions were rotary evaporated to 25 mL, hexane exchanged three times with 50 mL of hexane, and further evaporated to 1 mL.

PCDD/Fs were isolated from the above atmospheric, leaf, and corn kernel sample extracts by silica gel column chromatography. Silica gel (Grace Davison, Baltimore, MD) was Soxhlet extracted for 24 h with dichloromethane. The silica gel was then activated at 160 °C for 24 h, deactivated with 1% water by weight, and equilibrated for 24 h. The silica was loaded into a 1.5 cm i.d. × 25 cm long column in a hexane slurry to a height of 20 cm and capped with 1 cm of anhydrous sodium sulfate. The sample was transferred onto the column and eluted with 75 mL each of hexane, 15% dichloromethane in hexane, and dichloromethane. PCDD/F eluted in the first two fractions. These fractions were combined, rotary evaporated to 25 mL, solvent exchanged three times with 50 mL of hexane, and concentrated to less than 1 mL for subsequent alumina column chromatography (to remove interfering organochlorine compounds).

Alumina (ICN Biomedicals, Inc., Costa Mesa, CA) was activated for 12 h at 160 °C. The alumina was dry loaded into a 0.5 cm i.d. × 9.5 cm Pasteur pipet to a height of 6.5 cm. The column was capped with 0.5 cm of anhydrous sodium sulfate and wetted with hexane. The sample was transferred onto the column and eluted with 8 mL each of hexane, 2% dichloromethane in hexane, and 40% dichloromethane in hexane. The PCDD/F eluted in the third fraction, which was concentrated to less than 20 μL under a gentle stream of nitrogen.

Procedural blanks (no sample) were run with every set of extracts. When PCDD/F were found in the blanks, data for that set of extracts were not used. Recoveries of known amounts of PCDD/F were 65−110% for the entire procedure for all matrixes.

Sample Analysis. Samples were analyzed on a Hewlett-Packard 5989A gas chromatographic mass spectrometer equipped with a 30 m × 250 μm i.d. DB-5MS capillary column with a 0.25 μm film thickness (J & W Scientific, Folsom, CA). Two microliters of the sample was injected in the splitless mode. The injection port was held at 285 °C. The GC temperature program started at 40 °C for 2 min, ramped at 30 °C/min to 210 °C, and ramped at 2 °C/min to 285 °C, where it was held for 10 min. The mass spectrometer was operated in the electron capture, negative ionization mode with the ion source temperature at 175 °C. The pressure of the reagent gas, methane, in the ion source was maintained at 0.43 Torr. Selected ion monitoring and relative response factors were used to quantitate all congeners. Detailed quantitation methods have been described elsewhere (*32*−*34*). The PCDD/F detection limits are 0.5−1 pg/g lipids, 0.5−1 fg/m^3, and 5−10 pg/g lipids for corn kernel, atmosphere, and corn leaf samples, respectively.

Results and Discussion

We have elected to quantitate and report PCDD/F concentrations as the sum of all congeners in each homologue group. While we recognize that many researchers are interested in only those congeners that are toxicologically significant (the 17 2,3,7,8-substituded congeners), we are interested in examining the overall environmental fates of all the tetra- through octachlorinated PCDD/F congeners.

We examined the partitioning of PCDD/F from the atmosphere to corn plants over the entire growing season,

TABLE 1. PCDD/F Homologue Concentrations for Each Atmospheric Sample (fg/m^3)

