

# Framework for the Interpretation of Measurements of SOC<sub>s</sub> in Plants

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Plant uptake of semivolatile organic compounds (SOC<sub>s</sub>) occurs primarily from the atmosphere via one of three processes: equilibrium partitioning between the vegetation and the gas phase, kinetically limited gaseous deposition, or wet and dry particle-bound deposition. Each of these processes depends on different atmospheric concentrations, plant properties, and environmental variables. Hence, in interpreting measurements of SOC<sub>s</sub> in plants, it is imperative that the major process responsible for the accumulation of a given compound be known. Beginning with basic equations describing gaseous and particle-bound deposition to vegetation, a framework for identifying the major uptake process and further interpreting measurements of plant concentrations is developed. This framework makes use of the relative differences in accumulation behavior as a function of the octanol–air partition coefficient ( $K_{OA}$ ) of the chemical. The mathematical analysis leads to two interpretive tools, both log–log plots, one of the quotient of the vegetation and gas-phase concentrations vs  $K_{OA}$  and one of the quotient of the vegetation and particle-bound concentrations vs the quotient of the particle-bound and gaseous concentrations. Each of these plots contains three distinct and easily recognizable segments, and each segment corresponds to one of the three deposition processes. When the experimental data are plotted and the three segments are identified, it is possible to determine the dominant uptake process for a given compound, and this in turn opens the door to further interpretation of the plant uptake behavior.

## Introduction

The uptake of semivolatile organic compounds (SOC<sub>s</sub>) from the atmosphere into plants has attracted considerable research interest in the last years (1). Plants are important as vectors of SOC<sub>s</sub> into terrestrial food webs and in particular into the grass/corn–cattle–milk/beef food chain that accounts for the largest portion of background exposure of the European and North American population to many persistent SOC<sub>s</sub> (2–6). Plants act as filters of atmospheric SOC<sub>s</sub>, removing them from the atmosphere and transferring them to soil (7). There have also been a number of attempts to use plants as biomonitors of atmospheric contamination with SOC<sub>s</sub> (e.g., refs 8–12).

Plant uptake of SOC<sub>s</sub> has been shown to occur primarily from the atmosphere (13, 14). SOC<sub>s</sub> in the atmosphere can deposit to plants via a number of mechanisms depending on the physical–chemical properties of the compound. There

are three basic deposition mechanisms: gaseous deposition, particle-bound deposition (wet and dry), and wet deposition of dissolved chemical, of which the third is of negligible importance for most SOC<sub>s</sub> because of their hydrophobic nature (7). The relative importance of the other two mechanisms is driven by the gas/particle partitioning of the compound: With decreasing volatility, organic compounds show a stronger tendency to partition from the gas phase onto atmospheric particles (15), which results in an increase in the importance of wet and dry particle-bound deposition as compared to gaseous deposition. In the case of gaseous deposition, it is necessary to differentiate between two different processes: equilibrium partitioning between the atmosphere and the vegetation and kinetically limited gaseous deposition. Equilibrium partitioning can be achieved when the vegetation/gas-phase partition coefficient ( $K_{VC}$ ) is relatively small, but when it is large, the transfer of chemical from the gas phase to the vegetation may be too slow for an equilibrium to be reached during the lifetime of the plant (16–18).

Each of these processes is governed by a different set of atmospheric concentrations, environmental parameters, and plant properties. Particle-bound deposition is a function of the particle-bound concentration in the atmosphere; the particle size distribution of the chemical; the quantity, frequency, and intensity of precipitation; and the ability of the plant surfaces to retain particles, among other things. Kinetically limited gaseous deposition is an integrative process that can be expected to depend on the gaseous concentration during the whole growth period of the plant, the age of the vegetation, wind speed, atmospheric stability, canopy structure, and leaf surface roughness. For equilibrium partitioning, the gaseous concentrations in the period prior to sampling are important as well as the temperature and the contaminant storage properties of the vegetation.

Clearly, in order to interpret concentrations of SOC<sub>s</sub> in plants, it is essential that the dominant process responsible for the plant uptake be known. Otherwise it is not possible to properly normalize the plant concentrations to atmospheric concentrations or to evaluate the environmental conditions and plant properties that have influenced the uptake. This has often been neglected in the past. In some papers it has been assumed that the uptake is purely particle-bound (e.g., refs 19 and 20), while in others it has been assumed that there was a vegetation/gas-phase partitioning equilibrium for all SOC<sub>s</sub> studied (e.g., ref 21). When these assumptions are not scientifically grounded, the resulting interpretation of the data is likely to be misleading. These problems have arisen because there has been no method available for identifying the dominant uptake process in field samples.

