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Estimating Partitioning and Transport of Organic Chemicals in the Foliage/Atmosphere System: Discussion of a Fugacity-Based Model

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■ The air-to-vegetation pathway may substantially contribute to human and food-chain exposure to organic chemicals since the surface area of the above-ground parts of vegetation by far exceeds the area the plants are growing on. A model for assessing the atmosphere-to-vegetation transfer of persistent organic chemicals is discussed. It is based on the fugacity concept and uses the 1-octanol/water and cuticle/water partition coefficients, aqueous solubility, and the saturation vapor pressure of the chemicals as input data. Equilibrium concentrations in plant tissues and air-to-vegetation bioconcentration factors can be estimated. Further, the model permits prediction of the compartment(s) in vegetation where a given chemical will preferentially accumulate. An approach for assessing semiquantitatively the potential for (re)volatilization of organics from leaves is also suggested. Various applications of the model are shown for reference compounds of widely differing physicochemical properties.

Introduction

The surface area of the above-ground parts of higher plants usually exceeds by far the area the plants are growing on. The greatest portion of the plant surface area is contributed by leaves and needles while the surfaces of stems and twigs generally play only a secondary role. The ratio of the sum of the projected leaf areas and the ground area on which the plants are growing (leaf area index; LAI) reaches values of 20 m^2/m^2 (*1*). The generally high values of LAI underline the importance of plant communities in the interception and accumulation of air-borne pollutants. Pollutants may arrive at the vegetation surface in the vapor phase, dissolved in droplets or in particulate form. The leaf surfaces are covered by a lipophilic membrane called the plant cuticle, which is made up of the biopolymer cutin (consisting of hydroxyalkanoic acid monomers) and associated waxlike lipids. The accumulation of lipophilic material in isolated cuticles has been extensively investigated (*2*).

The uptake into vegetation of organic substances from the atmosphere has been studied under controlled (*3–6*) and natural conditions (*7–14*). From these studies, it was concluded that the air-to-vegetation pathway may substantially contribute to human exposure to persistent organic chemicals. This, however, has been largely ignored in experimental research and applied risk assessment (*15*). Partitioning and transport in the foliage/atmosphere system plays also an important role in the emission of biogenic hydrocarbons whose role in the formation of tropospheric ozone is discussed controversely. Substantial amounts of these compounds are released to the atmosphere (*16*, *17*).

However, due to the lack of experimental data it is difficult to assess quantitatively the partitioning and transport processes in the foliage/atmosphere system. Estimates derived from a mathematical model of this system may therefore serve as first approximations. For the establishment of such a model, concepts originally developed for the analysis of large-scale partitioning of organic chemicals are applied to the modeling of the uptake into and the partitioning of organics within aerial plant biomass. A model describing the partitioning of lipophilic compounds between different compartments of the foliage/atmosphere system is presented and applied to reference compounds of widely differing physicochemical properties. Although it may not be true in every case, the reference compounds are assumed not to be subject to translocation and metabolism within the plant and thus resemble persistent chemicals with comparable physicochemical properties.

Input data to the model are the 1-octanol/water and the cuticle/water partition coefficients, aqueous solubility, and the saturation vapor pressure. These data are either available for a large number of substances or, in the case of the cuticle/water partition coefficient, can be estimated from fundamental properties (*2*). The model has three outputs: (1) prediction of equilibrium concentrations in different leaf tissues of compounds occurring in the environment or originating from the metabolism of plants, (2) estimates of air-to-vegetation bioconcentration equilibria, and (3) identification of the compartment(s) of preferential accumulation within leaves. An approach for assessing semiquantitatively the vapor-phase uptake or (re)volatilization of organics from leaves is also suggested. Work is under way in the author's laboratory to test experimentally the theoretical models discussed in this paper.

Theory

Model Leaf. A leaf of dimensions and properties representative for broad-leaved trees (and thus for a significant portion of plant biomass) is used in the partitioning model. The leaf is assumed to have a projected surface area of 50 cm^2 and a thickness of 0.3 mm. A thickness of 1 μm is used for both the adaxial and the abaxial cuticles. The water, acylgycerol (biomembrane and storage) lipid, and polar constituent (e.g., carbohydrates, proteins, electrolytes) contents are taken to be 920, 2, and 66 g/kg of fresh plant material, respectively (values determined for leaves of *Brassica oleracea* L. var. *capitata* L. f. *alba*, *18*). Thirty percent of total leaf volume is assigned to the intercellular air space.

On the basis of these assumptions the total leaf volume (V_L) of 1.5×10^{-6} m^3 can be divided into the following compartmental volumes (V_i) and volume fractions ($v_i = V_i/V_L$); $V_A = 4.5 \times 10^{-7}$ m^3 for the intercellular gas space ($v_A = 0.300$), $V_W = 9.7 \times 10^{-7}$ m^3 for the aqueous phase of the water-filled cell walls and the cytoplasm ($v_W = 0.645$), $V_K = 7.0 \times 10^{-8}$ m^3 for polar constituents ($V_K = 0.047$), $V_G = 2.1 \times 10^{-9}$ m^3 for glycerol lipids ($v_G = 0.001$) and $V_C = 1.0 \times 10^{-8}$ m^3 for the cuticle ($v_C = 0.007$). The specific masses of the leaf compartments are $\rho_A = 1.19$ kg/m^3 for the air space, $\rho_W = 1000$ kg/m^3 for the aqueous phase, $\rho_K = 1300$ kg/m^3 for the polar constituents, $\rho_G = 800$ kg/m^3 for the glycerol lipids and $\rho_C = 1100$ kg/m^3 for the cuticle phase. From these data an overall fresh weight density for the whole leaf of $\rho_L = 715$ kg/m^3 and a dry weight content of $\rho_D = 70$ kg/m^3 can be estimated. The leaf is

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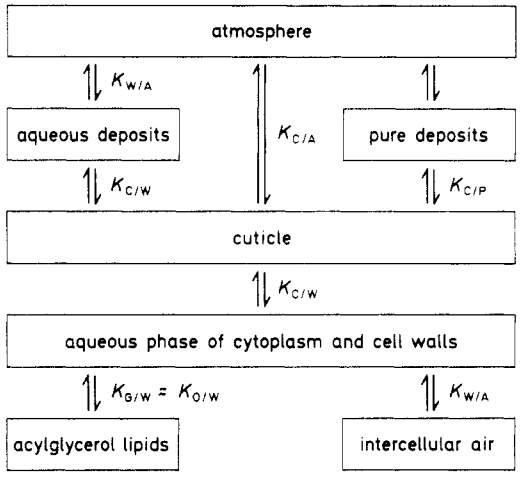

Figure 1. Schematic representation of the compartments included in the equilibrium partitioning model for the atmosphere/leaf system (partition coefficients K included).

further assumed to be hypostomatous, i.e., to have stomata only on its lower surface.

