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Uptake of Airborne Semivolatile Organic Compounds in Agricultural Plants: Field Measurements of Interspecies Variability

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The accumulation of semivolatile organic compounds (SOCs) in plants is important because plants are the major vector of these compounds into terrestrial food chains and because plants play an important role in scavenging SOCs from the atmosphere and transferring them to the soil. Agricultural plants are of particular interest because they are a key link in the atmosphere−fodder−milk/beef food chain that accounts for much of background human exposure to persistent lipophilic organic pollutants such as PCBs and PCDD/Fs. In this study the accumulation of PCBs, PCDD/Fs, PAHs, and some chlorobenzenes was determined in eight grassland species as well as maize and sunflower leaves collected simultaneously at a semirural site in Central Europe. Air samples were collected at the same site during the growth of these plants, and the particle-bound and gaseous concentrations were determined. A newly developed interpretive framework was employed to analyze the data, and it was established whether the accumulation of a given compound was due primarily to equilibrium partitioning, kinetically limited gaseous deposition, or particle-bound deposition. The interspecies variability in uptake was then examined, and it was found that for those compounds which had accumulated primarily via kinetically limited gaseous deposition and particle-bound deposition the variation among the 10 species was generally a factor of <4. For most of the plants this variation could largely be explained by differences in the surface area and horizontally projected surface area per unit plant volume. However, for the more volatile compounds for which the plant levels were determined by equilibrium partitioning, the interspecies variability exceeded a factor of 30. This variability was not related to the extractable lipid content or the cuticle volume fraction in the vegetation. Good agreement was found between the partition coefficients measured in the field and published values measured in the laboratory. The results indicate that the interspecies variability in the vegetation/gas-phase partition coefficient is larger than the variability in the net gaseous and particle-bound deposition velocities, yielding a greater interspecies variability in plant levels for more volatile SOCs.

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Introduction

The uptake of semivolatile organic compounds (SOCs) from the atmosphere into plants has attracted considerable research interest in recent years, in part because of the key role plants play in contaminant accumulation in agricultural food chains. Animal fat in the form of milk and meat (primarily beef) is the major source of background exposure of the European and North American populations to many persistent SOCs (*1*−*4*). This imparts the uptake of SOCs in agricultural food chains with a particular significance.

One factor that influences accumulation of SOCs in plants is the physical−chemical properties of the compound. Plant uptake of SOCs has been shown to occur primarily from the atmosphere (*5*, *6*). Depending on the properties of the compound, accumulation in plants is primarily determined by one of three processes: equilibrium partitioning between the vegetation and the gas phase; kinetically limited dry gaseous deposition; or particle-bound deposition to the vegetation (*7*, *8*). It is important to know which of these processes has been dominant, because each is controlled by a different set of chemical properties, meteorological conditions, and plant characteristics. When field data are considered, it is not immediately apparent which process has determined the uptake of a chemical in a given plant, and incorrect assumptions in this regard have in the past resulted in misleading interpretations and false conclusions. In an effort to address this difficulty, the considerable knowledge accumulated over the past years about the influence of physical−chemical properties on each of these processes was used to develop an interpretive framework for interpreting field measurements of SOCs in plants (*9*). However, the usefulness of this framework has yet to be demonstrated.

Another factor that can be expected to influence the accumulation of SOCs in plants is the properties of the plants. There is little information available on this subject, and what little there is is contradictory. Buckley (*10*) reported a 10-fold range in PCB concentrations (on a dry weight basis) in foliage from 18 plant species collected in New York state, suggesting pronounced interspecies variability. On the other hand, Gaggi et al. (*11*) determined the levels of PCBs and a number of organochlorine pesticides in the leaves of 12 different woodland species in Italy and found the range in the concentrations (on a dry weight basis) to be quite small, varying by at most a factor of 3 for most compounds and by a factor of 5 for PCBs. These authors concluded that the interspecies variability in plant concentrations was unimportant.

In this paper the interspecies variability in the accumulation of SOCs in agricultural plants is investigated; pasture species are focused on due to the importance of pasture grass as a vector of SOCs into the food supply. Ten species were collected simultaneously from a farm close to Bayreuth, Germany, and analyzed for a wide range of organic contaminants including polychlorinated benzenes, biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs) as well as polycyclic aromatic hydrocarbons (PAHs). By collecting mature plants from the same location, the influence of external variables such as air concentration, temperature, plant growth rate, and age could be eliminated or minimized. The interspecies variability is interpreted separately depending on which of the three uptake processes dominated for a given compound, because in each case different plant properties determine the uptake. This is accomplished using the interpretive framework proposed in ref *9*.

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TABLE 1. List of the Plants Studied and Their Properties

Latin name	common name	dry wt[a] (%)	surface area[b] ($m^2\ m^{-3}$)	horizontally projected surface area[c] ($m^2\ m^{-3}$)	extractable lipids[d] ($kg\ m^{-3}$)	cuticle fraction[e] ($m^3\ m^{-3}$)
Lolium multiflorum + *Lolium perenne*	ryegrass	32.2	14700	1900	6.8	0.008−0.016
Cirsium arvense	creeping thistle	20.4	4000	1500	4.4	
Taraxacum officinale agg.	dandelion	17.4	8800	1800	4.1	
Plantago lanceolata	ribwort plantain	22.0	6300	1900	2.3	
Achillea millefolium agg.	yarrow	29.5	5800	1800	4.6	0.002−0.005
Alchemilla vulgaris agg.	lady's mantle	27.6	8100	4000	6.6	
Helianthus annuus	sunflower, leaves	16.6	5300	2000	3.5	0.001−0.003
Leontodon autumnalis	autumn hawkbit	24.0	6100	530	4.5	
Trifolium repens	white clover	21.0	6600	3000	3.0	
Zea mays	corn/maize, leaves	24.2	8600	3000	5.4	

[a] Dry weight expressed as percent of fresh weight. [b] Superficial surface area of the vegetation normalized to the volume of the vegetation. [c] Projected horizontal surface area of the vegetation normalized to the volume of the vegetation. [d] Extractable lipids normalized to the volume of the vegetation. [e] Estimated volume fraction of the cuticle.