In this paper, a simple framework for identifying the dominant uptake process and interpreting plant concentrations of SOC<sub>s</sub> is developed based on the relative accumulation behavior of different compounds as a function of their physical–chemical properties. This framework is used in a subsequent paper to interpret the concentrations of polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) as well as hexachlorobenzene (HCB) and polycyclic aromatic hydrocarbons (PAHs) measured in 10 different agricultural plants sampled on a farm south of Bayreuth (22).

## Theory

Gaseous deposition to plants is a partitioning process driven by the gradient in chemical potential between the atmosphere

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and the plant. The simplest model describing this process is to treat the plant as a single homogeneous compartment that is in contact with the air. Although more complex multi-compartment models may be necessary to describe uptake in some plants (23), this one-compartment plant model has been found to be adequate for describing SOC uptake in the vegetation of a number of species (24, 25). The governing equation for the one compartment plant model is

$$d(VC_V)/dt = Av_G(C_G - C_V/K_{VG}) \quad (1)$$

where  $V$  is the volume of the plant or vegetation ( $m^3$ ),  $C_V$  is the concentration in the vegetation due to gaseous deposition ( $mol\ m^{-3}$ ),  $t$  is time (h),  $A$  is the surface area of the vegetation ( $m^2$ ),  $v_G$  is the mass transfer coefficient or deposition velocity describing the rate of transport from the bulk atmosphere to the plant surface ( $m\ h^{-1}$ ),  $C_G$  is the gaseous concentration in the bulk atmosphere, and  $K_{VG}$  is the vegetation/gas-phase equilibrium partition coefficient expressed on a volume/volume basis. Assuming  $V$ ,  $A$ ,  $v_G$ ,  $K_{VG}$ , and  $C_G$  to be constant and choosing  $C_V = 0$  at  $t = 0$  as the initial condition, eq 1 can be solved through separation of variables to give

$$C_V = K_{VG}C_G(1 - \exp[-Av_G t/(VK_{VG})]) \quad (2)$$

The mass transfer coefficient  $v_G$  can be defined using a two-resistance model (17):

$$v_G = (1/v_{GG} + 1/(K_{VG}v_{GV}))^{-1} \quad (3)$$

where  $v_{GG}$  is the mass transfer coefficient describing transport from the atmosphere to the surface of the vegetation ( $m\ h^{-1}$ ), and  $v_{GV}$  is the mass transfer coefficient describing transport from the surface of the vegetation to the contaminant reservoir in the plant ( $m\ h^{-1}$ ).

Note that  $v_{GG}$  incorporates both the turbulent mass transfer from the bulk atmosphere to the vicinity of the leaf surface and the diffusive mass transfer through the laminar boundary layer surrounding the leaf. When comparing chemical uptake in different plants, at different locations, or during different periods, it may be useful to separate  $v_{GG}$  into a turbulent and a laminar component in order to study the influence of micrometeorology on the plant accumulation of compounds for which  $v_{GG}$  is the governing parameter. However, the main purpose of this interpretive framework is to identify the dominant uptake mechanism for a given compound in a given plant as a prerequisite for such further interpretation, and for this application, it is simpler to leave  $v_{GG}$  as a bulk parameter.

The plant side mass transfer coefficient is also typically modeled as two parallel processes: transport through the cuticle and transport through the stomata. However, in the case of SOCs, the cuticle is a major storage organ in the plant. It has a very high capacity to store SOC, and as a result, the uptake via the stomata with their much smaller surface area is believed to be negligible (26).

It has been shown that the vegetation/gas-phase equilibrium partition coefficient  $K_{VG}$  of many SOCs can be described as a function of  $K_{OA}$ , the octanol-air partition coefficient (17, 25, 27):

$$K_{VG} = mK_{OA}^n \quad (4)$$

where  $m$  and  $n$  are constants that are specific for a given plant. This does not imply that octanol is a good surrogate for the SOC storage properties of the plant; this is only the case if  $n = 1$ . However, in the studies to date, a linear relationship between  $\log K_{VG}$  and  $\log K_{OA}$  has generally been observed.