Partitioning between Compartments. The partitioning of lipophilic organic molecules between the atmospheric environment, the leaf surface, and the interior of the leaf can be described by using a model system consisting of seven compartments (Figure 1). The polar fraction of leaves can be neglected when dealing with the partitioning of lipophilic substances. It is further assumed that the chemicals are not translocated and/or metabolized in the interior of the leaf or diluted by growth. Under these conditions, equilibrium partitioning between different leaf compartments can be described by partition coefficients (K).

Partitioning between the atmosphere and aqueous deposits on the surface of the cuticle as well as between the gaseous phase of the intercellular space and the aqueous phase of the adjacent water-saturated cell walls can be described by the air/water partition coefficients ($K_{A/W}$)

$$K_{A/W} = P^S/(C^S_W RT) = H/(RT) \quad (1)$$

where R and T are the ideal gas constant [in (Pa m^3)/(mol K)] and the absolute temperature (in K), respectively. Saturation vapor pressures (P^S in Pa) and aqueous solubilities (C^S_W in mol/m^3) have to be used for the physical state in which the chemical is present at the temperature given (*19*). The term P^S/C^S_W is equivalent to the Henry's law constant [H in (Pa m^3)/mol]. The cuticle/air partition coefficient ($K_{C/A}$) is estimated by

$$K_{C/A} = (K_{C/W} C^S_W RT)/P^S = (K_{C/W} RT)/H = K_{C/W}/K_{A/W} \quad (2)$$

In eq 2 the concentration in the cuticle of a substance in equilibrium with its saturated aqueous solution is formally expressed by $C^S_C = K_{C/W} C^S_W$. This assumes a linear sorption isotherm for the system cuticle/water, which has been found at low concentrations of organic solutes (*20–22*). Therefore, eq 2 will give a good estimate of $K_{C/A}$ for the low concentrations normally found for chemicals in the atmosphere. At high concentrations, the cuticle/water partition coefficient (and thus the Henry's law constant and $K_{C/A}$) would become increasingly concentration dependent and eq 2 is no longer valid. The acylglycerol lipid/water partition coefficient ($K_{G/W}$) is taken to be equivalent to the 1-octanol/water partition coefficient ($K_{O/W}$; ref 23). A glycerol lipid/air partition coefficient $K_{G/A}$ can be estimated analogously to eq 2 by substituting $K_{O/W}$ for $K_{C/W}$. The cuticle/pure substance partition coefficient ($K_{C/P}$) is given by

$$K_{C/P} = K_{C/W} C^S_W V_m \quad (3)$$

with the molar volume (V_m in m^3/mol) representing the reciprocal of the concentration of the substance in its pure state. The concentration in the cuticle at equilibrium with the pure substance is estimated from the product of the cuticle/water partition coefficient and the aqueous solubility.

Fugacity-Based Partitioning Model. A simple model, which allows prediction of the equilibrium concentrations and amounts of chemicals present in different compartments of the model leaf, is formulated. The theoeretical basis of this model is the fugacity concept developed for large-scale modeling (*24–26*). It is adopted here to the level of a plant leaf and its immediate surroundings, thus taking an intermediate place between environmental and toxicokinetic models. This concept is based on the fact that at equilibrium equal fugacities are established in all compartments of a system regardless of the nature or the physical state of the compartments. Thus, at equilibrium the overall fugacity f is equal to the fugacities in the different compartments according to

$$f = f_1 = f_2 = f_3 = \ldots = f_n \quad (4)$$

where the subscripts 1–n denote the compartments. It has been shown (*25*) that at low concentrations fugacity is linearly related to concentration by

$$C_i = Z_i f \quad (5)$$

with C_i representing the concentration (in mol/m^3) in compartment i and f (in Pa) the overall fugacity. The proportionality factor Z_i is called the fugacity capacity for the compartment i [in mol/(m^3 Pa)], which is a volume-based property depending on temperature, pressure, the nature of the substance, and, most importantly, on the properties of the medium.

The values of Z for the compartments included in the atmosphere/foliage model can be estimated from the aqueous solubilities and saturation vapor pressures of the compounds and from experimentally determined cuticle/water and 1-octanol/water partition coefficients by (*25*)

$$Z_A = 1/(RT) \quad (6)$$

$$Z_P = 1/(P^S V_m) \quad (7)$$

$$Z_W = C^S_W/P^S = 1/H \quad (8)$$

$$Z_C = Z_W K_{C/W} \quad (9)$$

$$Z_G = Z_W K_{O/W} \quad (10)$$

The subscripts denote the atmospheric and intercellular gas space (A), the pure solid or liquid (P), the aqueous (W), the cuticle (C), and the glycerol lipid (G) compartments, respectively. The overall fugacity capacity for the whole leaf (Z_L) is the sum of the compartmental fugacity capacities (Z_i) weighted by the volume fractions of the compartments (υ_i) according to

$$Z_L = \sum \upsilon_i Z_i \quad (11)$$

When the overall fugacity of a system in equilibrium is known, the concentrations of a given compound in the different compartments or in the whole leaf can be estimated from eq 5 and the appropriate fugacity capacities obtained from eqs 6 to 11. The amount of material (M_i) in each compartment i is $V_i C_i$ or, according to eq 5, $f Z_i V_i$ with V_i expressing the volumes of the different compart-

Table I. Physicochemical Properties of the Compounds Used for Model Calculations

compound	M_m, kg/mol	V_m,[c] cm³/mol	mp, °C	P^S, Pa	C_W^S, mol/m³	H,[d] Pa m³/mol
methanol[a]	0.032	37	−94	15200	∞	0.354
phenol[a]	0.094	119	41	83	871	0.095
2-NP[a]	0.139	132	45	11.9	9.35	1.27
4-NP[a]	0.139	132	114	0.0054	106	0.00005
2,4-D[b]	0.221	201	136	1	1.81	0.552
atrazine[b]	0.216	251	174	0.00004	0.139	0.0003
2,4,5-T[b]	0.256	226	153	0.005	0.861	0.0058
PCP[b]	0.266	208	190	0.002	0.045	0.044
HCB[b]	0.285	221	231	0.001	0.00014	7.14
perylene[b]	0.252	263	274	0.0000007	0.0000016	0.440
DEHP[b]	0.391	525	−55	0.0000011	0.000000059	18.6

[a] Melting points (mp), saturation vapor pressures (P^S, at 25 °C), and saturation concentrations in aqueous solution (C_W^S, at 25 °C) taken from ref 30. [b] Melting points, saturation vapor pressures (P^S, at 20 °C), and saturation concentrations in aqueous solution (C_W^S, at 20 °C) taken from ref 31. [c] Molar volumes (V_m) estimated by the LeBas method (*32*). [d] Henry's law constants estimated according to $H = P^S/C_W^S$.

ments. In those cases, where the total amount (M_L) of a substance contained in a leaf is known instead of overall fugacity, the latter can be estimated from

$$f = M_L/\Sigma(Z_i V_i) \qquad (12)$$

This overall fugacity can be used to calculate amounts and concentrations in the different leaf compartments. For a complete discussion of the thermodynamic basis and the potential of the fugacity approach the reader is referred to ref 24–29.

