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A Partition-Limited Model for the Plant Uptake of Organic Contaminants from Soil and Water

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In dealing with the passive transport of organic contaminants from soils to plants (including crops), a partition-limited model is proposed in which (i) the maximum (equilibrium) concentration of a contaminant in any location in the plant is determined by partition equilibrium with its concentration in the soil interstitial water, which in turn is determined essentially by the concentration in the soil organic matter (SOM) and (ii) the extent of approach to partition equilibrium, as measured by the ratio of the contaminant concentrations in plant water and soil interstitial water, α_{pt} (≤ 1), depends on the transport rate of the contaminant in soil water into the plant and the volume of soil water solution that is required for the plant contaminant level to reach equilibrium with the external soil-water phase. Through reasonable estimates of plant organic-water compositions and of contaminant partition coefficients with various plant components, the model accounts for calculated values of α_{pt} in several published crop-contamination studies, including near-equilibrium values (i.e., $\alpha_{pt} \cong 1$) for relatively water-soluble contaminants and lower values for much less soluble contaminants; the differences are attributed to the much higher partition coefficients of the less soluble compounds between plant lipids and plant water, which necessitates much larger volumes of the plant water transport for achieving the equilibrium capacities. The model analysis indicates that for plants with high water contents the plant-water phase acts as the major reservoir for highly water-soluble contaminants. By contrast, the lipid in a plant, even at small amounts, is usually the major reservoir for highly water-insoluble contaminants.

Introduction

The contamination of soils by pesticides and other substances leads to the subsequent contamination of crops/plants grown in these soils; many soil-incorporated pesticides are known to translocate to various crops/plants (1–6). Although the levels of contamination in plants depend in principle on the

levels in soil, the physicochemical properties of the contaminant, the particular plant species, and the soil type that sustains the plant, the current understanding of plant contamination in terms of these parameters remains limited for making effective a priori estimates of contaminant levels.

Interest in plant contamination began as early as the early 1950s when many organochlorine insecticides were introduced for pest control. Numerous studies on the levels of pesticide residues and other organic chemicals in crops/plants accumulated from contaminated soils have since been reported (1–16). Lichtenstein (1) observed that lindane was taken up much more readily by root crops (e.g., carrots and potatoes) from light mineral soils than from a muck soil to which about the same doses of the insecticide had been applied prior to the crop growth. In a later and more specific study on the effect of soil type on crop uptake, Harris and Sans (6) measured the levels of dieldrin accumulated by carrots, radishes, and other root crops from three well-characterized contaminated field plots in relation to the soil pesticide levels; the three soil types studied, a sandy soil, a clay loam, and a muck soil, differed widely in soil organic-matter (SOM) content (1.4 to 66.5%) and other soil constituents. The dieldrin concentrations were much lower for crops from the muck soil than from the sandy and clay soils; by contrast, the dieldrin concentration was considerably higher in the muck soil than in the two other soils. The concentrations in radishes and other crops were generally lower than those in carrots. A similar effect of soil type on plant uptake of organic contaminants was also recognized in later studies by others, e.g., by Topp et al. (12) on the uptake of some aromatic compounds by barley roots in laboratory experiments. Despite the observed influence of soil type on plant uptake, there has hitherto been no means of estimating the magnitudes of the correlations coefficients for contaminant levels in a wide variety of plants in a wide variety of soils.

Other studies have investigated the plant uptake of contaminants from nutrient (soil-free) solutions (17–20). The uptake by plants is considered to occur by passive and/or active transport, depending on the contaminant and plant type (17–19). Passive transport proceeds in the direction of decreasing chemical potential; active transport is against the chemical potential gradient, requiring expenditure of energy. The passive transport to plants may be treated as a series of contaminant partitions between plant water and plant organic components. In a carefully controlled laboratory system, Briggs et al. (18) studied the uptake from water solution by barley roots of two series of organic compounds, *O*-methylcarbamoyloximes and substituted ureas, which exhibit a wide variation in lipophilicity; they concluded that the root uptake of the compounds approached the equilibrium values in a relatively short time (24–48 h). The root concentration factors (RCFs), i.e., the ratios of chemical concentrations in roots and water (17), increased monotonically, but not proportionally, with the octanol–water partition coefficients (K_{ow} 's) of the compounds. Similar empirical correlations for contaminants with plant roots and leaves have also been observed (21). The level of a chemical that may arise in a given part of the plant is controlled presumably by both the plant circulation rate and the local composition specific to a particular part of the plant, assuming that the chemical metabolism does not affect the passive transport of the parent compound. Thus, the noted correlation with K_{ow} for chemical uptake by plant roots or by other tissues would vary in principle with the intrinsic local composition of the plant tissue. At this time, the compositional effect of

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the plant species or of the different tissues of a plant has not been sufficiently elucidated.