Substituting eqs 3 and 4 into eq 2, one obtains

$$C_V = mK_{OA}^n C_G (1 - \exp[-A(1/v_{GG} + 1/(mK_{OA}^n v_{GV}))^{-1} t / (VmK_{OA}^n)]) \quad (5)$$

Turning to particle-bound deposition, a simple model employed by Stevens and Gerbec (28) and later by Lorber et al. (29) is adopted based on the assumption that the net accumulation of particle-bound chemical in a plant is equal to the difference between deposition and erosion of particle-bound chemical:

$$d(VC_{VP})/dt = Av_P C_P - k_E VC_{VP} \quad (6)$$

where  $C_{VP}$  is the concentration in vegetation due to particle-bound deposition ( $mol\ m^{-3}$ ),  $v_P$  is the deposition velocity of particle-bound chemical to the surface of the vegetation ( $m\ h^{-1}$ ),  $C_P$  is the particle-bound concentration ( $mol\ m^{-3}$ ) normalized to the air volume, and  $k_E$  is the first-order rate constant describing erosion of particle-bound chemical from the plant surface ( $h^{-1}$ ).

The deposition velocity  $v_P$  lumps together both wet and dry deposition. As with  $v_{GG}$ , a more detailed description of  $v_P$  that includes the effects of particle size distribution of the compound, micrometeorology, precipitation physics, and plant properties on deposition of particle-bound SOC may be useful in interpreting plant concentrations of compounds taken up primarily via particle-bound deposition. However, the objective of this framework is to identify the mechanism primarily responsible for the uptake of a given compound in a given plant sample, and for this application, it is adequate to use this simple formulation.

It is assumed that the erosion of particle-bound contaminant from the plant surface is a first-order process. The erosion is certain to be a complex function of canopy turbulence, precipitation frequency and intensity, plant properties, etc. An erosion term is included in the framework to emphasize that the quantity of SOC that accumulates in a plant due to particle-bound deposition will be less than the amount deposited. As long as the erosion term is similar for different SOCs, the way in which this term is formulated does not influence the framework (see below).

Assuming  $V$ ,  $A$ ,  $v_P$ ,  $k_E$ , and  $C_P$  to be constant and integrating, one obtains

$$C_{VP} = [v_P A C_P / (V k_E)] [1 - \exp(-k_E t)] \quad (7)$$

It was recently proposed that the partitioning of SOCs between particles and the gas phase can also be predicted from  $K_{OA}$  (30):

$$C_P = B \times TSP \times K_{OA} C_G \quad (8)$$

where  $B$  is a constant ( $m^3\ \mu g^{-1}$ ) and TSP is the total suspended particulate matter or particle concentration in the air ( $\mu g\ m^{-3}$ ). It should be noted that  $B$  is a very small number, typically  $10^{-12}\ m^3\ \mu g^{-1}$  (30). Substituting into eq 7 yields

$$C_{VP} = [v_P A B \times TSP \times K_{OA} C_G / (V k_E)] [1 - \exp(-k_E t)] \quad (9)$$

Equations 5 and 9 can now be added to give the total concentration in the vegetation due to both gaseous and particle-bound deposition  $C_V$ :

$$C_V = mK_{OA}^n C_G (1 - \exp[-A(1/v_{GG} + 1/(mK_{OA}^n v_{GV}))^{-1} t / (VmK_{OA}^n)]) + [v_P A B \times TSP \times K_{OA} C_G / (V k_E)] [1 - \exp(-k_E t)] \quad (10)$$

or

$$C_V/C_G = mK_{OA}^n(1 - \exp[-A(1/v_{GG} + 1/(mK_{OA}^n v_{GV}))^{-1}t/(VmK_{OA}^n)]) + [v_p AB \times TSP \times K_{OA}/(V k_E)] [1 - \exp(-k_E t)] \quad (11)$$

## Interpretive Framework

Equation 11 describes the quotient of the vegetation and gas-phase concentrations as a function of  $K_{OA}$  and various properties of the plant/atmosphere system. This forms the mathematical basis for the interpretive framework. It is now assumed that the interchemical variability in plant accumulation of SOC's and hence in  $C_V/C_G$  is determined primarily by  $K_{OA}$  or, in other words, that all other variables in eq 11 are comparatively independent of the properties of the chemical. It is furthermore assumed that the overall mass transfer coefficient is determined by the air-side resistance (i.e.,  $1/v_{GG} \gg 1/(mK_{OA}^n v_{GV})$ ) (the validity of this assumption is discussed below). When  $K_{OA}$  is varied, three different cases or simplified forms of eq 11 are obtained. Each of these cases is dominated by a different uptake behavior. Hence, the hypothesis is that the dominant process governing plant uptake of a chemical can be determined from its  $K_{OA}$  value.