The model will be used to predict the partitioning of 11 reference compounds, namely, methanol, phenol, 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), (2,4-dichlorophenoxy)acetic acid (2,4-D), 6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine (atrazine), (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), pentachlorophenol (PCP), hexachlorobenzene (HCB), perylene, and 1,2-benzenedicarboxylic acid bis(2-ethylhexyl) ester (DEHP). These compounds have been selected because of their widely differing physicochemical properties (Table I) and the availability of data on their accumulation and transport in the plant cuticle. It must be emphasized that the data derived from the model will not represent in every case the actual behavior of the specific compounds as at least for some of them the assumption of persistence within the leaf is not valid. Throughout this work, the reference compounds are regarded as models for persistent organic chemicals with corresponding physicochemical properties.

Kinetics of Vapor-Phase Uptake and Loss. Partition coefficients are useful only if equilibrium is established between the different compartments of the atmosphere/foliage system (Figure 1). If it is assumed that translocation, metabolism, and growth dilution are absent (which is valid for persistent chemicals in mature leaves), uptake from and/or loss to the atmosphere are the sole processes limiting the time during which equilibrium between the compartments persists after the concentration of a chemical in the environment had changed.

Three common situations for the uptake in and loss of chemicals from plant foliage exist. The chemicals can be transported either in dissolved, in particulate (or adsorbed), or in gaseous form to and from the leaf surfaces. Unfortunately, unsufficient information is available on the factors determining the uptake of chemicals that are deposited on the outer surface of the cuticle in the solid state or adsorbed to particulate matter. In vapor-phase transport a molecule can take two different routes when the stomata of the leaf are open: the cuticular and the stomatal pathways. During periods of darkness and water stress plants usually close their stomata and only the cuticular pathway remains open. Stomata do not interfere with the transport of dissolved material because they are impermeable to aqueous solutions (*33*).

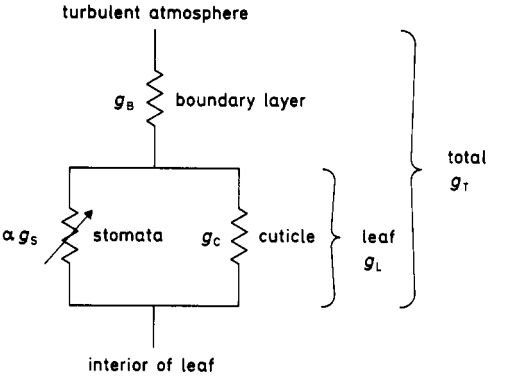

Figure 2. Conductance network for the vapor-phase transport of organics across the atmosphere/leaf interface. The conductance for the pathway through the stomata (g_S) varies with the degree of stomatal opening (α). The parentheses indicate leaf (g_L) and total (g_T) conductances.

The data on the transport properties of leaf cuticles and of stomata are sufficient for suggesting a first semiquantitative assessment of the kinetics of uptake and loss in the dissolved and gaseous state. The transport from or to aqueous solutions covering the outer surface of the cuticle has been described in detail (*2*). The vapor-phase transport of chemicals at the interface between the atmosphere and foliage has not yet been investigated with equal intensity. For a first tentative approximation, however, kinetic parameters can be deduced from values determined for the transport of water vapor between the leaf and the surrounding atmosphere.

Vapor-phase transport at the atmosphere/foliage interface can be described by a network of parallel and serial conductances or resistances (Figure 2). Conductances (g in m/s) are equivalent to mass-transfer coefficients. Adjacent to the leaf surface there is a unstirred air layer called the boundary layer, whose conductance depends on wind speed and leaf surface topography. An intermediate value of 1×10^{-2} m/s (*34*) is used for the boundary layer conductance of water vapor (based on concentrations in the vapor phase). A representative value for the water vapor conductance of leaf surfaces with open stomata is 1×10^{-3} m/s (*34*). The conductance (g) of a given chemical (on a vapor-phase basis) can be estimated from the conductance of water vapor (g^W) when the effect of molecular size on the diffusion coefficient is taken into account according to

$$g \simeq g^W(M_m^W/M_m)^{0.5} \qquad (13)$$

with M_m being the molar masses of water (superscript W) and the compound (*35*).

Table II. Partition Coefficients (at 25 °C and on a Volume Basis) for the Distribution of the Reference Compounds[a]

compound	log $K_{O/W}$[b]	log $K_{C/W}$[c]	log $K_{A/W}$	log $K_{C/A}$	log $K_{C/P}$	log $K_{L/A}$
methanol	−0.71	−1.11	−3.85	2.74	−1.15	3.66
phenol	1.39	1.55	−4.42	5.97	–[d]	4.38
2-NP	1.69	1.88	−3.29	5.17	−1.03	3.38
4-NP	1.92	1.83	−7.69	9.52	–[d]	7.77
2,4-D	2.50	2.51	−3.65	6.16	−0.93	4.16
atrazine	2.64	2.19	−6.94	9.13	−2.27	7.28
2,4,5-T	3.40	3.17	−5.63	8.80	−0.54	6.76
PCP	4.07	4.46	−4.75	9.21	−0.57	7.08
HCB	5.47	5.74	−2.54	8.28	−1.77	6.16
perylene	6.50	6.49	−3.75	10.24	−2.89	8.14
DEHP	7.86	7.26	−2.12	9.38	−3.25	7.42

[a] Subscripts denote 1-octanol/water (O/W), cuticle/water (C/W), air/water (A/W), cuticle/air (C/A), cuticle/pure substance (C/P), and whole leaf/air (L/A) partition coefficients. [b] From ref 38 with the exception of methanol (*39*), phenol and 2-NP (*22*), HCB and perylene (*40*), and DEHP (*41*); where appropriate, partition coefficients are given for the nondissociated species. [c] References: methanol (*39*), phenol and 2-NP (*22*), 2,4-D (*20*), and for the remaining compounds (*38*); where appropriate, partition coefficients are given for the nondissociated species. The values of $K_{C/W}$ had been determined on a mass basis (concentrations in mol/kg) and were recalculated for this table to a volume basis (concentrations in mol/m^3) by using a density of the cuticle phase ρ_C = 1100 kg/m^3. Values of log $K_{C/W}$ were determined for adaxial leaf cuticular membranes of *Citrus aurantium* with the exception of phenol and 2-NP, where adaxial leaf cuticles of *Ficus elastica* were used. [d] log $K_{C/P}$ values of 0.57 (phenol) and −0.02 (4-NP) are obtained from eq 3, which are obviously wrong.