sample	°C[a]	F4	F5	F6	F7	F8	D4	D5	D6	D7	D8	total
gas (7/9-11/1996)	20	36	58	68	13	N/A	<1	57	110	100	<20	440
particle (7/9-11/1996)	20	14	35	100	45	35	<1	27	84	270	460	1070
gas (7/26-28/1996)	21	48	91	93	32	15	<1	<0.3	170	220	480	1150
particle (7/26-28/1996)	21	4.2	13	33	33	71	<1	<0.3	130	540	1400	2200
gas (8/29-31/1996)	23	31	72	63	25	26	<1	12	58	75	37	400
particle (8/29-31/1996)	23	<0.2	22	100	68	110	<1	<0.3	34	110	280	720
gas (9/20-22/1996)	17	10	29	64	15	6.6	<1	<0.3	160	210	130	620
particle (9/20-22/1996)	17	1.7	7.7	27	21	42	<1	6.1	120	510	2300	3040
gas (10/29-31/1996)	11	16	29	29	7.1	5.1	<1	10	35	47	33	210
particle (10/29-31/1996)	11	1.2	18	31	11	28	<1	<0.3	41	27	240	400
gas (11/28-12/1/1996)	5	74	72	87	9.2	3.6	<1	23	69	37	25	400
particle (11/28-12/1/1996)	5	16	35	73	60	41	<1	12	86	220	290	830
gas (1/3-3/1997)	13	37	49	69	3.8	9.5	<1	11	39	51	60	330
particle (1/3-3/1997)	13	<0.2	29	83	31	34	<1	10	100	230	380	900
avg gas phase		36 ± 8[b]	57 ± 9	68 ± 8	15 ± 4	9.4 ± 3.3	<1	16 ± 7	90 ± 21	110 + 29	110 ± 64	510 ± 75
avg particle phase		5.3 ± 2.6	23 ± 4	64 ± 13	38 ± 8	52 ± 12	<1	7.9 ± 3.7	85 ± 14	270 ± 73	750 ± 290	1300 ± 300

[a] Average atmospheric temperature for the sampling period. [b] Standard errors.

TABLE 2. PCDD/F Homologue Concentrations for Each Corn Leaf Sample (pg/g lipids)

sample	F4	F5	F6	F7	F8	D4	D5	D6	D7	D8	total
corn (7/11/1996)	59	93	360	65	180	<10	<5	110	200	703	1800
corn (7/26/1996)	94	34	<10	<10	140	<10	71	230	230	1200	2000
corn (8/31/1996)	36	9.3	59	<10	75	<10	<5	94	130	240	640
corn (9/22/1996)	<2.5	66	<10	170	170	<10	59	<10	<10	9400	9900
corn (10/31/1996)	220	170	205	130	250	<10	180	420	330	740	2600
corn (12/2/1996)	300	370	410	110	410	<10	300	270	670	970	3800
corn (1/5/1997)	900	540	460	340	680	<10	480	1020	1070	2900	8400
avg	230 ± 120[a]	180 ± 75	210 ± 75	120 ± 44	270 ± 79	<10	160 ± 68	310 ± 130	380 ± 140	2300 ± 1200	4200 ± 1200

[a] Standard errors.

July to January. It may seem odd to include January as part of the growing season, even in southern Ohio. However, because of heavy rains and delays in planting, these corn plants were not harvested until January, at which time, they were sold for feed. Individual and average PCDD/F concentrations for the seven sets of atmospheric and corn leaf samples are given in Tables 1 and 2, respectively. As expected, PCDD/F concentrations in both the atmospheric gas and particle phases were similar to those found in remote locations such as Gothenberg, Sweden (*1*), and Trout Lake, WI (*35*). The lower chlorinated congeners were found primarily in the gas phase, while the higher chlorinated congeners were found primarily in the particle phase. Again, this is expected based on atmospheric gas-to-particle phase partitioning models (33).

All concentrations were below the detection limits (0.5−1 pg/g lipids) in the corn kernels. This indicates that PCDD/Fs are neither translocated through the stalk to the corn kernels nor directly accumulated from the atmosphere (due to the layers of husks surrounding the kernels). This is important. It implies that humans and animals, such as cows and poultry, can eat corn kernels without risking contamination of their tissues. We did, however, find PCDD/F in corn leaves; see Table 2. We normalized the individual corn leaf concentrations on a lipid basis to reduce the variability of the data (*15*, *20*, *23*, *36*).

For compounds such as PCDD/F, which exist in the atmosphere in both the gas and particle phases, we can define two vegetation-atmosphere partition coefficients:

$$K_{v,g} = \frac{\text{corn}_t}{\text{gas}}$$

$$K_{v,g} = \frac{\text{corn}_t}{\text{particle}} \quad (1)$$

where $corn_t$ is the total concentration of PCDD/F on the corn leaves on a lipid basis (pg/g lipid), *gas* is the atmospheric gas-phase PCDD/F concentration (fg/m^3), and *particle* is the atmospheric particle-phase PCDD/F concentration (fg/m^3). The atmospheric and corn plant samples must be collected at the same time and place. Converting units and using an air density of 1300 g/m^3, a dimensionless partition coefficient can be obtained. We calculated these corn/gas-phase and corn/particle-phase partition coefficients for all of the PCDD/F homologues measured for each of our seven paired corn leaf-atmospheric samples.