Case 1: Low  $K_{OA}$  values. In this case, the second term on the right-hand side of eq 11 goes to 0 (due to the very low value of  $B$ ), and the first term simplifies to

$$C_V/C_G = mK_{OA}^n \quad (12)$$

This is equivalent to eq 4 and describes equilibrium partitioning between the vegetation and the gas phase.

Case 2: Intermediate  $K_{OA}$  values. Here the second term in eq 11 is still small, but the exponential component of the first term approaches 1. Equation 11 is then approximated by

$$C_V/C_G = A(1/v_{GG} + 1/(mK_{OA}^n v_{GV}))^{-1}t/V \quad (13)$$

This is the case of kinetically limited dry gaseous deposition. Dry gaseous deposition is still the dominant uptake process, but the storage capacity of the vegetation for the chemical is so high that an equilibrium is not approached over the time of exposure.  $C_V/C_G$  is limited by the rate at which the chemical can be transported from the atmosphere to the plant storage compartment and by the time of exposure. Utilizing the assumption that the overall mass transfer coefficient is determined by the air-side resistance (i.e.,  $1/v_{GG} \gg 1/(mK_{OA}^n v_{GV})$ ), then this equation simplifies to

$$C_V/C_G = Av_{GG}t/V \quad (14)$$

Note that  $C_V/C_G$  is now independent of  $K_{OA}$ .

Case 3: High  $K_{OA}$  values. As  $K_{OA}$  increases further, the second term in eq 11 becomes more important as compared to the first (which remains constant with increasing  $K_{OA}$ ), and eventually the second term dominates:

$$C_V/C_G = [v_p AB \times TSP \times K_{OA}/(V k_E)] (1 - \exp(-k_E t)) \quad (15)$$

The levels in the vegetation are dominated by particle-bound deposition. When  $k_E t$  is large (which is generally the case for older vegetation since the half-lives for erosion of particles from vegetation are in the order of 2 weeks (29)), then eq 15 simplifies to

$$C_V/C_G = v_p AB \times TSP \times K_{OA}/(V k_E) \quad (16)$$

Combining the three cases, a plot of  $\log C_V/C_G$  against  $\log K_{OA}$  for a given vegetation sample should first give a straight line with a positive slope equal to  $n$ . This region contains those compounds that approach equilibrium partitioning.

This should be followed by a flat line representing case 2, those compounds where accumulation is dominated by kinetically limited gaseous deposition. Finally, the curve should then bend up to give a straight line with a slope of 1. This section contains those compounds taken up primarily by particle-bound deposition (see Figure 1).

In practice, it is extremely difficult to measure the gaseous concentration  $C_G$  for compounds with very high  $K_{OA}$  values (i.e., case 3 compounds in particular), because these compounds are virtually completely particle-bound in the atmosphere. In this case  $C_V/C_G$  cannot be determined. To circumvent this problem, it is necessary to plot  $C_V/C_P$ . Substituting eq 8 back into eq 16 (case 3), one obtains

$$C_V/C_P = v_p A/(V k_E) \quad (17)$$

Similarly, multiplying eq 14 (case 2) by  $C_G/C_P$  gives

$$C_V/C_P = Av_{GG}tC_G/(VC_P) \quad (18)$$

which describes kinetically limited gaseous deposition. Multiplying eq 12 for equilibrium partitioning (case 1) by  $C_G/C_P$  gives

$$C_V/C_P = mK_{OA}^n C_G/C_P \quad (19)$$

These three equations can be used to interpret a plot of  $\log C_V/C_P$  vs  $\log C_P/C_G$ . Since  $K_{OA}$  is proportional to  $C_P/C_G$  (eq 8) and  $n$  is close to 1, the first section of the plot describing equilibrium partitioning should begin with a region with a relatively flat slope equal to  $(n - 1)$  (eq 19). This should be followed by a segment with a slope of  $-1$  containing those compounds taken up mainly by kinetically limited gaseous deposition (eq 18). The third section of the curve described by eq 17 is in this case independent of  $C_P/C_G$  and hence flat (see Figure 2).