Experimental Section

Sampling. Vegetation samples were collected from a farm 1 km to the south of the University of Bayreuth, which lies on the southern outskirts of the city of Bayreuth. There were no major obstructions for >500 m to the east and west, the primary wind directions. The nearest major wind obstruction was a grove of trees 10 m in height located 70 m to the north. The greatest distance between sampling sites was 100 m, with the exception of the corn (400 m).

The samples were collected on September 15−16, 1995. Ten different plant species were sampled including eight grassland species from a meadow as well as *Zea mays* (corn) and *Helianthus annuus* (sunflower) (see Table 1). The meadow had last been mowed at the beginning of June so the vegetation had developed over a 15 week period. The *Zea* and *Helianthus* plants were 15 and 18 weeks old, respectively. Most of the plants were mature, having concluded the main growth phase at least 6 weeks prior to sampling.

Of the eight grassland species, five are common grassland species that are important components of cattle feed in Central Europe, whereas three have unusual characteristics which we thought might influence their contaminant uptake behavior: *Achillea millefolium* (yarrow) has very fine feathery leaves, *Alchemilla vulgaris agg.* (lady's mantle) has large hairy leaves that stand horizontally in the lower part of the canopy, and *Cirsium arvense* (creeping thistle) has particularly thick stiff leaves and often protrudes out of the canopy. The different species were not homogeneously distributed in the meadow. One area was dominated by *Lolium* and other grasses with scattered groups of *C. arvense*; a second contained primarily *Taraxacum officinale* and *Plantago lanceolata*; a third was a mixture of *Trifolium repens*, *Leontodon autumnalis*, *A. vulgaris*, and other species; *A. millefolium* grew as a monoculture. The *Zea* samples were taken 5−10 m from the edge of a large field, and the *Helianthus* were sampled from a 15 m wide thinly seeded hedge.

The plant samples were cut with scissors, sorted, packed in aluminum foil, and stored at −18 °C. For *Zea* and *Helianthus* several plants were selected and all of the leaves were harvested. The other parts of these plants were not analyzed.

Air samples were also collected continuously. During May, June, and July monthly samples were collected 150 m from the edge of a forest located 1 km to the west of the plant sampling site (*12*). During August and September air samples were collected directly on the meadow in 2 week intervals. The sampler, which employs a glass fiber filter and an XAD-2 adsorbent cartridge, is described in detail elsewhere (*13*, *14*).

Analysis. The plant samples were divided into two groups of five species. For each group one sample from each species was analyzed together with a blank. This was repeated four times, yielding four analyses for each species. The vegetation was first freeze-dried and then ground before being subjected to Soxhlet extraction in toluene for 16−18 h. Prior to extraction, an internal standard mixture containing 2 $^{13}C_6$ chlorobenzenes, 7 $^{13}C_{12}$ PCBs, 12 $^{13}C_{12}$ PCDD/Fs, and 14 deuterated PAHs was added to the extraction solvent.

The filter samples were Soxhlet extracted in toluene for 16−18 h, while the XAD samples were either Soxhlet extracted in toluene or extracted via elution with *n*-hexane/diethyl ether (10:1). The same internal standard mixture was applied as with the plant samples.

Following extraction 25% of the extract was set aside for the PAH analysis (one-third) and for archiving (two-thirds). The remainder was cleaned up using a mixed H_2SO_4−silica gel/NaOH−silica gel column followed by an aluminum oxide column that separated the PCBs and chlorobenzenes from the PCDD/Fs. A detailed description is given in ref *15*. For the plant samples a further purification of the PCB/chlorobenzene fraction was necessary. This was accomplished with gel permeation chromatography (GPC) using 40 g of Bio-Beads SX-8 (Bio-Rad) in a 24 mm i.d. column and toluene as the solvent. The PAH fraction was cleaned up using a silica gel/alox column and this same GPC column (*16*).

The HRGC/HRMS analyses were performed on a VG-Autospec Ultima using a 25 m DB-5 MS capillary (0.25 mm i.d. × 0.25 μm film thickness for PCBs and PAHs, 0.25 mm i.d. × 0.10 μm for PCDD/Fs). The measurements were conducted using EI ionization at a mass resolution of 8000−10000. The compounds analyzed were pentachlorobenzene (QCB), hexachlorobenzene (HCB), the PCB congeners with IUPAC numbers 17+18 (+ indicates coellution), 16+32, 28+31, 52, 44, 64, 95, 101+90, 149, 153, 138+158, 187, 180, 202, and 196+203, the homologue sums for the Cl_4−Cl_8DD/Fs, phenanthrene, fluoranthene, pyrene, triphenylene + chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, indeno[1,2,3-*c*,*d*]pyrene, benzo[*g*,*h*,*i*]perylene, dibenz[*a*,*h*]anthracene, and coronene.