Most current models for the plant uptake of contaminants from soil, water, or air are formulated on a differential mass-balance basis in terms of the rates of contaminant interface transfer, plant growth and transpiration, and contaminant metabolism along with some estimated transfer coefficients (13, 14, 22–24). While these models are intended primarily for delineating the net plant-uptake rates of contaminants with time from given external source(s), the model calculations depend sensitively on the accuracy of the assumed transfer rates and coefficients. In this study we present a partition-limited model for the passive uptake of contaminants either from soil or from external water to plants, taking explicit account of the contaminant level in either soil or water and the plant composition. The model formulation sets the upper (equilibrium) limit for the level of a contaminant in a plant with respect to the external-source level, against which the actual approach to equilibrium of the contaminant in the plant at the time of analysis can then be estimated. This novel model feature is fundamental to the understanding of the levels of different contaminants in a plant and in different plants. Although the present model may be part of a more extended model involving active contaminant transport and metabolism, it seems best at this time to limit our immediate interest to the passive uptake of the parent contaminant species. The model is here applied to several published studies on contaminant uptake by some crops. Although some required data have had to be estimated, the preliminary results are encouraging.

Theoretical Considerations

Consider first the simpler case of a partition-limited model for the plant uptake of nonionic contaminants from a soil-free nutrient solution by passive transport through the plant vascular system. Here water is both the solvent for the contaminant and the medium that carries it to plant roots (and to other water-contacted surfaces) and eventually to other parts of the plant via the plant vascular system. The overall plant uptake process is driven by the external-water concentration and is considered to consist essentially of a series of partition uptakes, with the understanding that the contaminant concentrations within the plant may or may not come to full equilibrium with the external water solution. On the other hand, for any given volume element inside the plant, local equilibrium is assumed for a contaminant between sap water and the various organic constituents within that volume element. With these considerations, the concentration of a contaminant either in the whole plant or in a specific part of the plant (C_{pt}), expressed as the mass of contaminant per unit wet mass of the plant, can be equated with the contaminant concentration in external water (C_w) at the time of sample analyses

$$C_{pt} = \alpha_{pt} C_w [f_{pom} K_{pom} + f_{pw}] \quad (1)$$

in which $f_{pom} + f_{pw} = 1$ and

$$f_{pom} K_{pom} = \sum f_{pom}^i K_{pom}^i, \quad i = 1, 2, 3, \dots, n \quad (2)$$

In eq 1, K_{pom} is the contaminant partition coefficient between plant organic matter and water, f_{pom} is the total weight fraction of the organic matter in the plant, and f_{pw} is the weight fraction of water in the plant, either for the whole plant or for a specific part of it. In eq 2, the $f_{pom} K_{pom}$ term is expressed as the sum of contributions from all plant organic components according to their specific partition coefficients (K_{pom}^i) and weight fractions (f_{pom}^i). The term α_{pt} is called “the quasi-equilibrium factor”, which describes the approach to equilibrium of any absorbed contaminant in the plant (or in a part of it) with

respect to the same contaminant in external water phase. In this model it may be viewed as the ratio of the respective concentrations in plant water and external water. Thus, $\alpha_{pt} = 1$ denotes the state of equilibrium. The magnitude of α_{pt} (≤ 1) is a measure of the extent of approach to equilibrium. If passive transport is the dominant uptake process, α_{pt} should not exceed 1, except for highly unusual situations; if the uptake involves an active process, α_{pt} may however exceed 1. In principle, with passive transport, if the concentrations in whole plant and external water are at equilibrium, all parts of the plant must be at equilibrium. However, when equilibrium is not attained with the whole plant, the α_{pt} value may vary with the local composition of the plant and its proximity to the contaminant source. Further rationale for variation in α_{pt} will be presented later. The α_{pt} value for a contaminant with a plant (or a selected part of it) is thus determined with inputs of C_{pt} and C_w together with the overall (or local) plant compositions and the respective partition coefficients. Once the value of α_{pt} is known, it may then be used to predict C_{pt} from C_w and other associated parameters.

We now consider the model formulation for the more typical case of plants in contaminated soils. For plant growth, the water content in soil must well exceed the water content at the plant's wilting point. This means that the soil interstitial (pore) space contains bulklike water with dissolved nutrients and contaminants available for plant-root uptake. Therefore, as before, water is the transfer medium. The approach to model the contaminant uptake from soil is in essence to relate the contaminant concentration in plants to the effective concentration in soil interstitial (or pore) water.

The concentration of a contaminant in soil interstitial water (C_w) can in principle be determined experimentally for a given loading of the contaminant in a soil (C_s), in which C_w is related to C_s as

$$C_s = K_d C_w \quad (3)$$

where K_d is the soil-water distribution coefficient specific to a contaminant on a given soil. K_d is largely independent of C_w when the ratio of C_w to S_w (water solubility) is moderately large but may be a function of C_w for certain contaminant-soil systems at very small C_w/S_w (25 and references therein). On the other hand, as rationalized below, reasonable and convenient estimates of C_w for relatively nonpolar contaminants on most soils can be achieved based on the observed effect of soil organic matter (SOM) on contaminant sorption by water-saturated soils.