Figure 2 also has its limitations, since it is difficult to measure the particle-bound concentrations of volatile compounds with low  $K_{OA}$  values (i.e., many case 1 substances). Hence, in practice a combination of Figures 1 and 2 must be used to interpret vegetation concentrations, the former for compounds with lower  $K_{OA}$  values for which  $C_G$  can be reliably determined, and the latter for compounds with higher  $K_{OA}$  values for which  $C_P$  can be reliably determined. Since there are many compounds for which both  $C_G$  and  $C_P$  are measurable, the two plots overlap, yielding information on the overall consistency of the approach.

## Discussion

A prerequisite for using this interpretive framework is a knowledge of the gaseous and particle-bound concentrations as well as the concentrations in vegetation. To effectively use it, it is necessary to analyze many SOC's that cover a broad range of  $K_{OA}$ . If the range is limited, it may be difficult to identify the transitions from one case/process to another. This is particularly true of the transition from equilibrium partitioning to kinetically limited gaseous uptake. Values of  $n$  as low as 0.57 have been measured for some plant species (27), and hence, the change in slope between the first two sections of Figure 1 can be quite small. Given the analytical error associated with ultra-trace analysis of SOC's in plants and the atmosphere, the point of transition can be easily missed if there are too few data points or if the  $K_{OA}$  values do not extend at least a factor of 10 above and below the point of transition.

It is essential to note that a large number of assumptions have been made in developing the framework. Many of these assumptions are of little or no consequence for the main purpose of the framework—the identification of the dominant process of compound accumulation. For instance, in inte-

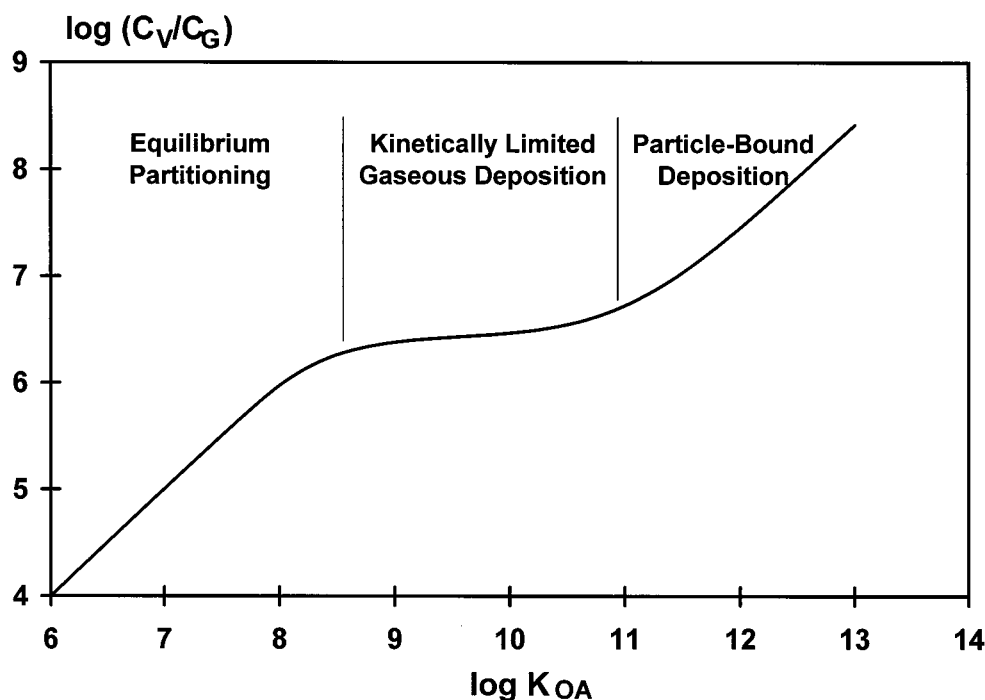


FIGURE 1. Illustrative plot of  $\log(C_V/C_G)$  vs  $\log K_{OA}$  for identifying the primary process of plant uptake of more volatile SOCs.