The conductance of the leaf (g_L) is the sum of the stomatal (g_S) and the cuticular conductances (g_C)

$$g_L = g_C + \alpha g_S \tag{14}$$

with $\alpha = 0$ when all stomata are closed and $\alpha = 0.5$ when the stomata are open. The model leaf is taken to be hypostomatous like the leaves of many tree species. In this case, stomata occur only on half the total surface area and therefore $\alpha = 0.5$. The total vapor-phase flux into or out of the leaf is the sum of the invariable cuticular flux plus the variable flux through the stomata, which depends on the degree of stomatal opening (Figure 2). The total conductance (g_T) additionally includes the conductance of the boundary layer (g_B):

$$1/g_T = 1/g_L + 1/g_B \tag{15}$$

Equation 15 takes into account that the leaf and boundary layer conductance are in series (Figure 2).

The kinetics of the volatilization of a chemical from the leaf or its vapor-phase uptake can tentatively be described by eqs 16 and 17, respectively:

$$C_L/C_L^\circ = \exp(-g_T A t/V_L K_{L/A}) \tag{16}$$

$$C_L/C_L^\infty = 1 - \exp(-g_T A t/V_L K_{L/A}) \tag{17}$$

where C_L is the overall concentration of the chemical in the leaf at time t. C_L° is the concentration within the leaf at $t = 0$, i.e., just before volatilization starts; C_L^∞ is the leaf concentration when equilibrium has been achieved during vapor-phase uptake. In eqs 16 and 17 it is further assumed that during volatilization the concentration of the chemical in the atmosphere remains zero and that during uptake into the leaf no chemical is present within the leaf at the beginning and that the atmospheric concentration does not change. A, V_L, and g_T are the total leaf area (2 times the projected area), the leaf volume, and the total conductance (on a vapor basis). The leaf/air partition coefficient $K_{L/A}$ can be estimated according to

$$K_{L/A} = C_L/C_A = \upsilon_A + \upsilon_W/K_{A/W} + \upsilon_C K_{C/A} + \upsilon_G K_{G/A} \tag{18}$$

Both the atmosphere and the interior of the leaf are assumed to be well-mixed. This assumption is valid since diffusional transport in the interior of the leaf is by several orders of magnitude faster than the transport across the atmosphere/foliage interphase (*2*). The total amount of chemical within the leaf also includes the fraction that is sorbed by the cuticle. This situation can be adequately treated by eqs 16 and 17 because the transport limiting barrier of the cuticle is a very thin skin at its outermost boundary (*37*).

Results and Discussion

Partition Coefficients for the Atmosphere/Foliage System. The experimentally determined partition coefficients (on a volume basis) for the reference compounds in the systems 1-octanol/water (which is regarded as being equivalent to the acylglycerol lipid/water system) and cuticle/water range over more than 8 orders of magnitude (Table II). It has been shown that a linear relationship exists between the logarithms of both quantities as well as between aqueous solubility and $K_{C/W}$ (*2*).

The air/water partition coefficients calculated according to eq 1 range over more than 5 orders of magnitude (Table II) according to the variation of the Henry's law constants (Table I). The extreme values of the cuticle/air partition coefficients estimated according to eq 2 are 550 for methanol and 1.7×10^{10} for perylene. All lipophilic compounds (with $K_{O/W} > 1$) have log $K_{C/A}$ values from 5.17 to 10.24, which demonstrates that the cuticle is, on a volume basis, highly favored during air/cuticle partitioning and thus can be expected to effectively scavenge lipophilic molecules from the surrounding air. Even polar compounds like methanol with high vapor pressures will, under equilibrium conditions, accumulate several hundred times in the plant cuticle in relation to the adjacent atmosphere.

Under certain circumstances pure solid or liquid residues of organic compounds are deposited on the cuticle surface. Such residues may develop when the water of rain, fog, or dew or the solvent of pesticide spray droplets has evaporated. The partitioning between the cuticle and the pure substance on its surface can be estimated from eq 3. These partition coefficients have values smaller than unity ranging from 0.0006 (DEHP) to 0.29 (4-NP). As the molar volumes of the reference substances vary only by somewhat more than 1 order of magnitude (Table I), the large variation of the cuticle/pure substance partition coefficients can, according to eq 3, be attributed mainly to the variation of the saturation concentrations in aqueous solution. The first term on the right side of eq 3 is the cuticle/water partition coefficient, which has been shown to be also correlated with aqueous solubility (*2*). With phenol and 4-NP, nominal $K_{C/P}$ values of 3.7 and 0.95, respectively, are calculated when eq 3 is applied. These values are

Table III. Fugacity Capacities (at 25 °C) for the Reference Compounds in the Compartments of the Atmosphere/Foliage System[a]

compound	fugacity capacity, mol/(m³ Pa)				
	Z_P	Z_W	Z_C	Z_G	Z_L
methanol	1.78	2.90	0.225	0.565	1.87
phenol	101	10.5	372	258	9.63
2-NP	637	0.786	59.6	38.5	0.963
4-NP	1.40×10^6	1.96×10^4	1.33×10^6	1.63×10^6	2.36×10^4
2,4-D	4.98×10^3	1.81	586	572	5.84
atrazine	9.96×10^7	3.48×10^3	5.38×10^5	1.52×10^6	7.53×10^3
2,4,5-T	8.85×10^5	172	2.55×10^5	4.33×10^5	2.33×10^3
PCP	2.40×10^6	22.5	6.49×10^5	2.64×10^5	4.82×10^3
HCB	4.52×10^6	0.140	7.69×10^4	4.13×10^4	580
perylene	5.43×10^9	2.29	7.06×10^6	7.23×10^6	5.67×10^4
DEHP	1.73×10^9	5.36×10^{-2}	9.76×10^5	3.89×10^6	1.07×10^4

[a] Subscripts denote pure substance (P), water (W), cuticle (C), acylglycerol lipid (G), and whole leaf (L) fugacity capacities.