Soil is known to behave primarily as a dual sorbent for nonionic organic compounds of limited water solubilities, in which the mineral matter acts as an adsorbent (26–30) and the SOM as a partition medium (31–34). In water solution, the soil uptake of relatively nonpolar contaminants consists mainly of partition into SOM because of the strong suppression by water of their adsorption on mineral matter (26–28). Thus, the effective concentration of the contaminant in a hydrated soil is the concentration that is normalized to the SOM content of the soil (31–34), i.e.,

$$C_{som} = C_s / f_{som} \quad (4)$$

where C_{som} is the SOM-normalized contaminant concentration in soil and f_{som} is the weight fraction of the SOM in soil. Assuming local equilibrium for contaminants between soil particles and interstitial water, the contaminant C_w in soil interstitial water, which will be designated as the driving force for contaminant transport, is related to C_{som} as follows

$$C_w = C_{som} / K_{som} \quad (5)$$

where K_{som} is the contaminant partition coefficient between

SOM and water; K_{som} is practically concentration-independent, with the possible exception at very low C_w/S_w with some special soils, such as those which contain a significant amount of high-surface-area carbonaceous material (HSACM) (25, 35–38). The magnitude of K_{som} is determined by the contaminant and SOM properties. For contaminants of limited water solubilities, the K_{som} values are usually much greater than 1. The SOM properties for soils from widely dispersed geographic sources have been found to be relatively comparable (39), which allows for a fairly general assessment of the influence of soil sorption on the contaminant uptake by plants. Thus, while the direct determination of C_w , or the evaluation of C_w from the established relation with C_s , helps to capture the possible sorption nonlinearity, sufficiently accurate estimates of C_w can be readily obtained for low-polarity contaminants from C_{som} and K_{som} for soils sufficiently high in SOM and low in HSACM. The latter approach is especially merited for analysis of earlier published studies where the K_d data are usually unavailable.

With the above considerations, the uptake of a relatively nonpolar contaminant from a soil by plants can then be formulated to a good approximation by substituting $C_{\text{som}}/K_{\text{som}}$ for C_w in eq 1, i.e.,

$$C_{\text{pt}} = \alpha_{\text{pt}}(C_{\text{som}}/K_{\text{som}})[f_{\text{pom}}K_{\text{pom}} + f_{\text{pw}}] \quad (6)$$

Eq 6 is an alternative form of eq 1 that accounts for the effect of soil sorption on the contaminant concentration in soil interstitial water. The use of $C_{\text{som}}/K_{\text{som}}$ in eq 6 circumvents the need for the experimentally cumbersome determination of C_w in soil interstitial water. The value of α_{pt} in eq 6 can be determined as before with the additional inputs of C_{som} and K_{som} .

The water content and organic composition of plants may vary considerably either between plant types or between the different parts of a plant. The partition limits for a given contaminant inside a plant from the water phase to different parts of the plant would therefore vary with the overall and local plant composition. Most root and leaf crops are composed of large amounts of water and polar organic constituents, such as carbohydrates, cellulose, and proteins, and lesser amounts of lipids. From the partition standpoint (eq 2), the most striking differences in contamination between plants would likely be exhibited with relatively nonpolar lipid-soluble contaminants by plants that differ radically in their lipid contents. These differences would occur because of the much higher partition capacities of these contaminants with lipids than with polar organic matter (40, 41). For the more water-soluble solutes, the partition capacities from water to either nonpolar lipids or relatively polar carbohydrates and proteins should be small to moderate.

Because the value of α_{pt} characterizes the approach to equilibrium of a contaminant between external water and the plant (or a part of the plant) at the time of the experiment, it must depend in part on the contaminant partition capacity of the plant organic matter. For a plant with a given lipid content, a polar contaminant with a low K_{lip} (lipid-water) could exhibit a higher α_{pt} than a relatively nonpolar contaminant with a significantly higher K_{lip} , because the attainment of partition equilibrium for the latter requires a much greater volume of water transport within the plant. Thus, the magnitude of α_{pt} may be expected to be a function of the contaminant partition coefficient, the plant water-organic composition, and the plant water-transport rate. Finally, the contaminant uptake by plants through direct diffusion to the outer layers of plant roots is expected to contribute to the rate of local and overall plant uptake and would therefore affect the local and/or overall α_{pt} value before the contaminant in plant and external water reaches equilibrium. The significance of the contaminant uptake by diffusion relative

to that by transport of external water into plant's vascular system would depend on the specific system involved but should not in principle make $\alpha_{\text{pt}} > 1$. We now check the model against the pertinent available literature data on plant contamination. The present analysis is restricted to systems with relatively nonreactive nonionic compounds in water or soil. The ionizable compounds are also excluded from consideration because of the possibility of their plant uptakes to involve active transport to certain plant organic constituents.

Results and Discussion

Uptake by Barley Roots from Water. Starting with the simplest system, consider the uptake by the roots of a barley (*Hordeum vulgare* cv. Georgie) of various *O*-methylcarbamoyloximes and substituted ureas from nutrient water solution, as reported by Briggs et al. (18). The experiments consisted of measuring the root concentration factor ($\text{RCF} = C_{\text{pt}}/C_w$) for each of these ^{14}C -labeled compounds individually in replicated laboratory systems after the 10-day-old barley plants were transferred to nutrient solution with the test compound for 24 and 48 h. The authors indicated that the RCF values for the parent compounds alone, or for the parent compounds plus their metabolites, were very similar after 24 and 48 h. The 24–48 h averaged RCF values of the parent compounds (with reported data uncertainties of $\pm 5\%$) and their octanol-water partition coefficients (K_{ow} 's) are presented in Table 1.