In addition to the wet weight and dry weight, the superficial surface area, extractable lipid content, and cuticle size of the different plant species were measured. The projected surface area of the vegetation was determined using an area meter. This was multiplied by 2 for leaves to obtain the superficial surface area. A factor of 3.14 was used for stems and flowers (where analyzed). Due to their unusual form, cross sections of *A. millefolium* leaves were examined under the microscope to obtain estimates of the circumference/diameter ratio (2.66). The extractable lipid content was

TABLE 2. Reproducibility of the Plant Analyses

compound	CV[a]	compound	CV[a]
Cl_4DD	0.07	pentachlorobenzene	0.18
Cl_5DD	0.12	hexachlorobenzene	0.10
Cl_6DD	0.11	PCB 17+18	0.14
Cl_7DD	0.13	PCB 16+32	0.15
Cl_8DD	0.10	PCB 28+31	0.10
Cl_4DF	0.11	PCB 52	0.12
Cl_5DF	0.09	PCB 44	0.12
Cl_6DF	0.10	PCB 64	0.13
Cl_7DF	0.14	PCB 95	0.13
Cl_8DF	0.12	PCB 101+90	0.11
phenanthrene	0.15	PCB 110	0.09
fluoranthene	0.13	PCB 149	0.10
pyrene	0.14	PCB 153+132	0.11
triphenylene + chrysene	0.12	PCB 158+138	0.11
benzo[*b*]fluoranthene	0.19	PCB 187	0.11
benzo[*k*]fluoranthene	0.19	PCB 180	0.11
benzo[*e*]pyrene	0.18	PCB 202	0.17
benzo[*a*]pyrene	0.23	PCB 196+203	0.11
indeno[1,2,3-*c*,*d*]pyrene	0.23		
benzo[*g*,*h*,*i*]perylene	0.14		
dibenz[*a*,*h*]anthracene	0.21		
coronene	0.23		

[a] Coefficient of variation for the four parallel analyses of the compound averaged over all 10 species.

determined using a standard method (*17*) involving Soxhlet extraction of freeze-dried ground plant material in petroleum ether for 14 h. The size of the cuticle was determined microscopically following staining of leaf cross sections with Sudan IV.

Results and Discussion

The air concentrations measured in this study were low compared to most reports in the literature and in good agreement with previous measurements at this and other semirural sites in southern Germany (*12*, *18*−*20*). This suggests that the proximity of the small city of Bayreuth did not have a significant impact on the atmospheric levels of the chemicals. The gaseous concentrations of the PAHs with five and more rings lay in the range of the blanks and hence could not be quantified. The particle-bound concentrations of QCB, HCB, and the tri- and tetrachlorinated PCBs could not be quantified for the same reason.

The properties of the different plants are summarized in Table 1. It is surprising how little interspecies variation there is despite the wide range of plants chosen for this study. This is particularly true for the total extractable lipid, which ranges over just a factor of 2.2 with very good agreement between the two parallel measurements.

Quality of the Plant Data. With a few sporadic exceptions, the standard recoveries were good and no evidence of interferences or chromatographic problems was observed. The laboratory blanks were generally low and posed no problem to the analytical quantitation. Only for QCB, PCB 202, and Cl_8DF did the average blank exceed 20% of the quantity in the samples, and this was only the case for a few of the plant samples analyzed. In just two cases did the blank exceed one-third of the quantity in the sample, and these two data points (QCB in one *Zea* and one *Lolium* sample) were discarded.

The reproducibility of the plant analyses is illustrated in Table 2, which gives the coefficient of variation of the concentrations of each chemical in the four parallel samples analyzed averaged over all 10 plant species. With the exception of QCB and several of the primarily particle-bound PAHs, all of the values are <0.15. This is a very good result for ultratrace analysis of organic contaminants and indicates that the plant data are of high quality. The complete data set is available as Supplementary Information.

Interchemical Variability in Plant Accumulation. The interchemical variability in plant accumulation was examined using the interpretive framework presented in ref *9*. The log of the quotient of the concentration in vegetation C_V and the concentration in the gas-phase C_G was plotted against log K_{OA} (taken from ref *12*) for those compounds for which gaseous concentrations could be measured. Similarly, the log of the quotient of the plant concentration and the particle-bound concentration C_P was plotted against the log of the quotient of the particle-bound and gaseous concentrations for those compounds for which the particle-bound concentration could be reliably determined. If in the latter case the gaseous concentrations could not be quantified, the limit of quantification was used. The average gaseous concentrations for the three air samples covering the 6 weeks preceding sampling were used for those compounds for which the achievement of a partitioning equilibrium between the gas phase and the plants was thought to be possible (QCB, HCB, the PCBs, phenanthrene, fluoranthene, and pyrene), because in this case the early exposure history of the plants is erased, the plant levels being determined by recent exposure. In all other cases the average concentrations between the beginning of July and September 15 were used. Note that this does not have a large influence on the results, because for most compounds the air concentrations varied by a factor of <3 between the air samples.

The results are plotted for each of the 10 species studied in Figures 1 and 2. According to the interpretive framework (*9*), Figure 1 should begin with a region of increasing log(C_V/C_G) with increasing log K_{OA}, which contains those compounds that approached a partitioning equilibrium. This should be followed by a flat region which includes compounds taken up primarily by gaseous deposition but that did not approach a partitioning equilibrium. Finally, log(C_V/C_G) should begin to increase at high log K_{OA} as a result of particle-bound deposition. This behavior can be seen for each of the 10 species in Figure 1. All compounds show a positive slope on the left-hand side of the plot. Note, however, that the slope varies considerably, from quite flat for *Helianthus* to quite steep for *Lolium*. This is a first indication that there is considerable interspecies variability for compounds that approach a partitioning equilibrium. Moving to the middle of Figure 1, the different species all have a plateau at a log(C_V/C_G) of ∼7. This is followed by a second increase that sets in when log K_{OA} exceeds ∼11. This increase is not as pronounced as the one on the left-hand side of the curve.

This is where Figure 2 is useful, because it incorporates the most involatile compounds. According to the interpretive framework log(C_V/C_P) should be quite flat for compounds with low C_P/C_G values. Compounds in this portion of the curve approach a partitioning equilibrium. This should be followed by a region in which log(C_V/C_P) decreases with a slope of 1. Here one finds compounds that accumulate primarily as a result of kinetically limited gaseous deposition. Toward the right of the diagram C_V/C_P should become constant. This area contains those compounds taken up mainly as a result of particle-bound deposition. Referring to Figure 2, in each of the plants all chemicals with the exception of the PAHs show this predicted behavior. The first plateau is short because the particle-bound concentrations could not be determined for the most volatile compounds. However, the second two elements of the figure are very apparent, with a linear decrease in log(C_V/C_P) for C_P/C_G between about 0.02 and 5, followed by a lower plateau at a log(C_V/C_P) value of ∼6.5.