Table IV. Equilibrium Fugacities and Concentrations (25 °C) of the Reference Compounds in the Model Leaf When a Concentration of 10 μg of Each Chemical per kg of Fresh Weight Is Assumed[a]

compound	f, Pa	concn, mol/m³				
		C_A	C_W	C_C	C_G	C_L
methanol	91.0	3.67×10^{-2}	264	20.5	51.4	170
phenol	5.93	2.39×10^{-3}	62.2	2210	1530	57.1
2-NP	40.4	1.63×10^{-2}	31.7	2410	1550	38.9
4-NP	1.64×10^{-3}	6.61×10^{-7}	32.2	2180	2680	38.7
2,4-D	4.21	1.70×10^{-3}	7.62	2470	2410	24.6
atrazine	3.28×10^{-3}	1.32×10^{-6}	11.4	1770	4980	24.7
2,4,5-T	9.08×10^{-3}	3.66×10^{-6}	1.56	2310	3930	21.1
PCP	4.31×10^{-3}	1.74×10^{-6}	9.70×10^{-2}	2800	1140	20.8
HCB	3.34×10^{-2}	1.35×10^{-5}	4.68×10^{-3}	2570	1380	19.4
perylene	3.84×10^{-4}	1.55×10^{-7}	8.78×10^{-4}	2710	2780	21.8
DEHP	1.26×10^{-3}	5.08×10^{-7}	6.76×10^{-5}	1230	4900	13.5

[a] Subscripts denote air (A), water (W), cuticle (C), acylglycerol lipid (G), and mean leaf concentrations (L).

obviously wrong, probably due to activity coefficient effects or due to erroneous data for aqueous solubility.

Concentrations of Chemicals in Leaf Compartments. The equilibrium concentrations and amounts of a given chemical in the different compartments of a leaf can be estimated from eq 5 if the overall fugacity and the fugacity capacities Z_i (eqs 6–11) are known. While at 25 °C the fugacity capacity of air (atmosphere and intercellular space) has a constant value of 4.04×10^{-4} mol/(m³ Pa) regardless of the chemical considered (eq 6), the fugacity capacities for the pure state and the aqueous, cuticle, and acylglycerol phases of the leaf vary widely between the reference compounds (Table III). This variation is due to differences in vapor pressure, molecular volume, the Henry's law constant, and the 1-octanol and cuticle/water partition coefficients.

Given the fugacity capacities and the compartment volumes it is possible to calculate the overall fugacity (eq 12) and thus the concentrations in individual compartments (eq 5) when the total amount of material present in the leaf is known. Assuming for example a content of 10 μg/kg of fresh leaf material for each reference compound, overall fugacities ranging from 91 (methanol) to 3.84×10^{-4} (perylene) Pa are obtained (Table IV). The concentrations in the aqueous phase of the leaf, which is the largest compartment both on a volume and mass basis, range from 264 (methanol) to 6.76×10^{-5} (DEHP) mol/m³. In comparison to the aqueous concentrations, the concentrations in the intercellular air space (second largest compartment by volume) are predicted to be lower by factors from 133 (DEHP) to 4.9×10^7 (4-NP). This is due to the low Henry's law constants of the chemicals included in this study, while considerable concentrations in the intercellular air may be found with more volatile compounds. Reflecting the close relationship between the 1-octanol and cuticle/water partition coefficients, the concentrations in the cuticle and the acylglycerol lipid phases are within the same order of magnitude. The concentrations in these two lipid phases, which both make up only small volume fractions, are by factors from 35 (phenol) to 1.8×10^7 (DEHP) higher than those in the aqueous phase. The only exception is methanol, whose equilibrium concentrations in the cuticle and the lipid phases are less than those in the aqueous phase of cytoplasm and cell walls.

The concentrations of all reference compounds (except methanol) in the cuticle and acylglycerol phases are at least 1 order of magnitude [factors ranging from 39 (phenol) to 135 (PCP)] higher than the overall concentrations predicted for the whole leaf, while the intercellular air concentrations are much lower (Table IV). Due to the large volume fraction of the aqueous compartment and the comparably high water solubility, the mean and the aqueous-phase concentrations differ by up to a factor of 14 for methanol, phenol, 2-NP, 4-NP, 2,4-D, atrazine, and 2,4,5-T, while with PCP, HCB, perylene, and DEHP the aqueous concentrations are 2 to more than 5 orders of magnitude lower. This demonstrates that overall concentrations of chemicals in plant material are of limited value in analyzing the phytotoxic potential, the accumulation, or the uptake into food chains. In these cases, the concentrations in those compartments must be known, where the chemicals develop their physiological activity or are transformed into biologically active or inactive derivatives. The model discussed here cannot, however, predict the form into which a chemical may be transformed by physiological processes within the plant. Further, the sites of preferential accumulation of a chemical within

Table V. Compartmental and Overall Concentrations (25 °C) in Equilibrium with a Constant Background Contamination Level of $f = P^S/10000$ and Air-to-Vegetation Bioconcentration Factors[a]

compound	concn, mol/m³					
	C_A	C_W	C_C	C_G	C_L	log $B_{V/A}$[b]
methanol	6.13×10^{-4}	4.41	0.342	0.859	2.85	1.89
phenol	3.35×10^{-6}	8.71×10^{-2}	3.09	2.14	8.00×10^{-2}	2.61
2-NP	4.80×10^{-7}	9.35×10^{-4}	7.09×10^{-2}	4.58×10^{-2}	1.15×10^{-3}	1.61
4-NP	2.18×10^{-10}	1.06×10^{-2}	0.717	0.882	1.27×10^{-2}	6.00
2,4-D	4.04×10^{-8}	1.81×10^{-4}	5.86×10^{-2}	5.72×10^{-2}	5.84×10^{-4}	2.39
atrazine	1.61×10^{-12}	1.39×10^{-5}	2.15×10^{-3}	6.07×10^{-3}	3.01×10^{-5}	5.51
2,4,5-T	2.02×10^{-10}	8.61×10^{-5}	0.127	0.216	1.16×10^{-3}	4.99
PCP	8.07×10^{-11}	4.50×10^{-6}	0.130	5.29×10^{-2}	9.64×10^{-4}	5.31
HCB	4.04×10^{-11}	1.40×10^{-8}	7.69×10^{-3}	4.13×10^{-3}	5.80×10^{-5}	4.39
perylene	2.82×10^{-14}	1.60×10^{-10}	4.94×10^{-4}	5.06×10^{-4}	3.97×10^{-6}	6.37
DEHP	4.44×10^{-14}	5.90×10^{-12}	1.07×10^{-4}	4.27×10^{-4}	1.18×10^{-6}	5.65

[a] Subscripts denote air (A), water (W), cuticle (C), acylglycerol lipid (G), and overall leaf (L) concentrations. [b] Vegetation/air bioconcentration factors (eq 19) on a mass basis and adjusted to leaf dry weight.

plant material can be determined. This information can be used when assessing the entry of chemicals into food chains or the risk potential of different eating habits (e.g., peeling or not peeling fruit).