The K_{ow} 's for many of the compounds in Briggs et al. (18), such as the more lipophilic benzaldehyde *O*-methylcarbamoyloximes, were obtained either by indirect experimental methods or by empirical calculations. No information on the water-organic composition of the barley roots was provided. However, an approximate composition for barley roots (*Hordeum vulgare*) is given by Trapp et al. (13); it comprises 87.5% water and 1% lipids by weight. It is assumed that the remainder consists mainly of carbohydrates and cellulose, with traces of proteins and nutrients, for a total of 11.5 wt %. We assume further that the partition coefficients of the compounds with the relatively polar carbohydrates, cellulose, and proteins are practically the same. Since octanol is known to mimic biological lipids closely in contaminant partition (40), the lipid-water partition coefficients (K_{lip} 's) are assumed to be the same as the corresponding K_{ow} 's.

On the premise of the above assumptions, the $f_{\text{pom}}K_{\text{pom}}$ term in eq 2 for barley roots can be simplified as the sum of the contributions by carbohydrates and lipids, i.e.,

$$f_{\text{pom}}K_{\text{pom}} = f_{\text{ch}}K_{\text{ch}} + f_{\text{lip}}K_{\text{lip}} \quad (7)$$

where the subscripts "ch" and "lip" designate carbohydrates and lipids, respectively. Substituting eq 7 into eq 1 with the assumed barley root composition (13) leads to

$$C_{\text{pt}} = \alpha_{\text{pt}}C_w[f_{\text{pw}} + f_{\text{ch}}K_{\text{ch}} + f_{\text{lip}}K_{\text{lip}}] \quad (8)$$

or

$$\alpha_{\text{pt}} = (C_{\text{pt}}/C_w)/[0.875 + 0.115K_{\text{ch}} + 0.01K_{\text{ow}}] \quad (9)$$

Calculations of the estimated α_{pt} values for contaminants require values for the individual carbohydrate-water partition coefficients (K_{ch} 's); these are not available. However, the K_{ch} values are expected to be small because of the high polarity of carbohydrates. For example, the cellulose-water partition coefficients for benzene ($\log K_{\text{ow}} = 2.13$) and carbon tetrachloride ($\log K_{\text{ow}} = 2.83$) are 0.56 and 1.75 (41), respectively, where the cellulose is similar in composition to the carbohydrates. As an approximation, we thus assume K_{ch} to be 0.1 for compounds with $\log K_{\text{ow}} < 0$; 0.2 for $\log K_{\text{ow}}$

TABLE 1. Calculated Quasi-Equilibrium Factors (α_{pt}) from Root Concentration Factors (RCF) of Pesticides and Related Compounds from Water into Barley Roots (*Hordeum vulgare* cv. Georgie) over a Period of 24–48 h (18)

compound	log K_{ow}	RCF	α_{pt}
<i>O</i> -Methylcarbamoyloximes			
aldoxycarb	-0.57	0.66	0.74
oxamyl	-0.47	0.91	1.02
acetone <i>O</i> -methylcarbamoyloxime	-0.13	0.95	1.06
aldicarb	1.08	0.94	0.90
benzaldehyde <i>O</i> -methylcarbamoyloxime	1.49	1.48	1.19
4-chlorobenzaldehyde <i>O</i> -methylcarbamoyloxime	2.27	2.80	0.98
3,4-dichlorobenzaldehyde <i>O</i> -methylcarbamoyloxime	2.89	5.61	0.64
3-phenylbenzaldehyde <i>O</i> -methylcarbamoyloxime	3.12	8.72	0.61
3-(3,4-dichlorophenoxy)benzaldehyde <i>O</i> -methylcarbamoyloxime	4.6	81.1	0.20
Substituted Ureas			
3-methylphenylurea	-0.12	0.73	0.82
phenylurea	0.80	1.20	1.25
4-fluorophenylurea	1.04	1.10	1.06
3-(methylthio)phenylurea	1.57	0.94	0.72
4-chlorophenylurea	1.80	2.00	1.28
4-bromophenylurea	1.98	3.17	1.63
3,4-dichlorophenylurea	2.64	5.86	1.09
4-phenoxyphenylurea	2.80	7.08	0.97
4-(4-bromophenoxy)phenylurea	3.7	34.9	0.68

= 0.1–0.9; 0.5 for log K_{ow} = 1.0–1.9; 1 for log K_{ow} = 2.0–2.9; 2 for log K_{ow} = 3.0–3.9; and 3 for log K_{ow} \geq 4.0. With the assumed barley-root composition, the partition contribution by carbohydrates becomes unimportant relative to that by the lipids for compounds with log K_{ow} > 3.0.

The thus calculated α_{pt} values for the compounds are listed in the last column of Table 1. They are generally consistent with the overall hydrophilic-to-lipophilic trend of the solutes in that the water-soluble compounds have α_{pt} values close to 1 and that the α_{pt} values for lipophilic compounds (high K_{ow} values) are less than 1. This relatively smooth transition is reflective in part of the passive transport of contaminants into the different plant-root organic matrices and in part of the spatial uniformity of the contaminant concentration in external water. As seen for both *O*-methylcarbamoyloximes and substituted ureas with $K_{ow} \leq 500$ or so, the α_{pt} values are, within the uncertainties from all sources, essentially 1, suggesting that the passive uptake of these relatively water-soluble compounds by barley roots comes closely to equilibrium within 24–48 h, while for compounds with increased lipophilicity, i.e., those with $K_{ow} > 1000$, the α_{pt} values are clearly below 1. With the assumed composition for barley roots, the calculation shows that for compounds with $K_{ow} \leq 10$, the contaminant level in root water accounts for more than 85% of the total root uptake; for compounds with $K_{ow} = 100$, the uptake by the root water and the root lipid each contributes about 50% to the total uptake; for compounds with $K_{ow} > 1000$, the total root uptake is predominated by the lipid uptake.