The PAHs show a somewhat different behavior. The plateau on the right-hand side of the figure is very pronounced due to the large number of strongly particle-bound PAHs,

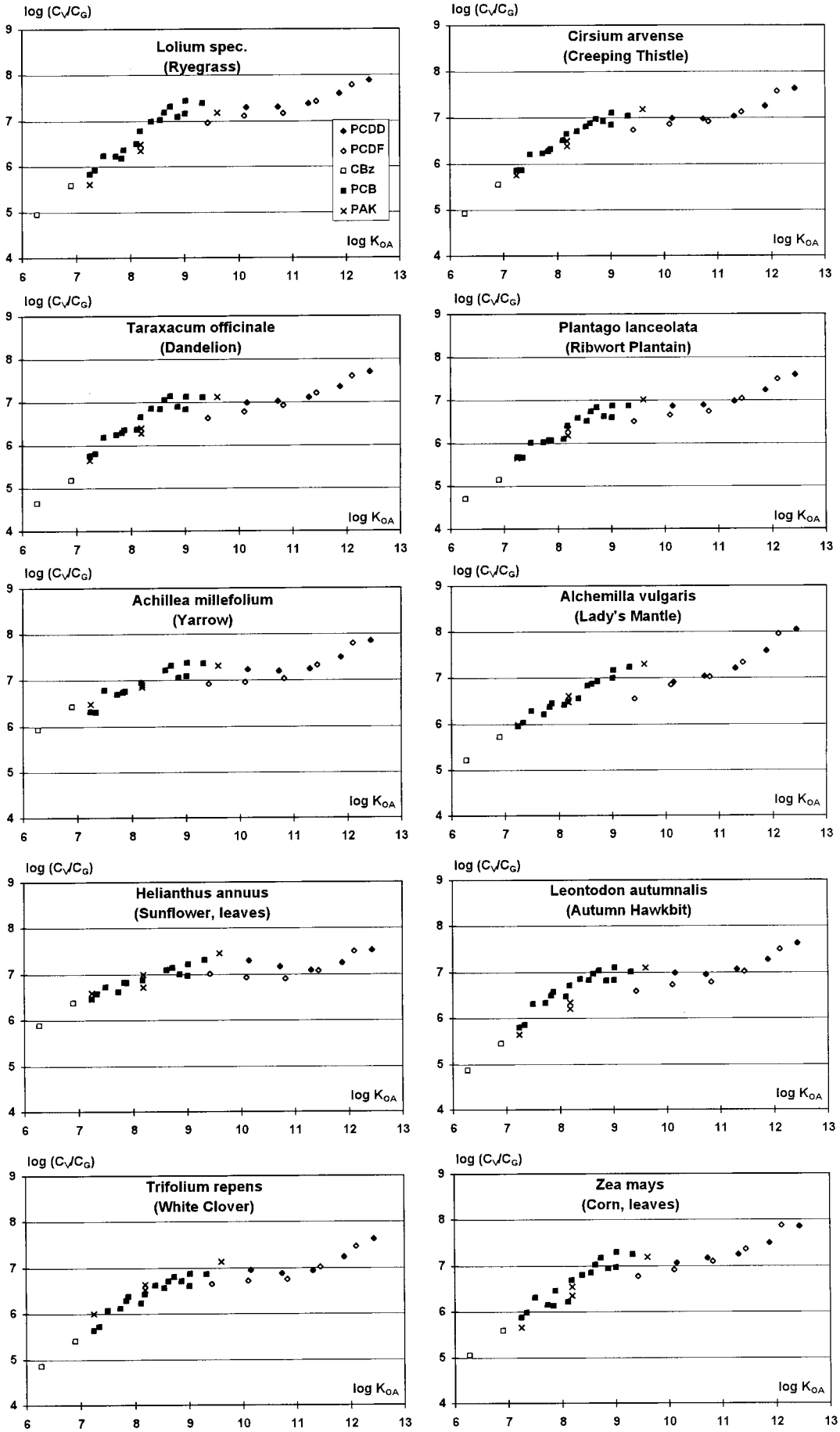

FIGURE 1. Plot of log(C_V/C_G) vs log K_{OA} for each of the 10 plant species.