Prediction of Bioconcentration. Another application of the equilibrium partitioning model for plant leaves is to predict the concentrations of a persistent chemical in plant foliage as a whole or in its compartments when the substance is occurring at a constant background contamination level in the environment. This may help to evaluate the role of vegetation in the environmental fate of chemicals or to estimate the concentrations of chemicals in plant material and its different compartments from an ecotoxicological or physiological viewpoint.

For demonstrative purposes, it is assumed that the chemical has a fugacity in the environment 10 000 times lower than its vapor pressure at environmental temperatures. By use again of eq 5 and the fugacity capacities calculated for the different leaf compartments and the whole leaf (Table III), the leaf and compartmental concentrations can be estimated (Table V). Due to differences in vapor pressures and polarities, the leaf equilibrium concentrations obtained for the reference compounds range from 2.85 to 1.18×10^{-6} mol/m³ equivalent to 375 mg/kg (methanol) and 0.6 μg/kg (DEHP) of fresh weight. The calculated overall and compartmental concentrations are not only valid for the model leaf but may equally apply to the total leaf mass of vegetation provided the volume ratios are comparable to those assumed for the model leaf.

The fugacity-based partitioning model for the leaf/atmosphere system can also be applied to estimating bioconcentration factors ($B_{V/A}$), which generally are defined as the ratio of the equilibrium concentrations in the vegetation (in kg/kg of dry mass) and in the atmosphere (kg/kg). The bioconcentration factors thus can be obtained from

$$B_{V/A} = (C_L/C_A)(\rho_A/\rho_D) = K_{L/A}(\rho_A/\rho_D) \qquad (19)$$

where $K_{L/A}$ is the leaf/air partition coefficient (eq 18) and ρ_D is the dry weight content per cubic meter of fresh leaves. Values of $B_{V/A}$ for the reference compounds range from 41 (2-NP) to 2.3×10^6 (perylene) (Table V). They are a direct measure for the accumulation of organic chemicals in the total leaf mass of vegetation, which is taken as one homogeneous phase.

Recently, the question of how the air-to-vegetation bioconcentration factors might depend on fundamental physicochemical properties has been raised (*15*). This problem can be analyzed by using the partitioning model presented here. Replacing $K_{L/A}$ in eq 19 by eq 18 and

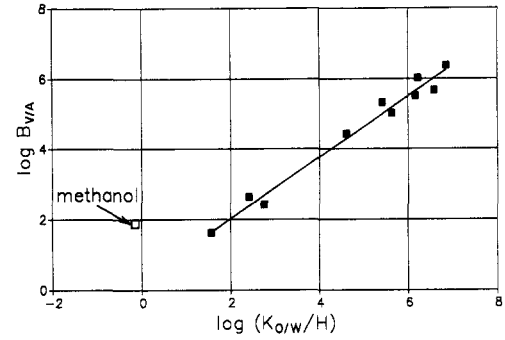

Figure 3. Correlation of the air-to-vegetation bioconcentration factors (log $B_{V/A}$) estimated for the reference compounds and log ($K_{O/W}/H$).

substituting eqs 1 and 2 for $K_{A/W}$, $K_{C/A}$, and $K_{G/A}$ we obtain

$$B_{V/A} = (\rho_D/\rho_A)$$
$$(\upsilon_A + \upsilon_W RT/H + \upsilon_C K_{C/W} RT/H + \upsilon_G K_{O/W} RT/H) \qquad (20)$$

For lipophilic compounds of low volatility, υ_A is negligible, as shown by the vanishingly low air space concentrations of the reference compounds (Table V). With highly lipophilic compounds ($K_{C/W} \simeq K_{O/W} \gg \upsilon_W/\upsilon_C + \upsilon_G$), the term containing υ_W can also be omitted, as only small fractions of the total amount of the chemical contained in the leaf are actually dissolved in the aqueous phase. Since $K_{G/W}$ is practically equal to $K_{O/W}$ and $K_{C/W}$ has been shown to be almost linearly related to $K_{O/W}$ (*2*), it can be concluded from eq 20 that the vegetation/air bioconcentration factor of lipophilic compounds should be directly proportional to the ratio $K_{O/W}/H$. Indeed, a linear relationship is obtained when the bioconcentration factors (on a mass and dryweight basis) are plotted vs the ratio of 1-octanol/water partition coefficients and Henry's law constants (Figure 3). Only the $B_{V/A}$ value of methanol is not related to $K_{O/W}/H$, which is not surprising because the total amount of metanol is dissolved in the aqueous phase. Provided relationships of this type are confirmed by experimental tests, they may be used to estimate bioconcentration factors needed for assessing the role of vegetation in the fate of chemicals in the environment (*15*, *42*).

The equilibrium partitioning approach can also be helpful to study the distribution of chemicals present in their pure (solid or liquid) state on the surfaces of leaves. As indicated above, such residues frequently result from rain, fog, dew, and pesticides spray droplets when the water or any other solvent has evaporated. Then the driving force for partitioning is the fugacity of the pure compound on the outer side of the cuticle, which is equal to its sat-

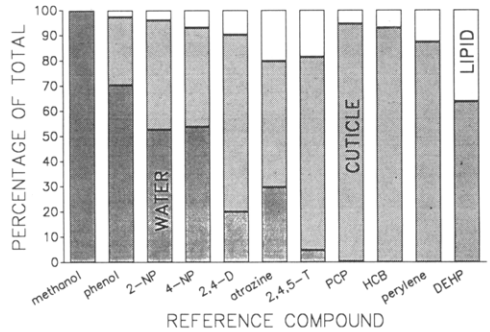

Figure 4. Equilibrium distribution among leaf compartments of the relative amounts (M_i/M_L) of the reference compounds. Relative amounts contained in the intercellular air space are ≤0.0001 and thus are omitted.

uration vapor pressure at the temperature given. However, equilibrium conditions will be attained under these conditions only with a very limited number of chemicals whose water solubility, saturation vapor pressure, and translocation and metabolism rates are low enough that small amounts of material are sufficient to saturate the system for an appreciable period of time.