The calculated α_{pt} values depend sensitively on the assumed lipid content and the accuracy of the K_{ow} values for compounds having $K_{ow} > 100$; this sensitivity increases proportionally with increasing K_{ow} of the compound. As to the K_{ow} , it is not uncommon for the reported values to be in error by a factor of 2–3, especially for compounds with large K_{ow} 's (42). In view that the variation of the α_{pt} values in Table 1 is supportive of passive transport, one may verify the relative K_{ow} values of the compounds in terms of their measured RCF (or C_{pt}/C_w) values. Here, for example, the RCF values for 4-bromophenylurea, 3,4-dichlorophenylurea, and 4-phenoxyphenylurea are 3.17, 5.86, and 7.08, respectively; the corresponding measured K_{ow} values are 95, 436, and 631. Thus, based on the measured RCF values, the K_{ow} for 4-bromophenylurea seems to be too low, by nearly a factor

of 2, relative to the values for the other two compounds. The relatively high α_{pt} = 1.63 for 4-bromophenylurea, compared to the values for the other two compounds (where $\alpha_{pt} \approx 1$), may be an artifact of the calculation, rather than a manifestation of active uptake. Similarly, the α_{pt} value for 3-(3,4-dichlorophenoxy)benzaldehyde *O*-methylcarbamoyloxime could be somewhat too low, as the estimated K_{ow} seems somewhat too high.

The less-than-1 α_{pt} values (i.e., the very small RCFs) for highly polar aldoxycarb (0.74) and 3-methylphenylurea (0.82) in Table 1 are noted with interest, since their uptake by root lipids and carbohydrates would be small relative to that by root water. Briggs et al. (18) attributed the small RCFs of highly polar chemicals to difficulties in passing through the lipid membranes in the root, thus resulting in selective rejection of the chemicals at the membrane barriers. The low α_{pt} values could also result from the high ionic strength in root water that increases the activity (and thus decreases the solubility) of neutral compounds (43). However, the high α_{pt} value (1.02) for equally polar and soluble oxamyl in Table 1 suggests that other effects may be relevant. Overall, the results indicate that the concentrations of compounds with $K_{ow} \leq 1000$ in barley roots are reasonably close to equilibrium with external water after 24–48 h; for compounds with $K_{ow} > 1000$, accurate K_{lip} values are required to determine the approach to equilibrium.

Uptake by Barley Seedlings from Soil. Although there are numerous reports in the literature on the contaminant uptake by plants/crops from soils, only a few provide the corresponding soil contaminant levels; even in studies where the levels in soil are reported, the requisite data on the SOM (or K_d) values is often not available. In others, the incorporation of contaminants into soils has not reached a stable condition, because either of insufficient time of incorporation or of instability of the compounds (e.g., a large dissipation by vaporization). The following model calculations are performed for those systems that are considered to be relatively stable and where the data on SOM contents are reported.

Trapp et al. (13) measured the concentrations of a herbicide (atrazine) and other chlorinated hydrocarbons in barley seedlings (*Hordeum vulgare*) germinated from a contaminated soil. The crop uptake was separately investigated for each of the ^{14}C -labeled contaminants in a closed

TABLE 2. Calculated SOM-Normalized Soil Concentrations (C_{som})ⁱ, Soil-Interstitial-Water Concentrations ($C_w = C_{\text{som}}/K_{\text{som}}$), and Quasi-Equilibrium Factors (α_{pt}) of Pesticides and Chlorinated Compounds Based on the Concentrations in Soil (C_s) and Barley Plants (C_{pt}) after 1-Week Plant Uptake (13)

compound	log K_{ow} ^a	log K_{som}	C_s ^b ppm	C_{som} ^b ppm	C_w ^c ppm	C_{pt} ^b ppm	α_{pt} ^c
atrazine	2.71	2.17 ^d	0.84 (0.98)	24 (28)	1.6×10^{-1}	1.02 (2.53)	1.0
1,2,4-trichlorobenzene	3.98	2.70 ^e	0.65 (0.75)	19 (21)	3.8×10^{-2}	0.70 (1.33)	0.19
1,2,3,5-tetrachlorobenzene	4.65	3.42 ^f	1.13 (1.18)	32 (34)	1.2×10^{-2}	1.93 (3.54)	0.35
dieldrin	4.55	3.69 ^g	2.07 (2.08)	59 (59)	1.2×10^{-2}	1.14 (1.24)	0.27
hexachlorobenzene	5.50	4.19 ^f	1.86 (1.88)	53 (54)	3.4×10^{-3}	2.19 (2.21)	0.20
2,4,6,2',4'-PCB	5.92	4.57 ^f	2.15 (2.16)	61 (62)	1.6×10^{-3}	2.54 (2.77)	0.19
DDT	6.36	5.34 ^h	2.10 (2.16)	60 (62)	2.7×10^{-4}	0.70 (0.88)	0.11