Because the samples were collected over a range of temperatures, the partitioning expressed by K_v is likely to change as a function of temperature. The standard ther-

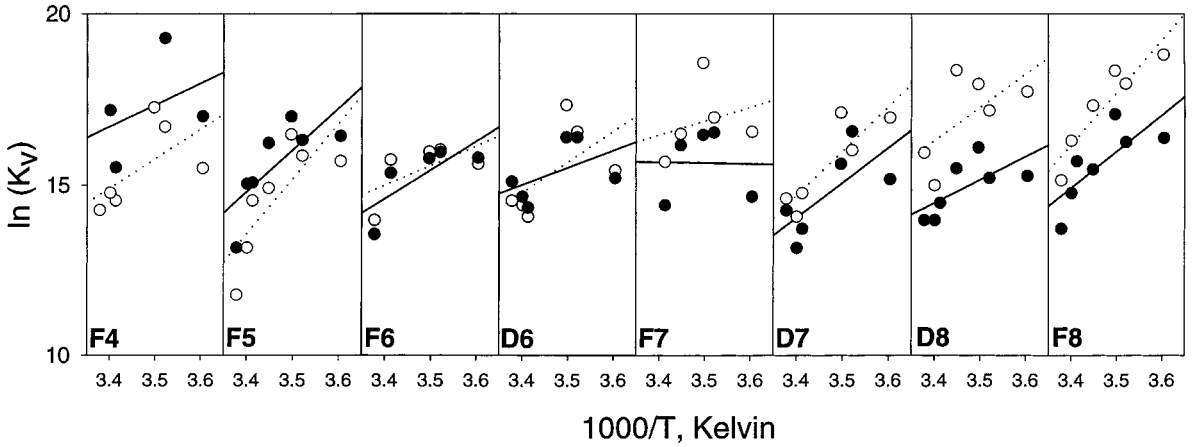

FIGURE 1. Natural logarithms of K_v versus $1/T$ for PCDD/F homologues. The letters F and D refer to dibenzofurans and dibenzo-*p*-dioxins, respectively. The numbers indicated the level of chlorination. Open circles are $K_{v,g}$ values relative to the atmospheric gas phase; the dotted lines are the regressions for these data. Filled circles are $K_{v,p}$ values relative to the atmospheric particle phase; the solid lines are the regressions for these data.

modynamic expression relating partition coefficients to temperature is

$$\frac{d(\ln K)}{d(1/T)} = \frac{\Delta H_{va}}{R} \qquad (2)$$

where T is the temperature of the system (K), ΔH_{va} is the enthalpy of phase change between vegetation (v) and air [a (J/mol)], and R is the gas constant (8.314 J/°C mol). Although we have defined ΔH_{va} as an enthalpy, as discussed above, it is not clear if this phase change is at equilibrium; therefore, these values could be considered empirical constants describing the partitioning process. In our case, T in eq 2 is the average, atmospheric temperature during the time of the sample collection. Equation 2 has been used before to explain atmosphere-vegetation partitioning of polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) as a function of atmospheric temperature (*22*, *23*). On the basis of eq 2, plots of the natural logarithm of $K_{v,g}$ or $K_{v,p}$ versus $1/T$ should be linear, and the lines should have slopes proportional to the ΔH_{va} values. These plots for both the $K_{v,g}$ and $K_{v,p}$ values are shown in Figure 1, which shows data for all homologues except for the tetra- and pentachloro dioxins (D4 and D5), neither of which were detected in a sufficient number of samples to make these data analysis procedure valid. Nondetects, which resulted in zero for one or the other partition coefficients, have been eliminated from these plots. Because of low degrees of freedom, few of the regression lines are statistically significant; however, several trends are apparent.

All but one of the slopes (see Figure 1) are positive, indicating that as the ambient temperature decreases, PCDD/Fs increasingly partition from the atmosphere to the corn leaves. This relationship indicates that the partitioning of PCDD/F between the atmosphere and corn leaves is, in fact, dependent on temperature. It has been suggested that accumulation of particle-phase PCDD/F during the growing season, dilution as the vegetation grows, or erosion of particles from the leaf surfaces could confuse the temperature effect (*16*, *17*, *22*). The first effect would tend to increase the concentrations of the higher homologues as the growing season progresses or as the temperature decreases, while the last two effects would have the opposite result. Although it is true that some combination of all these effects could mimic the temperature effect, we believe that this is unlikely. Therefore, the temperature effect is too strong and too general to be explained by a combination of other miscellaneous effects.