Distribution of Total Amounts among Leaf Compartments. A different point of view and a general description of the equilibrium partitioning within the leaf can be obtained when the distribution between the leaf compartments is given in relative units. The ratio of the amount of a chemical in compartment i (M_i) and its total amount in the whole leaf (M_L) is given by

$$M_i/M_L = \upsilon_i Z_i/Z_L \qquad (21)$$

These fractions clearly express the combined effects of the polarity of the chemicals and of the relative volume sizes of the different foliage compartments (Figure 4). Judging from fractional amounts, the two most important compartments in the leaf are the aqueous and the cuticle phases even though their volume fractions differ widely ($\upsilon_W = 0.645$ and $\upsilon_C = 0.007$). The acylglycerol lipid compartment, which is assumed to contribute only 0.1% to the total volume of the model leaf, plays an intermediate role. On an amount basis the intercellular air space is negligible for the partitioning of the compounds investigated here.

The relative importance of the aqueous and the cuticle phases depends on the polarity of the compound. All of the methanol (99.9%) and most of the phenol (70%) and the two nitrophenols (54%) present in the leaf will be found in the aqueous phase of cytoplasm and cell walls. Appreciable fractions of atrazine (30%), 2,4-D (20%), and 2,4,5-T (5%) will also be dissolved in the aqueous compartment, while the aqueous phase of the leaf is practically free of PCP, HCB, perylene, and DEHP (Figure 4). On the other hand, the cuticle dominates the partitioning of all compounds with $K_{O/W}$ values equal to and higher than that of 2,4-D, with the exception of atrazine. Between 77 and 94% of all 2,4,5-T, PCP, HCB, perylene, and probably also DEHP (whose $K_{O/W}$ and thus $K_{G/W}$ appear to be overestimated due to experimental problems) will partition into the cuticle phase. No methanol and only 27–43% of the total amount of the three phenols should be found in the cuticle.

These results clearly show that even a very thin plant cuticle is an important compartment for the accumulation of persistent lipophilic compounds from the environment. For highly nonpolar compounds, both concentrations and relative amounts will be high in the cuticle compartment, which makes up 180–1500 kg/hectare of temperate forests and agricultural plant communities (*20*). However, no general answer can be given to the question of whether bioconcentration is a surface phenomenon only (*15*). In fact, the compartment where the largest amount of a chemical may be found depends on the lipophilicity of the substance (Figure 4). But even when most of the material is contained in the cuticle, only small amounts of the chemical will be washed away by rain or during food preparation due to asymmetric transport properties of plant cuticles (*37*). Such dynamic phenomena, which go beyond the static equilibrium view presented here, are the subject of current research.

Table VI. Conductances (at 25 °C and Based on Vapor-Phase Concentrations) for Estimating Vapor-Phase Uptake and Volatilization of Reference Compounds[a]

	conductance × 10^5, m/s				
compound	g_C	g_S	g_T^{open}	g_T^{closed}	$\frac{g_T^{open}}{g_T^{closed}}$
phenol	1.25	43.7	22.0	1.25	17.6
2-NP	0.199	36.0	17.3	0.199	87.1
4-NP	798	36.0	250	248	1.01
2,4-D	0.125	28.5	13.7	0.125	110
atrazine	88.0	28.9	75.6	67.4	1.12
2,4,5-T	22.2	26.5	31.3	20.5	1.53
PCP	224	26.0	124	120	1.03
HCB	29.8	25.1	36.3	26.7	1.36
perylene	90.5	26.7	74.8	67.6	1.11
DEHP	4.27	21.5	14.0	4.19	3.35

[a] Values of g_C were experimentally determined for isolated leaf cuticular membranes of *Citrus aurantium* with two adjacent aqueous phases (*43*) and were transformed to a vapor-phase basis by dividing them by $K_{A/W}$ (*36*); g_C for phenol and 2-NP were measured with cuticular membranes from *Ficus elastica* leaves (*22*). Stomatal conductances (g_S, vapor-phase driving force) were calculated according to eq 13. Total conductances (g_T) were calculated from eq 15 with $\alpha = 0.5$ (g_T^{open}) and $\alpha = 0$ (g_T^{closed}).

Kinetics of Uptake and Loss. As far as persistent chemicals are concerned, the equilibrium partitioning of a chemical between the different compartments of mature plant foliage may only be disturbed by the uptake from or the loss into the surrounding atmosphere. When the kinetics of transport across the atmosphere/foliage interface are known, the boundary conditions can be derived within which the assumption of equilibrium partitioning is valid. Information about the kinetics of uptake and loss of chemicals across plant surfaces may also prove useful for the analysis of foliar penetration of pesticides (*2*) and the emission of biogenic hydrocarbons.

For assessing the kinetics of vapor-phase uptake of chemicals from the atmosphere or their (re)volatilization from the interior of foliage, the following approach is suggested: The total conductance of the leaf/atmosphere interface (g_T) is made up (eq 15) by the conductances of the leaf (g_L) and the boundary layer of unstirred air surrounding it (g_B). The leaf conductance is the sum of the conductances for the cuticular (g_C) and the stomatal (g_S) pathways (eq 14). The experimentally determined values for the cuticular conductance of the reference compounds (adjusted to concentrations in the vapor phase) vary from 1.25×10^{-4} (2,4-D) to 7.98×10^{-3} (4-NP) m/s (Table VI). Cuticular conductances of lipophilic nonelectrolytes are correlated with 1-octanol/water partition coefficients and molar volumes (*2*, *43*). The estimates for the stomatal conductance (g_S on vapor-phase basis; eq 13) range from 2.15×10^{-4} (DEHP) to 4.37×10^{-4} (phenol) m/s (Table VI). The conductances for the boundary layer (g_B) are assumed to be 1 order of magnitude larger.

The total conductances of leaves with open stomata and their boundary layers (vapor-based) range from 1.37×10^{-4}

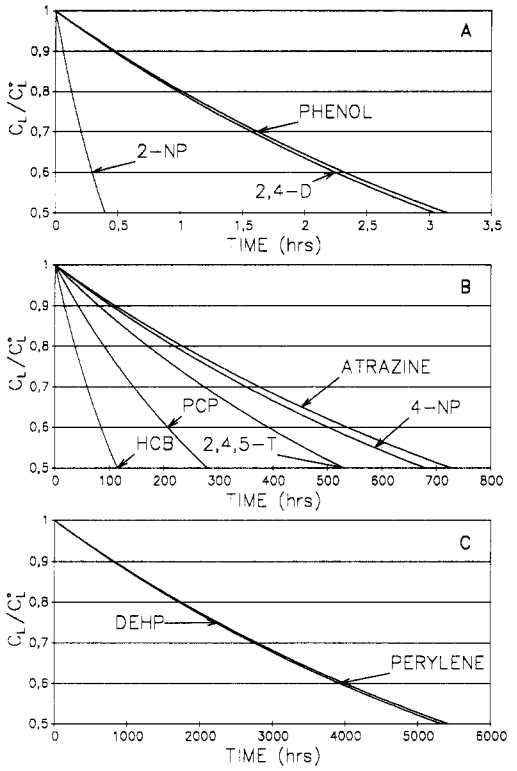

Figure 5. Time courses for the decrease of (C_L/C_L°) of the reference compounds due to volatilization with open stomata (eq 16).