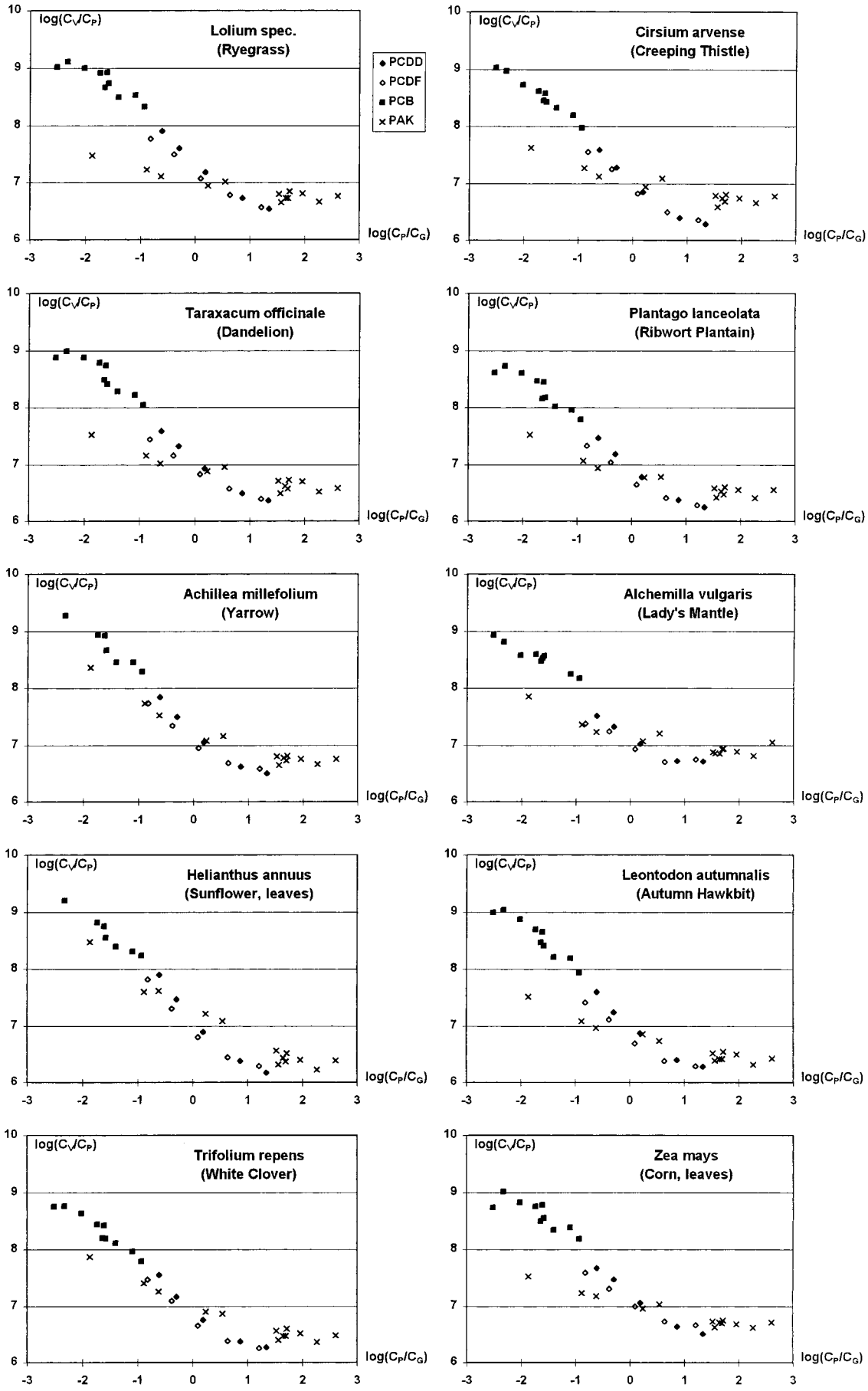

FIGURE 2. Plot of $\log(C_V/C_P)$ vs $\log(C_P/C_G)$ for each of the 10 plant species.

TABLE 3. Compounds Taken up Primarily via the Same Deposition Process in All Plants

equilibrium partitioning	kinetically limited gaseous deposition	particle-bound deposition
pentachlorobenzene	PCB 180	Cl_8DD
hexachlorobenzene	PCB 196+203	Cl_8DF
PCB 17+18	Cl_4DD	benzo[*b*]fluoranthene
PCB 16+32	Cl_5DD	benzo[*k*]fluoranthene
PCB 28+32	Cl_5DF	benzo[*e*]pyrene
	Cl_6DF	benzo[*a*]pyrene
		indeno[1,2,3-*c*,*d*]pyrene
		benzo[*g*,*h*,*i*]perylene
		dibenz[*a*,*h*]anthracene
		coronene

but this plateau lies higher than for the PCDD/Fs. This difference has also been observed in the deposition of these compounds below forest canopies near Bayreuth and indicates that the particle-bound deposition velocity is higher for the PAHs than for the PCDD/Fs (*12*). This may be due to differences in the particle-size distribution between these families of compounds (*21*).

A further anomaly in Figure 2 is the fact that in most species the three most volatile PAHs lie considerably below the other compounds in the central portion of the plot and do not show a pronounced decreasing trend with increasing C_P/C_G. Referring to Figure 1, it can be seen that the three most volatile PAHs lie in the left-hand portion of this curve, which indicates that their uptake was controlled by equilibrium partitioning. This is not inconsistent with the trend in Figure 2, because the interpretive framework predicts that C_V/C_P for compounds in the equilibrium partitioning group should be relatively independent of C_P/C_G. However, in Figure 2 these PAHs are found in the C_P/C_G range where the other compounds show kinetically limited gaseous uptake. This is due to the fact that the PAHs show higher particle-bound fractions at a given K_{OA} value than the other compounds. This stronger tendency of PAHs to partition to particles means that the window in which kinetically limited gaseous deposition dominates is very small for the PAHs. With the exception of chrysene−triphenylene, plant uptake of the PAHs was controlled by either equilibrium partitioning or particle-bound deposition.

The fact that almost all of the 40 compounds from five different families of chemicals fit on to the curves on these two plots indicates that the interpretive framework presented in ref *9* is very useful for the interpretation of field data for SOCs in vegetation. About 60% of the compounds studied were on both plots, so there was sufficient overlap to establish the internal consistency of the framework. Good results were also obtained with a similar framework for interpreting contaminant deposition to forest canopies (*22*). Despite the simplifying assumptions made, the framework functions very well. However, the example of the PAHs in Figure 2 demonstrates that careful interpretation of the results is nevertheless necessary.

Many compounds were always in either the left-hand segment, the middle segment, or the right-hand segment of Figures 1 and 2 for all species. On the basis of the framework, these are compounds for which the uptake in all plants was always dominated by equilibrium partitioning (left segment), kinetically limited gaseous deposition (middle segment), or particle-bound deposition (right segment). These compounds (see Table 3) will be used to further investigate the interspecies variability.