^a Values cited by Trapp et al. (13) except for dieldrin taken from ref 44 and hexachlorobenzene and DDT from ref 42. ^b Values outside the parentheses are for the parent compounds; values within the parentheses are sums of parents and metabolites. ^c Calculated only for the parent compounds. ^d Data from ref 45. ^e Data from ref 26. ^f Estimated from the correlation of ref 26: $\log K_{\text{som}} = 0.904 \log K_{\text{ow}} - 0.779$. ^g Data from ref 46. ^h Data from ref 47. ⁱ The SOM content is 3.5 wt %.

aerated laboratory system. After the barley seedlings had been in contact with the soil for 1 week, plant and soil samples were taken for analysis of the parent compound and its metabolites in both soil and plants; however, the metabolites were not identified. The soil contained 2.06% organic carbon, or approximately 3.5% in SOM, and was maintained at 20% water during the experiment. The measured concentrations of the parent compounds and their metabolites in both soil and plants (roots + shoots) are given in Table 2. For our model calculations, the concentrations in soil have also been normalized to the SOM.

For whole barley seedlings, the composition was taken by the authors to be 87.5% water and 1% lipids. As before, we further assume that the remaining 11.5% consists essentially of carbohydrates and cellulose, on which the contaminants exhibit the same partition coefficients. With these assumptions together with eq 5, eq 6 may then be expressed as

$$C_{\text{pt}} = \alpha_{\text{pt}} C_{\text{som}} [f_{\text{pw}} + f_{\text{ch}} K_{\text{ch}} + f_{\text{lip}} K_{\text{lip}}] / K_{\text{som}} \quad (10)$$

or

$$\alpha_{\text{pt}} = K_{\text{som}} (C_{\text{pt}} / C_{\text{som}}) / [0.875 + 0.115 K_{\text{ch}} + 0.01 K_{\text{ow}}] \quad (11)$$

With the relatively high K_{ow} values of the parent compounds in Table 2 and the assumed lipid content, the contributions to total barley uptake by plant water and cellulose would be quite small or negligible relative to that by lipids, as reasoned earlier. Although the levels of metabolites in soil and plants are a useful indicator of the contaminant fate, no calculations could be performed for the metabolites as their chemical identities are not known. The K_{som} values of the parent compounds in Table 2 are taken from various sources (26, 42, 44–47) to complete the calculation of the α_{pt} values.

The calculated α_{pt} values for the compounds except 1,2,4-trichlorobenzene are quite consistent with the expected counter-trend between α_{pt} and K_{ow} , despite that the calculated α_{pt} values for lipophilic compounds depend sensitively on the accuracy of the K_{ow} and K_{som} values. The noted results on α_{pt} are consistent with the model approach by substituting $C_{\text{som}}/K_{\text{som}}$ for C_w in soil interstitial water. For 1,2,4-trichlorobenzene in soil, the system was recognized to be unstable because of its high volatility (13); the total recovery of this compound and its metabolites from soil and plants was only 70%, whereas the recoveries for all other compounds exceeded 96%. Based on the model calculations, the uptake of atrazine by plant water and carbohydrates constitutes about 20% of the total, with the rest of atrazine being taken up by lipids. The total uptakes of other less water-soluble contaminants are exclusively by the small amount of lipids, with the different α_{pt} values reflecting the relative efficiencies

of the compounds inside the plants for approaching equilibrium with external soil water. One notes with interest that atrazine, with a moderate $\log K_{\text{ow}} = 2.71$, gives rise to $\alpha_{\text{pt}} = 1$ despite that the amount of metabolites in the plant is more than that of the parent species. This suggests that the metabolic process or formation of metabolites in plants does not seem to retard the plant passive uptake of the parent compound.

Although the α_{pt} value of a contaminant is partly a function of the plant water uptake and transport, it could also be affected by other mechanisms. Consider here, for example, the α_{pt} value (about 0.1) for DDT with $K_{\text{lip}} \approx K_{\text{ow}} = 2.3 \times 10^6$ on barley seedlings containing about 1% lipids. Since the plant is considered to be about 90% water, the total plant mass is about the same as the plant-water mass. If all the DDT uptake by barley seedlings were to come only from absorption of the external soil water through the plant vascular system (i.e., as a consequence of the plant transpiration), the needed transport mass of water for DDT at $\alpha_{\text{pt}} = 0.1$ would exceed 2000 times the plant mass. Since this amount appears to be unreasonably high in a short-term experiment, the DDT uptake is more likely also facilitated by mass diffusion from interstitial water into or across the root surfaces of the plant. Moreover, had such a high water transport mass been involved, the α_{pt} values for contaminants with much lower K_{ow} 's (e.g., dieldrin and tetrachlorobenzene) would have been much closer to 1 than observed, because the transport masses required to saturate the lipid phase are much less for these contaminants.