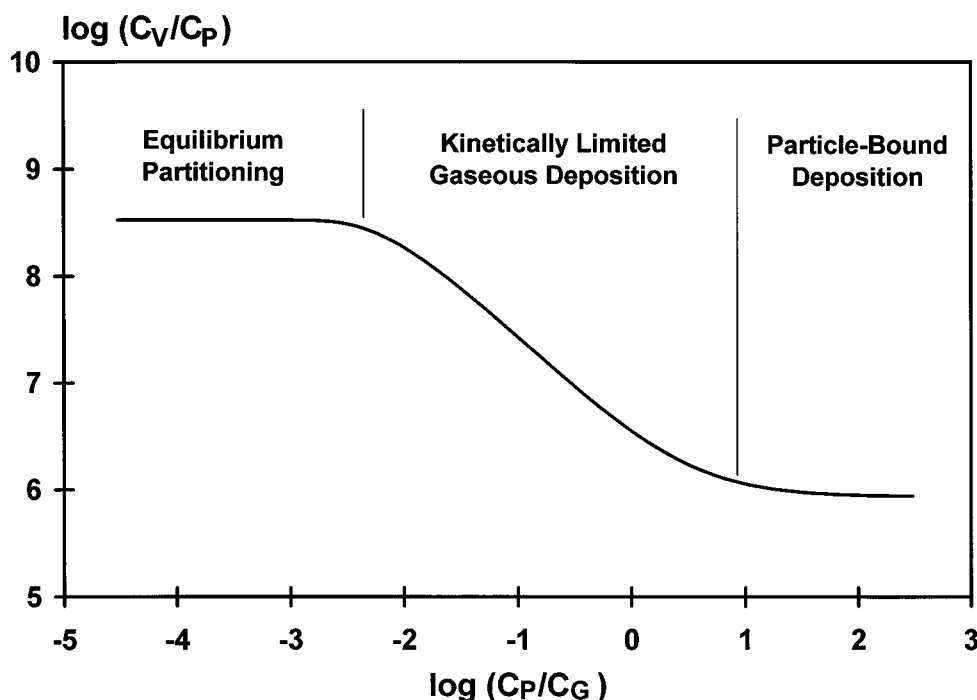


FIGURE 2. Illustrative plot of  $\log(C_V/C_P)$  vs  $\log C_P/C_G$  for identifying the primary process of plant uptake of less volatile SOCs.

grating it was assumed that  $A$ ,  $v_G$ ,  $v_P$ ,  $C_P$ , and  $k_E$  were constant with time. It is clear that these parameters are not constant; they are very variable with time. However, their relevance for the framework lies in the integrated values of  $Av_{GG}C_G dt$  and  $(Av_P C_P - k_E VC_{VP}) dt$  being the same for all compounds, and this is not compromised by changes in these parameters with time. Consider, for example, the case when  $v_{GG}$  dramatically increases shortly before the vegetation is sampled. For a chemical taken up primarily by kinetically limited gaseous deposition, the total amount of deposited chemical will increase (chemicals falling in the other two segments will be unaffected). However, this increase will be the same for all compounds, with the net result that the second segment will be shifted upward, while the form of

the curves in Figures 1 and 2 and the utility of the framework remain unaffected.

Of more concern are parameters that influence the partitioning equilibrium and the assumptions relating to interchemical variability, since in these cases deviations from the behavior predicted by the framework can be expected if the assumptions are not valid for a particular compound, plant species, or set of environmental conditions. These more critical assumptions are addressed below.

(a) All chemicals are persistent in the plant. If a chemical is subject to transformation following deposition, it will lie below the lines in Figures 1 and 2 if these have been defined using persistent chemicals. While it has been shown that some SOCs may be metabolized in plant cells (31), the



experimental evidence suggest that most SOC's are very persistent in plants. For instance, the half-lives of SOC's measured in clearance experiments with intact leaves lie in the range of weeks to months (17, 23, 24, 32), which indicates that metabolism is not a relevant factor for the accumulation of these compounds. The reason for the high persistence of SOC's may lie in their sequestration in nonviable plant tissues such as the cuticle.