TABLE 3. Calculated and Literature Values for Various Thermodynamic Terms

homologue	ΔH_{va} (gas)[a]	ΔH_{va} (particle)[a]	$\ln(K_{v,p}) - \ln(K_{v,g})$[b]	$-\log(P^0)$[c] (Torr)
F4	72	53	1.9	5.17
F5	130	100	1.4	5.75
F6	48	70	−0.45	6.36
D6	75	42	0.39	6.43
F7	34		−0.65	7.01
D7	110	86	−0.36	7.04
D8	81	57	−1.7	7.70
F8	130	88	−1.1	7.71

[a] Calculated enthalpies of phase change (kJ/mol) between the corn leaves and the atmospheric gas and particle phases, respectively. [b] Predicted values at 25 °C from the lines in Figure 1. [c] Average subcooled liquid vapor pressures at 25 °C; note that the vapor pressures in ref *33* are incorrect but that the corrected data are given here.

We calculated the enthalpies of phase change (ΔH_{va}) by multiplying these slopes (see Figure 1) by the gas constant, and these results are shown in Table 3, columns 2 and 3. While few of these values are statistically significant, most of them are in the range 80 ± 30 kJ/mol, values which are compatible with the literature. For example, values for PAH ranged 82−92 kJ/mol (*23*), and values for PCB ranged 54−140 kJ/mol (*22*). In another study, ΔH_{va} was shown to vary for PCB depending on the type of vegetation examined (*20*), and these values ranged 57−130 kJ/mol. Our values in corn leaves for PCDD/F are comparable with literature values for other semivolatile organic compounds in vegetation. We can also compare our ΔH_{va} values with enthalpies of vaporization, ΔH_v, of PCDD/F. Literature values for ΔH_v range 94−110 kJ/mol (*16*), an average of 104 ± 6 kJ/mol. Again, our values overlap this range. This result also suggests that the effect of temperature is real and not an artifact due to other variations during the growing season.

Vapor pressure also has an effect on atmospheric vegetation partitioning. It can be shown that

$$\ln(K_{v,p}) - \ln(K_{v,g}) = \ln\left(\frac{\text{gas}}{\text{particle}}\right) \propto \ln(P^0) \qquad (3)$$

where P^0 is the compound's subcooled liquid vapor pressure (*33*). The homologues shown in Figure 1 are arranged from left to right in order of decreasing vapor pressure. Notice that the F4 particle-phase line lies *above* the gas-phase line by 1−2 natural log units but that the D8 particle-phase line lies *below* the gas-phase line by 1−2 natural log units.

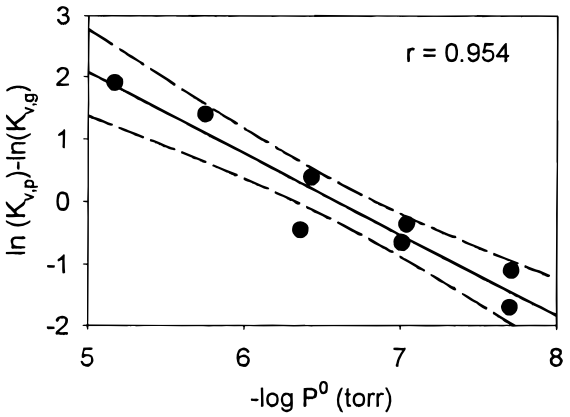

FIGURE 2. $\ln(K_{v,p}) - \ln(K_{v,g})$ versus $-\log P^0$; see Table 3; the dashed lines are the 95% confidence intervals.

Furthermore, there is a regular progression. As the vapor pressure decreases, (from left to right), the lines get closer together (see F4 to F5), cross (F6 and D6), and then get further apart (D7 to D8). In other words, as the vapor pressure decreases, the expression $\ln(K_{v,p}) - \ln(K_{v,g})$ goes from positive to about zero to negative as predicted by eq 3. We used the regression lines shown in Figure 1 to determine the difference between $\ln(K_{v,p})$ and $\ln(K_{v,g})$ at a fixed temperature, 25 °C. These differences are given in the fourth column of Table 3. The strong relationship between $\ln(K_{v,p}) - \ln(K_{v,g})$ and vapor pressure (see last column of Table 3) is illustrated in Figure 2. Clearly, vapor pressure plays an overwhelming role on the partitioning of both the atmospheric gas and particle phases to vegetation.

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