(2,4-D) to 2.50×10^{-3} (4-NP) m/s. The unstirred boundary layer significantly affects the transport only of those chemicals that have a high volatility from water and/or a high cuticular permeability (perylene, $g_L^{open}/g_T^{open} = 1.39$; PCP, 1.91; atrazine, 1.35; 4-NP, 3.27). When the stomata are closed the effect of the boundary layer resistance on total conductance is only slightly reduced (e.g., perylene, $g_L^{closed}/g_T^{closed} = 1.34$).

The total conductance may be employed to estimate semiquantitatively the time courses of vapor-phase uptake into or loss of chemicals from foliage (eqs 17 and 16, respectively). Revolatilization kinetics of the reference compounds from the model leaf are shown in Figure 5. With stomata open, 2-NP is the most easily volatilized reference compound. After only 3.7 and 48 min, 90 and 50%, respectively, of the originally present amount can be expected to be still sorbed or dissolved in any of the leaf compartments. 2,4-D and phenol are also fairly volatile with half-lives within the leaf of 3.05 and 3.15 h, respectively (Figure 5A). An intermediate level of volatility from the leaf can be assigned to HCB, PCP, 2,4,5-T, 4-NP, and atrazine with half-lives ranging from 115 to 728 h (Figure 5B). Ten percent losses are estimated to occur after 17.5–111 h. The least volatile compounds are expected to be perylene and DEHP, whose half-lives extend to 222 and 226 days, respectively (Figure 5C). The kinetics of revolatilization of methanol cannot be estimated, as g_C values are not available for this compound.

The effect of closed stomata as compared to open ones on the estimated kinetics of vapor-phase transport across the atmosphere/foliage interface is expressed by the ratio g_T^{open}/g_T^{closed} (Table VI). The kinetics of transport in the vapor phase of all but four compounds are practically not affected by the closure of the stomata. Only for 2,4-D, 2-NP, phenol, and DEHP, the conductances increase by factors ranging from 3.4 to 110 when the stomata are open. Significant effects of stomatal closure on the (re)volatilization from and the vapor-phase uptake into plant leaves thus can only be found with compounds of low cuticular permeability (Table VI) and comparably high Henry's law constants (Table I). In latter property leads to high concentrations in the intercellular air space, which is directly connected to the stomata.

Such semiquantitative revolatilization kinetics permit estimation of the time limits within which it is valid to assume equilibrium partitioning in the atmosphere/leaf system if only a single pulse of chemical has been applied to it or when a lasting and constant background pollution level had suddenly changed. The half-lives or any other times estimated by eq 16 characterize the "memory" of the leaf following a pulse event when the atmosphere is again free of the chemical. The "memory" of leaves and its variation with the air/water partition coefficient, the cuticular conductance, and the leaf geometry must be kept in mind when interpreting experimental data on the uptake of chemicals via aerial parts of plants (*3–14*). Frequently, samples are taken only once at a given location, and uptake as well as revolatilization kinetics are unknown. In these cases it is impossible to decide whether the concentrations of chemicals found in plant material are at equilibrium with and therefore may be used as indicators for the atmospheric contamination level. In fact, they may represent the more or less faded "memory" of a single pulse event or even the combination of both a constant background concentration and a recent pulse. In reality, the problem is even more intricate, as uptake or revolatilization are only two of a number of major processes able to disturb equilibrium partitioning. A full description of the dependence on time of equilibrium partitioning within plant foliage would also have to include the rates of uptake from and loss to aqueous and solid phases at the surface of the cuticle and the rates of translocation, metabolism, and dilution due to growth.

Registry No. 2-NP, 88-75-5; 4-NP, 100-02-7; 2,4-D, 94-75-7; 2,4,5-T, 93-76-5; PCP, 87-86-5; HCB, 118-74-1; DEHP, 117-81-7; methanol, 67-56-1; phenol, 108-95-2; atrazine, 1912-24-9; perylene, 189-55-0; 1-octanol, 111-87-5.

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Estimating the Effects of Dispersed Organic Polymers on the Sorption of Contaminants by Natural Solids. 2. Sorption in the Presence of Humic and Other Natural Macromolecules

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■ A triphase distribution model was used in conjunction with experimental observations to characterize the effects of humic polymers dispersed in an aqueous phase on the sorption of hydrophobic organic compounds from that phase by natural solids. The organic compound-humic substance binding constants employed in the model were estimated by using a partition equation that takes into account the solubility of the solute in both the aqueous and organic polymer phases as developed in the first paper of this two-part series. Experimental results and model predictions indicate that the sorption of moderately hydrophobic compounds by lacustrine sediments is relatively unaffected by the presence of humic polymers, but that the sorption of highly insoluble organic contaminants by the same sorbents is sensitive to small amounts of background organic polymers. The observations support earlier analyses by other investigators regarding the impact of the organic subphases on the fate and transport of pollutants in natural aquatic systems.

Introduction

The presence of dissolved or suspended organic macromolecules in natural waters has been observed to affect the sorptive behavior of many particle-reactive micropollutants. This phenomenon may have serious implications with respect to understanding and modeling the bioavailability, toxicity, fate, and transport of such contaminants. The first paper of this two-part series presented a conceptual thermodynamic model for the binding of sparingly soluble organic compounds to humic substances (*1*). In this paper an attempt is made to predict the effect of these natural organic polymers on solute sorption by using a simple triphase distribution model.

Triphase distribution models involving aqueous, solid, and dispersed polymer or colloid phases have been invoked in a number of instances (*2-5*) to explain the so-called "solids effect". These effects are frequently observed in experimental measurement of the sorption of target compounds by natural solids. Triphase distribution models are generally predicated upon three basic assumptions: (1) the total amount of target compound residual in the aqueous phase (i.e., not sorbed by the solid) comprises both free and polymer "bound" solute; (2) binding of the solute by the organic polymers in question and sorption of both solutes and polymers can be described in terms of partitioning relationships; and (3) equilibrium conditions exist

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