(b) The gaseous concentration is constant. Changes in the gaseous concentration will disturb an existing air/vegetation partitioning equilibrium. The speed with which the system reacts to such a perturbation depends on the vegetation/gas-phase partition coefficient. Compounds with high  $K_{VG}$  values react more slowly than compounds with low  $K_{VG}$  values, since chemical must be exchanged with a larger volume of air in order to cause a comparable change in vegetation concentration. The gaseous concentrations in the environment are variable with time, and hence the vegetation/air system will generally not reach a true partitioning equilibrium. Instead, the system will approach an operational equilibrium that reflects an average concentration over a time period characteristic for the response characteristic of the system. For a chemical with a low  $K_{VG}$  (and hence  $K_{OA}$ ) value, the operational equilibrium might be defined by an average gaseous concentration over the past day; for less volatile compounds that approach equilibrium, the relevant time frame might be a month; for compounds where kinetically limited gaseous deposition is dominant, it is the complete growing period, which may be several months or years. The use of an appropriate gaseous concentration is important for calculating  $C_V/C_G$  in Figure 1. Fortunately, the gaseous concentrations of many SOC's are relatively constant during the growing season, and this effect is of little concern for the framework. However, caution must be exercised when pronounced changes in the gaseous concentration occurred in the weeks prior to sampling. If only the most recent concentration is used and there has been a decreasing trend in gaseous concentration over time, then the left-hand portion of Figure 1 will tend to curve upward. Conversely, if the concentrations have increased over time there will be a downward curving.

(c) The vegetation/gas-phase partition coefficient  $K_{VG}$  is constant over time. The partition coefficient  $K_{VG}$  can change as the properties of the plant change. More importantly, it is known to be a strong function of temperature (33). Changes in temperature will cause changes in  $K_{VG}$  and thus disturb an existing vegetation/gas-phase partitioning equilibrium. The reaction of the vegetation/air system to this perturbation is analogous to that described above for changes in  $C_G$ : For a volatile compound with a low  $K_{VG}$  value, the plant concentrations react relatively quickly to changes in  $K_{VG}$  caused by temperature, whereas for a less volatile compound with a higher  $K_{VG}$ , the plant concentrations react more slowly. Thus a different "average" temperature may be applicable to two different compounds that approach equilibrium. For instance, a distinct increase in temperature in the week preceding plant sampling might result in a decrease in the vegetation concentration of a compound with a lower  $K_{VG}$ , whereas a chemical with a higher  $K_{VG}$  would react more slowly, and the plant concentration would still reflect the earlier temperature/partitioning conditions at the time of sampling. A quantitative analysis of this effect for ryegrass indicated that it is of little practical relevance for SOC's. A simulated step decrease in temperature of 10 °C resulted in at most a 70% increase in plant concentration after 100 h (33). The reason for the limited influence is that the more rapid kinetics of compounds with low  $K_{VG}$  tends to be compensated by a lower enthalpy of phase change and, hence, temperature dependence of  $K_{VG}$ . However, it is conceivable that this effect is of significance for plants that

experience exceptionally rapid gaseous exchange kinetics (e.g., exposed to high winds) and/or for compounds that have low partition coefficients together with unusually high enthalpies of phase change.

(d) The particle-bound deposition velocity  $v_p$  and the erosion time constant  $k_E$  are the same for all compounds. A common value of  $v_p$  would seem a reasonable assumption as long as the compounds are associated with the same particles. This is a reasonably good assumption within a class of compounds with a common source such as the PCDD/Fs or the PAHs (34, 35). However, there are few studies of the particle-size fractionation of different SOC classes in the same air mass, and there may be differences in  $v_p$  between classes. If  $v_p$  is constant for a given class of compounds, a constant value of  $k_E$  would seem reasonable as long as the compounds remain with the particles while on the vegetation (i.e., do not diffuse into the cuticle) and are eroded with the particles. There is little information in the literature with which to evaluate the magnitude of possible interchemical differences in  $v_p/k_E$  for SOC's. A study of deposition to forests near Bayreuth suggested that  $v_p/k_E$  is different for PAHs and PCDD/Fs, but more work is needed (36). The framework presented here may be helpful in this regard; different values of  $v_p/k_E$  would result in parallel lines for the different substance groups in the right-hand segment of Figures 1 and 2.