Overview of Interspecies Variability in Plant Uptake. To compare the uptake in the different species, the chemical concentrations were normalized to the concentration of the same compound in *Lolium* (both on a dry weight basis). The resulting quotients are plotted as a function of log K_{OA} in Figure 3. The five to seven ring PAHs are plotted on the right-hand side of the figure using arbitrarily selected log K_{OA} values between 13 and 15. This approach was taken because Figure 2 had shown that the uptake of these compounds was clearly dominated by particle-bound deposition. According to Figures 1 and 2, the uptake behavior of compounds with log K_{OA} <∼9 was determined by equilibrium partitioning; for 9 < log K_{OA} < 11 kinetically limited gaseous deposition dominated, and for log K_{OA} > ∼11 particle-bound deposition was most important. Referring to Figure 3, the interspecies variability in deposition via kinetically limited gaseous deposition and particle-bound deposition is quite small, varying by generally a factor of <4 and at most by a factor of 8 among the 10 species. In contrast, the variation in equilibrium partitioning behavior is very pronounced, ranging up to a factor of 37.

These results suggest that the importance of interspecies variability in plant uptake of SOCs depends on the properties of the compound. The variability, at least within this agricultural ecosystem, is quite small for less volatile compounds. However, for more volatile SOCs, which include most of the PCBs and organochlorine pesticides, the vari-

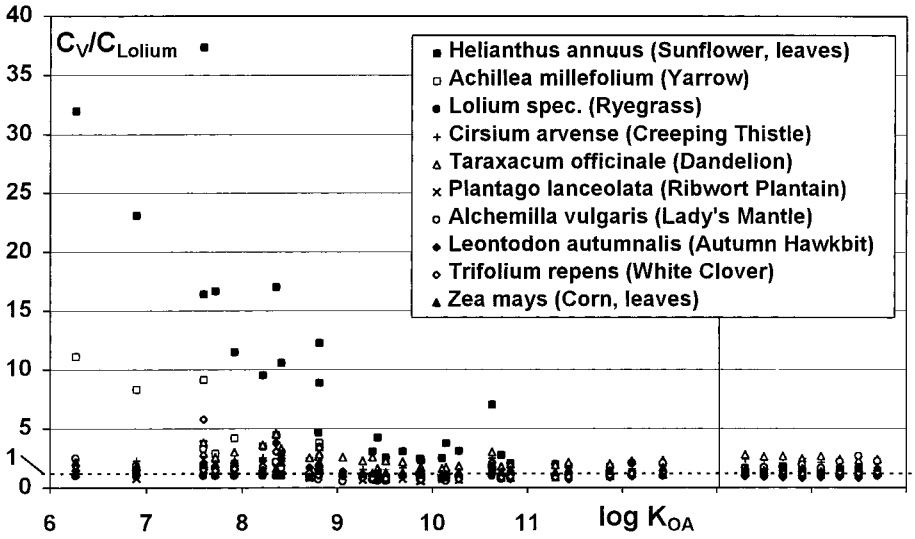

FIGURE 3. Plot of the plant concentrations normalized to the concentrations in *Lolium* vs log K_{OA} for all compounds and all plant species.

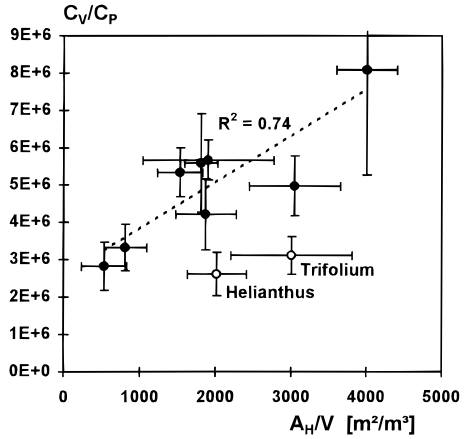

FIGURE 4. Plot of the average C_V/C_P for the eight PAHs that were taken up primarily through particle-bound deposition (see Table 3) vs the horizontal projected surface area of the vegetation normalized to vegetation volume A_H/V. The error bars give the standard deviation of the estimates of C_V/C_P and A_H/V.

ability is very large, in agreement with the findings of Buckley (*10*). It has been suggested that the choice of plant material for biomonitoring of SOCs with plants is irrelevant, because the interspecies variability in plant levels is low (*23*, *24*). This position is clearly refuted in Figure 3.

Interspecies Variability in Plant Uptake via Particle-Bound Deposition. It is interesting to attempt to identify factors responsible for the interspecies variability. Using the simple model described in ref *9*, the particle-bound deposition can be described as

$$C_V/C_P = v_P A/(Vk_E) \quad (1)$$

where v_P is the average particle-bound deposition velocity (m h^{-1}), A is the surface area that the deposition occurs to (m^2), V is the volume of the plant (m^3), and k_E is a time constant describing loss of particle-bound chemical from the leaf surface (h^{-1}). On the basis of this equation, C_V/C_P should be related to the normalized surface area of the plant A/V. To start with, only dry particle-bound deposition via sedimentation and wet particle-bound deposition will be considered, because these pathways contribute a large portion of the particle-bound deposition of SOCs to terrestrial surfaces in the Bayreuth area (*12*, *25*). In this case a reasonable definition for A would be the horizontal projected surface area of the plant A_H, because this is the surface that receives the deposition. In Figure 4 the average C_V/C_P (on a volume basis) for the eight PAHs that were taken up primarily through particle-bound deposition (see Table 3) is plotted against A_H/V (from Table 1). A linear relationship was obtained for eight of the plant species, with a correlation coefficient of 0.74 and an average deviation between the predicted and measured C_V/C_P of 15%. This indicates that a large part of the interspecies variability in the accumulation of particle-bound contaminants can be attributed to differences in A_H/V. The corollary of this is that v_P/k_E values are similar for these eight plant species. The particle-bound deposition velocity v_P is expected to be the same, because wet deposition and particle sedimentation rates are not influenced by plant properties. This implies that the time constants for weathering of contaminants deposited via these pathways are also approximately the same for these plants, which is more surprising.