The results in Table 2 reveal that although the α_{pt} values for compounds with high lipid-to-water solubility ratios (i.e., those with high K_{ow} 's) are significantly less than 1, their concentration factors from soil interstitial water (C_w or $C_{\text{som}}/K_{\text{som}}$) to the plant (C_{pt}), i.e., the C_{pt} -to- C_w ratios, are markedly higher than for relatively water-soluble compounds (e.g., atrazine). As manifested in Table 2, the C_{pt} -to- C_w ratio increases largely with increasing K_{ow} because a net increase in K_{ow} outweighs the resulting decrease in α_{pt} , as exemplified, for example, by the data of dieldrin and DDT. As such, extremely water-insoluble DDT with a small $\alpha_{\text{pt}} = 0.11$ exhibits nevertheless a large concentration factor, about 2600, from soil interstitial water into the barley, based on the assumed lipid content (1%) and lipid-water partition coefficient (K_{ow}). Here the concentration of DDT inside the plant is only about 10% of the equilibrium value with respect to the soil-interstitial-water concentration; the theoretical concentration factor at equilibrium would be about 10 times greater than observed. The small α_{pt} values for DDT and other compounds with large lipid-to-water solubility ratios may be attributed to insufficient amounts of external-water transport into the plant circulatory system for these compounds to achieve the equilibrium partition capacities.

TABLE 3. Calculated SOM-Normalized Soil Concentrations (C_{som})^a, Soil-Interstitial-Water Concentrations ($C_w = C_{\text{som}}/K_{\text{som}}$), and Quasi-Equilibrium Factors (α_{pt}) of Dieldrin and DDT Based on the Concentrations in Soils (C_s) and Root Crops (C_{pt}) in Field Plots after a Growing Season (θ)

system	C_s , ppm	C_{som} , ppm	C_w , ppm	C_{pt} , ppm	α_{pt}
Dieldrin					
sandy soil/carrots	0.48	34	6.9×10^{-3}	0.12	0.24
clay soil/carrots	1.1	31	6.3×10^{-3}	0.11	0.24
muck/carrots	3.9	5.9	1.2×10^{-3}	0.02	0.23
sandy soil/radishes	0.48	34	6.9×10^{-3}	0.02	0.08
clay soil/radishes	1.1	31	6.3×10^{-3}	0.05	0.22
muck/radishes	3.9	5.9	1.2×10^{-3}	0.01	0.23
DDT					
clay soil/carrots	0.34	9.4	4.3×10^{-5}	<0.01	<0.05
muck/carrots	15	23	1.1×10^{-4}	0.01	0.02
clay soil/radishes	0.34	9.4	4.3×10^{-5}	<0.01	<0.10
muck/radishes	15	23	1.1×10^{-4}	0.01	0.04

^a The SOM content is 1.4% for the sandy soil, 3.6% for the clay soil, and 66.5% for the muck.

Uptake by Root Crops from Different Soils. A very instructive work on the effect of soil type on contaminant uptake by crops is that of Harris and Sans (θ), who measured the uptake of dieldrin and DDT by several root crops from three contaminated field plots of widely different soil types. Each of the three field plots maintained stable levels of dieldrin and DDT during the growing season. The three soils studied consisted of a Fox sandy loam (1.4% SOM), a clay soil (3.6% SOM), and a muck (66.5% SOM). The plots were seeded during mid May; the growing season varied with the crop type and lasted, for example, about 1 month for radishes (Sparkler White Tip) and 3 months for carrots (Nantes). Soil insecticide-residue levels before seeding and after harvesting were measured, and no significant changes were observed. The levels of dieldrin and DDT in crops and soils observed by Harris and Sans (θ) are given in Table 3. In addition to the original insecticide concentrations in soils (C_s), the SOM-normalized soil concentrations (C_{som}) are also presented.

Calculations of the α_{pt} values for dieldrin and DDT with each soil/crop system have been made using the K_{ow} and K_{som} values from Table 2 and the assumed compositions of the root crops. Among the root crops studied (carrots, radishes, turnips, and onions), carrots showed the highest uptake from the soils and radishes exhibited trace levels, while the uptake by turnips and onions was near or below the detection limit (<0.01 ppm). For DDT, the observed levels in these crops were mostly below the detection limit and thus the data were more limited and less precise. The present analysis is confined largely to the dieldrin levels in carrots and radishes and to a lesser extent to the DDT levels in these two crops. The inclusion of the DDT data for analysis is mainly to substantiate the relative order in α_{pt} between DDT and dieldrin.

According to the USDA Nutrient Database (www.nal.usda.gov/fnic/foodcomp/), a fully grown carrot (*Daucus carota*) has a lipid content of about 0.19%, whereas a baby carrot (*Daucus carota*) contains 0.53% lipids. The lipid content for the carrot (Nantes) used by Harris and Sans is unknown. As a working basis, we assume a lipid content of 0.2% for carrots. Similarly, according to the USDA Nutrient Database, the lipid content for radishes varies between the varieties, with most values around 0.1%, and no information is available for the species used by Harris and Sans (θ). We assume a lipid content of 0.1% to be representative of most radish varieties. With the K_{ow} values for dieldrin and DDT, the crop uptake should be controlled predominantly by the lipid uptake. Contributions by carbohydrates and plant water are therefore ignored.

The calculated α_{pt} values for dieldrin and DDT follow the expected order. The α_{pt} values for dieldrin with carrots from three different soils are nearly constant and practically the

same as the value found for dieldrin with barley seedlings (Table 2). This uniformity of α_{pt} values is more than anticipated, considering the differences in crop type and growth time and the potential nonuniformity in contaminant concentration and soil SOM content over the root-accessible soil zone. The use of $C_{\text{som}}/K_{\text{som}}$ for C_w in eq 6 results in a practically linear relation between C_{pt} and C_{som} (as reflected by the consistent α_{pt} values) for dieldrin/carrots on the three soils of widely different properties. As may be seen, if the C_s values are not normalized to the SOM contents, the C_s/C_{pt} ratios vary radically, showing no obvious correlation. Similar results are noted for dieldrin with radishes and for DDT with carrots and radishes; however, the data here show more uncertainties where the contamination levels in the crops were either near or below detection limits (<0.01 ppm) (θ).