(e) The air-side resistance is higher than the plant-side resistance. In studies of azelea (17) and ryegrass (33), the air-side resistance has been found to be higher than the plant-side resistance for SOC's. In his review of plant accumulation, Riederer (26) reports a linear relationship between the half-life in a plant with a low permeability cuticle and  $K_{OW}$  for compounds with  $\log K_{OW} > 3$ , which is also indicative of the dominance of the air-side resistance. There have been no studies to date that have demonstrated that the plant-side resistance limits the uptake of an SOC, which is subject primarily to kinetically limited gaseous deposition. Hence, the assumption made here is well grounded. However, it cannot be ruled out that there are plants with very low permeabilities for which the plant-side resistance dominates, and in this case it is useful to consider the consequences for the framework. The simplified equation for case 2 (kinetically limited gaseous deposition) would become

$$C_V/C_G = A v_{GV} K_{VG} t / V \quad (20)$$

or

$$C_V/C_G = A v_{GV} m K_{OA}^n t / V \quad (21)$$

All three sections of Figure 1 would then show slopes of  $n$  or 1, and it would be difficult to differentiate between the three processes. If  $v_{GV}$  was constant, then all compounds would either be at equilibrium or the same distance from equilibrium, and neither Figure 1 nor Figure 2 would be of assistance in identifying which process was dominant. If, in addition,  $n$  was also equal to 1, then the uptake of **all** compounds would be dominated by either gaseous deposition **or** particle-bound deposition. Since in both cases the rate of uptake would be proportional to  $(A K_{OA} / V)$ , the relative magnitude of  $(v_p B \times TSP / k_E)$  and  $(v_{GV} m t)$  would determine which mechanism dominated.

(f)  $v_{GG}$  is the same for all chemicals. As was noted above,  $v_{GG}$  incorporates both the turbulent and the diffusive components of gaseous mass transfer from the atmosphere to the surface of the vegetation. The turbulent mass transfer is independent of the properties of the chemical. However, the diffusive mass transfer is proportional to the diffusion coefficient of the chemical in air. The diffusion coefficient is approximately proportional to the reciprocal of the square root of the molecular weight. The molecular weights of SOC's

subject to kinetically limited gaseous deposition generally lie in the range of 150–500. This corresponds to a variation in the diffusion coefficient of less than a factor of 2. Thus, if the diffusive mass transfer controls the air side resistance,  $v_{GG}$  will be different from compound to compound, but the variability will be small.

(g)  $B$  is the same for all chemicals. While there is some evidence that the gas/particle partitioning coefficient is proportional to  $K_{OA}$ , the database for the correlation is small, and the variability in  $B$  between compounds is large (30). It is possible that different families of compounds will have different values of the proportionality constant  $B$ .  $B$  affects the uptake of particle-bound compounds, and a change in  $B$  would result in a parallel shift of segment 3 in Figure 1. In Figure 2, where the behavior of compounds subject to particle-bound deposition is more readily seen, the transformation using  $C_G/C_P$  means that changes in  $B$  will result in parallel shifts in segments 1 and 2.

(h) It is important to note that even though assuming most of the parameters to be constant over time is not a principal problem, particular difficulties can arise if the temporal variability of two parameters is correlated. For instance, if one compound shows a diurnal cycle in  $C_G$  with maximum concentrations during the daytime while a second compound with the same average concentration displays a cycle with a maximum at night, the kinetically limited gaseous deposition of the latter chemical is likely to be less due to the diurnal cycle of  $v_{GG}$  (with lower values during the night as a result of more frequent stable atmospheric conditions).

In summary, the assumptions discussed above are not expected to influence the utility of the framework in most cases. The deviations arising from the assumptions are likely to be less than the analytical error associated with determining  $C_V/C_G$ ,  $C_V/C_P$ , and  $C_P/C_G$ , which can easily be a factor of 2. Errors of this order of magnitude can also be expected when estimating  $K_{OW}$  (for plotting Figure 1). Of the assumptions discussed above, the largest uncertainty is associated with the uniformity of  $B$ , and particular attention should be paid to this point when different families of compounds are being plotted together.

As with any model of complex environmental processes, the interpretive framework must be used judiciously and should be augmented by a careful analysis of the data. However, it is believed that it will be useful as an initial step in interpreting field measurements of SOCs in plants, especially in identifying the primary process responsible for the chemical uptake. Having constructed the diagrams, the next step is to return to eqs 12, 14, and 16 and to verify the plausibility of the partition coefficients and mass transfer coefficients. One can then use the simple models of each process to interpret the influence of environmental parameters and plant properties on the uptake, revising and improving them as necessary.

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