It is interesting to note that the extrapolation of the regression line in Figure 4 intersects the *y*-axis well above 0. In other words, this plot suggests that a theoretical plant that possesses no horizontal surface area to capture sedimenting deposition would still accumulate particle-bound chemical. This uptake can be interpreted as the contribution due to the deposition of small particles via diffusion/impaction. This deposition occurs to all plant surfaces, not just to the projected horizontal surface, and hence C_V/C_P for diffusion/impaction should not be related to A_H/V, but rather to A/V. The equation for overall particle-bound deposition can then be broken down into two terms

$$C_V/C_P = (v_P/k_E)_S(A_H/V) + (v_P/k_E)_{D/I}(A/V) \quad (2)$$

where the subscripts S and D/I refer to deposition via sedimentation (both wet and dry) and diffusion/impaction, respectively. It was thought that fitting the data using this equation might yield an improvement over the relationship shown in Figure 4, where $(v_P/k_E)_{D/I}(A/V)$ is in effect assumed to be constant for all species. However, regressions using A_H/V together with either A/V or the gaseous mass transfer coefficient v_{GG} (see below) as a measure of the interspecies variability in the particle-bound deposition due to diffusion/impaction yielded slightly poorer results. This is likely due to the uncertainty in the measured values, which precludes an interpretation at this level of complexity.

Two species, *Trifolium* and *Helianthus*, lie well below the regression line in Figure 4. Although there is no apparent explanation for *Helianthus*, in the case of *Trifolium* this may be due to the wax structure on the plant surface. Some plants are known to build crystalline wax structures, which make the plant surface virtually nonwettable. Water falling on the surface rolls off in the form of droplets. Particles on the surface adhere to the surface of the droplets and are efficiently removed from the plant surface (*26*). Hence, the surfaces of these plants can be expected to be relatively free of particles. Of the plants studied here, *Trifolium* is the one species where the surface remains unwettable. *Alchemilla* shows this characteristic to some extent, as do young plants of *Zea* and *Lolium*, but the wax structure erodes with age and older plants do not have this cleaning function (*27*). In terms of the mathematical model, k_E is much larger for *Trifolium* than for the other species.

Interspecies Variability in Plant Uptake via Kinetically Limited Gaseous Deposition. Turning to kinetically limited gaseous deposition, the equation for this process derived from the simple model in ref *9* is

$$C_V/C_G = Av_{GG}t/V \quad (3)$$

where v_{GG} is the average mass transfer coefficient for transport of gaseous SOCs from the atmosphere to the plant surface (m h^{-1}). This equation suggests that C_V/C_G should also be related to the normalized surface area of the plant A/V. Because gaseous deposition occurs to all surfaces of the plant, it would seem more appropriate to use the total surface area of the plant in this case. In Figure 5 the average C_V/C_G for those compounds that were taken up primarily via kinetically limited gaseous deposition (see Table 3) is plotted against A/V (see Table 1). For seven of the plant species a good linear relationship between C_V/C_G and A/V was obtained with a correlation coefficient of 0.88. The linear regression yielded a *y*-intercept close to zero. Thus, a simple model in which the mass transfer coefficient is assumed to be constant describes the interspecies variability in kinetically limited dry gaseous deposition well for seven of the species studied.

The mass transfer coefficient v_{GG} can be estimated from the slope of Figure 5. With the exposure time t set equal to 100 days or 2400 h, a v_{GG} value of 0.55 m h^{-1} is obtained. This can be transformed into a gaseous deposition velocity to the canopy by multiplying by twice the leaf area index. Assuming this to be 5, the gaseous deposition velocity is ~5 m h^{-1}. This is quite low but plausible, lying in the range of gaseous deposition velocities reported in the literature (*28*). It is

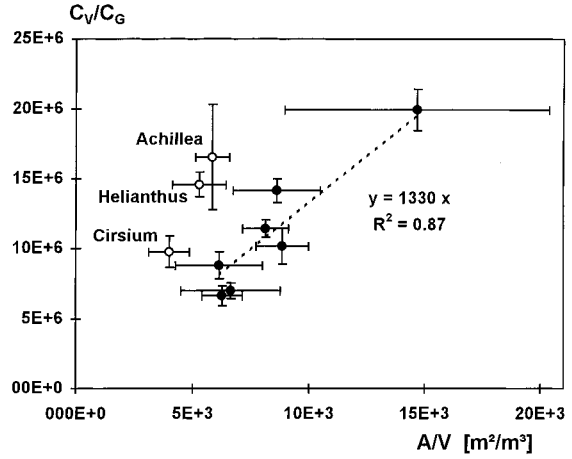

FIGURE 5. Plot of the average C_V/C_G for those compounds that were taken up primarily via kinetically limited gaseous deposition (see Table 3) vs the superficial surfaces area of the vegetation normalized to vegetation volume *A/V*. The error bars give the standard deviation of the estimates of C_V/C_P and *A/V*.

somewhat above the value determined for deposition of gaseous PCDD/Fs to soil (*25*) and well below the value determined for gaseous deposition of SOCs to forests (*12*).

Of the 10 species studied, 3 are not described well by this model and lie considerably above the regression line in Figure 5: *Cirsium*, *Helianthus*, and *Achillea*. For *Cirsium* and *Helianthus* this is attributed to the exposed locations of the vegetation. *Cirsium* grew as clumps that stood well above the surrounding *Lolium* canopy, whereas *Helianthus* formed a narrow and ragged canopy that stood 1.5 m above the surrounding vegetation. Due to their greater exposure to the atmosphere, higher mass transfer coefficients were to be expected for these two species. This cannot be said of *Achillea*, which was well integrated in the pasture canopy. However, *Achillea* was the only plant with very fine feathery leaves, and it may be that this reduces the laminar boundary layer surrounding the leaves, leading to higher mass transfer coefficients.