Effect of Plant Composition on Uptake. The generally lower uptake of dieldrin by radishes than by carrots appears to result largely from the difference in their lipid contents. This effect is illustrated by the finding that the C_{pt}/C_w ratios for dieldrin with a given soil for radishes are about one-half the values for carrots, which are in accord with the presumed difference in their lipid contents. Moreover, the present dieldrin concentration factor (C_{pt}/C_w) with carrots correlates well with the dieldrin concentration factor with barley seedlings described earlier, in which a 5-fold difference in crop lipids leads to about a 5-fold difference in C_{pt}/C_w values. Although the close agreement of the data in both cases seems a bit fortuitous for reasons as stated earlier, the results are suggestive of plant lipids as the major factor for the observed difference in plant uptakes of lipophilic contaminants. This view is further supported by the results of Lichtenstein (θ) on the uptakes of lipophilic aldrin, dieldrin, heptachlor, and heptachlor epoxide from a soil by carrots, radishes, beets, potatoes, onions, and lettuce. In this experiment, the field plots of a Carrington silt loam were treated with high insecticide levels on which various crops were seeded, and soil and crop contaminant levels were analyzed at the harvest; however, information on the SOM content of the soil was not available. An essential portion of the Lichtenstein's data on soil and crop contaminant levels is given in Table 4.

Data in Table 4 reveal that the whole-crop levels of these relatively water-insoluble pesticides in radishes (Early Scarlet Globe), beets (Detroit Dark Red), potatoes (Russet Sebago), onions (Yellow Globe Danvers), and lettuce (Great Lakes) were all significantly lower than in carrots, despite significant variations in relative contaminant levels with different crops. Although the lipid contents for all these crops are very low, carrots appear to have a comparatively greater lipid content than others according to the USDA Nutrient Database. Thus, the levels for each of the pesticides in these crops seem to

TABLE 4. Concentrations of Aldrin, Dieldrin, Heptachlor, and Heptachlor Epoxide in Carrington Silt Loam and Crops in Field Plots after a Growing Season (2)

soil/crop	concentrations in soil and crops (ppm)			
	aldrin	dieldrin	heptachlor	heptachlorepoide
soil	3.1	1.8	4.2	0.78
radishes	0.05	0.13	trace	0.12
beets	trace	0.17	0.03	0.12
potatoes (whole)	0.11	0.31	0.29	0.49
potatoes (peels)	0.63	1.82	3.03	2.35
potatoes (pulp)	trace	0.16	trace	0.24
onions	trace	0.05	NA ^a	NA ^a
carrots	0.36	0.55	1.34	NA ^a
lettuce	0.03	0.17	trace	0.05

^a Data not available.

be influenced most by the plant lipids. Significant variations in relative contaminant levels among crops may stem from various unspecified sources, such as the analytical sensitivity, the sample preparation loss with soil and crops, and other factors mentioned previously. Detailed evaluations of individual contaminant levels with these crops require the SOM content of the soil, accurate lipid data, and accurate K_{ow} and K_{som} values which are not readily available.

An interesting observation by Lichtenstein (2) is that the contaminant concentrations in the peels (skin) of potatoes are considerably higher than those in either whole potatoes or their pulps (Table 4). Although the mass-diffusion effect would make the concentrations higher in the peels than in the pulps, it is not clear without the relevant lipid data whether this disparity is caused solely by the mass diffusion or in addition by the lipid-content difference. A similar but more pronounced disparity was later reported by Lichtenstein (3) for the uptake of dieldrin from soil by carrots and by Mattina et al. (16) for the uptake of chlordane by carrots, potatoes, and beets. The exact cause of this phenomenon is yet to be investigated.

In summary, the proposed partition-limited model appears to give a satisfactory account of the passive transport of various contaminants from soil and water into a small number of crops. The effective concentration of a contaminant in soil for plant uptake is identified to be the concentration in soil interstitial (pore) water, which for the systems examined can in turn be reasonably well estimated from calculated C_{som} and K_{som} . For a contaminant at a location within the plant, local equilibrium is assumed to exist between plant water phase and various plant organic components; however, the local concentration may or may not be in equilibrium with external water. The quasi-equilibrium factor (α_{pt}) that measures the approach to equilibrium with external water depends presumably on plant contaminant-uptake capacity and water transport volume as well as on contaminant diffusion into water-contacted plant surfaces. In general, highly water-soluble contaminants may be expected to approach equilibrium with external water much more efficiently than relatively water-insoluble contaminants. An inverse correlation exists between the α_{pt} and K_{ow} values for contaminants with high lipid-to-water solubility ratios on a plant. For plants with a high water content, highly water-soluble contaminants occur mainly in the plant-water phase, as their uptakes by lipids and other plant matters are either small or insignificant. By contrast, the plant uptake of highly water-insoluble contaminants is predominated by the lipid uptake, even though the lipid content may be very low. Although the model remains to be further tested by more extensive experiments, it does provide improved insights to all the examples thus far investigated.

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