It should be noted that there is evidence indicating that the true surface area of the vegetation and not the superficial surface area used here is a better base of reference for describing the interspecies variability in the uptake kinetics of more polar organic compounds in vegetation (*29*). However, in the cited work the uptake rate was determined by a resistance within the plant, whereas for the SOCs in this study the uptake rate is limited by the rate of transport from the atmosphere to the plant surface.

Interspecies Variability in Plant Uptake via Equilibrium Partitioning. The interspecies variability was greatest for those compounds that approached a partitioning equilibrium between the vegetation and the gas phase. The governing equation is in this case

$$C_V/C_G = K_{VG} \quad (4)$$

where K_{VG} is the equilibrium partition coefficient. C_V/C_G can thus be viewed as a field estimate of a partition coefficient. One could surmise that the interspecies variability in K_{VG} is determined primarily by the lipid content of the vegetation. To test this hypothesis, C_V/C_G was plotted against the extractable lipid content (see Table 1) for pentachlorobenzene, for which the uptake was dominated by equilibrium partitioning. The results are illustrated in Figure 6. There is clearly no relationship between the field estimate of the partition coefficient and the extractable lipid content of the vegetation. Of particular note are the comparatively high partition coefficients for *Helianthus* and *Achillea*.

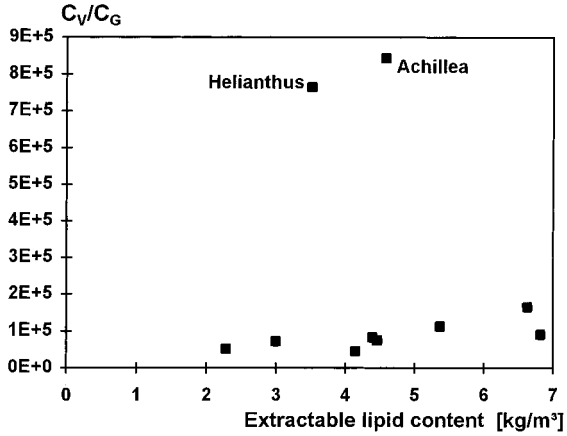

FIGURE 6. Plot of C_V/C_G for pentachlorobenzene vs the extractable lipid content of the 10 plant species.

Because the cuticular membrane has a high capacity to store SOCs (*30*) and is not extracted with petroleum ether, it was thought that the high C_V/C_G values for *Helianthus* and *Achillea* might be due to particularly thick cuticles. To test this, the fractional contribution of the cuticle to the leaf volume was determined for *Helianthus*, *Achillea*, and *Lolium*. The results are given in Table 1 and indicate that the volume fraction of the cuticle is not higher for *Helianthus* and *Achillea* than for *Lolium*, refuting the hypothesis.

The large interspecies variability in C_V/C_G for more volatile SOCs is in agreement with a recently published laboratory study, in which differences in K_{VG} of up to a factor of 20 between different grassland species were determined for lower chlorinated PCBs (*31*). In this earlier paper it was concluded that the interspecies variability was the result of differences in the quality of lipophilic material in the vegetation, not in the quantity. The differences in quality were expressed in different slopes when log K_{VG} was plotted against log K_{OA}, a slope of 1 indicating that octanol is a good model for the SOC storage properties of the vegetation, a slope of <1 indicating that the vegetation behaved as a more polar solvent than octanol, and a slope of >1 indicating that it behaved as a less polar solvent. These differences in slope are apparent in Figure 1, with *Helianthus* and *Achillea* showing particularly shallow slopes compared to the other species. There is full qualitative agreement between this field study and the laboratory study described in ref *31*, where the slope was lowest and the partition coefficients of the lower chlorinated PCBs highest for *Achillea* when compared with *Lolium*, *Trifolium*, *Plantago*, and another species.

To quantitatively compare the results of the field study and the laboratory study, the field estimate of the partition coefficient for PCB 28+31 was compared with the partition coefficient for the same compound measured in the laboratory for the four species common to both studies. The laboratory partition coefficient was interpolated to a temperature of 14 °C. This was the average temperature during the 2 weeks prior to plant sampling. Very good agreement was found between the field and laboratory estimates of log K_{VG}: 6.24 vs 6.14 for *Lolium*, 6.07 vs 6.14 for *Trifolium*, 6.01 vs 6.20 for *Plantago*, and 6.78 vs 6.86 for *Achillea*. This is strong evidence that the laboratory method yields reliable estimates of K_{VG} that are valid under field conditions.

Concluding Discussion. To verify the consistency of the interpretive framework employed to identify the primary deposition processes, it is important to demonstrate the plausibility of the parameters derived using the model. It was shown that the field estimates of the equilibrium partition coefficients are in excellent agreement with laboratory measurements, and the gaseous deposition velocities fell

within the range reported in the literature. This reinforces the usefulness of the framework for interpreting the plant data.

The interpretation of the interspecies variability in particle-bound deposition and kinetically limited gaseous deposition must be regarded as tentative. More study incorporating a broader range of plant species is required to attain a good understanding of the factors influencing these processes. However, this is of secondary importance because the interspecies variability in plant uptake of SOCs via these processes would appear to be relatively small. The variability in plant uptake via partitioning is much greater, indicating that future research should focus on developing a better understanding of the plant characteristics affecting this process. It is clear that not just the quantity but more importantly the quality of the plant storage compartment for SOCs is very variable. Because the cuticle plays an important role in this regard, interspecies differences in cuticle chemistry need to be more closely studied.

Acknowledgments

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Supporting Information Available

Tables of abbreviations and log K_{OA} values, air concentrations, and plant concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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