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Effects of Polar and Nonpolar Groups on the Solubility of Organic Compounds in Soil Organic Matter

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Vapor sorption capacities on a high-organic-content peat, a model for soil organic matter (SOM), were determined at room temperature for the following liquids: *n*-hexane, 1,4-dioxane, nitroethane, acetone, acetonitrile, 1-propanol, ethanol, and methanol. The linear organic vapor sorption is in keeping with the dominance of vapor partition in peat SOM. These data and similar results of carbon tetrachloride (CT), trichloroethylene (TCE), benzene, ethylene glycol monoethyl ether (EGME), and water on the same peat from earlier studies are used to evaluate the effect of polarity on the vapor partition in SOM. The extrapolated liquid solubility from the vapor isotherm increases sharply from 3–6 wt % for low-polarity liquids (hexane, CT, and benzene) to 62 wt % for polar methanol and correlates positively with the liquid's component solubility parameters for polar interaction (δ_p) and hydrogen bonding (δ_h). The same polarity effect may be expected to influence the relative solubilities of a variety of contaminants in SOM and, therefore, the relative deviations between the SOM–water partition coefficients (K_{om}) and corresponding octanol–water partition coefficients (K_{ow}) for different classes of compounds. The large solubility disparity in SOM between polar and nonpolar solutes suggests that the accurate prediction of K_{om} from K_{ow} or S_w (solute water solubility) would be limited to compounds of similar polarity.

Introduction

Soil/sediment organic matter (SOM) is recognized as the predominant sorbent in the sorption of nonionic organic contaminants from water by ordinary soils (with the exception of those having extremely low SOM contents), and the sorption by amorphous SOM occurs essentially by partition (solubility) (*1–10*). The weak adsorption of organic compounds by soil minerals in water is attributed to the strong competitive adsorption of water on polar mineral surfaces. The sorption (partition) coefficients of solutes between SOM and water (K_{om}) show an approximate inverse relation to their water solubilities (S_w) and an approximate linear relation to their octanol–water partition coefficients (K_{ow}), because both K_{om} and K_{ow} are controlled mainly by the reciprocal of S_w (*1–3, 11–16*). That the K_{om} values are usually lower than the respective K_{ow} values for low-polarity solutes (by about 1 order of magnitude) may be ascribed to the higher polarity of SOM relative to octanol, which reduces the solubility of low-polarity compounds. While polar compounds are expected to have higher solubilities, and therefore higher K_{om} values relative to K_{ow}, there has been a lack of a detailed account of the various types of molecular forces that affect the solubility of various substances in SOM.

Since SOM contains both polar and nonpolar functional groups, significant differences in solubilities of various (polar and nonpolar) organic compounds in SOM may result from differences in their combined molecular

interactions with SOM via dispersion forces (London forces), polar interaction, and H-bonding. Therefore, although good correlations are usually found between K_{om} and S_w (*2, 13, 15*) or between K_{om} and K_{ow} (*2, 13–16*) for compounds of similar polarity, one would not expect a single correlation of this kind to be accurate for groups of solutes exhibiting wide variations of polarity. In polar SOM, one would expect polar liquids to exhibit higher solubilities because polar interaction and H-bonding are more powerful molecular forces than nonpolar (dispersion) forces. This expectation comes from the finding that polar ethylene glycol monoethyl ether (EGME) (*17*) exhibits a significantly higher solubility in dry peat than relatively nonpolar liquids such as carbon tetrachloride (CT), trichloroethylene (TCE), and benzene (*10*). A comprehensive analysis of polarity effects requires a large set of solubility data of liquids representing a wide range of polarities. In aqueous systems, the saturation of water in SOM would enhance the polarity of SOM and could further affect the partition differences of polar versus nonpolar compounds. The noted discrepancy in many reported empirical equations relating K_{om} to S_w or K_{om} to K_{ow}, especially between polar and nonpolar compounds (*2, 13–16*), may be partially attributed to the variation of solubilities in SOM.

To provide an account of the polarity effect on solubility in SOM on the premise of the partition model, we took as model compounds a number of volatile liquids and measured their solubilities in SOM by their vapor sorption (partition) capacities on a high organic-content peat that was used earlier (*8–10*), the peat being a model for SOM. Vapor sorption data were determined for *n*-hexane, 1,4-dioxane, acetone, nitroethane, acetonitrile, 1-propanol, ethanol, and methanol to supplement earlier data for CT, TCE, benzene, EGME, and water on the same peat. These liquids encompass a range of polar and nonpolar groups such that their solubilities in SOM can be evaluated in terms of their respective dispersive forces, polar forces, and H-bonding capabilities. The use of intact peat rather than a fractionated soil organic component is intended to give a better representation of the solubility data in a whole SOM. Previous studies show that the K_{om} values of solutes derived from this peat are comparable with those from other soils (*9*). The peat has a low mineral content and a low BET surface area, and therefore no significant surface adsorption of vapors is anticipated.

Experimental Section

The peat sample used in this experiment is from the same batch that was used in previous studies (*8–10*). The peat is a reference sample of the International Humic Substances Society, collected from Everglades, FL. The field sample was prepared to pass through an 80-mesh sieve and then uniformly mixed for sorption experiments. The sieved sample has an organic content of 86.4% on a dry weight basis and a BET-(N_2) surface area of 1.3–1.5

m²/g (*10, 17*). The moisture-free and ash-free elemental content of the sample is as follows: C (57.1%), H (4.49%), O (33.9%), N (3.6%), and S (0.65%). *n*-Hexane, 1,4-dioxane, acetone, nitroethane, acetonitrile, methanol, and 1-propanol are all either reagent grade or spectrophotometric grade (99+%) from Aldrich Chemical Co. Ethanol is a highly pure material (99.95+%) from USI Chemical Co. All these solvents were used as received.

The apparatus and procedure for vapor sorption of selected liquids have been described elsewhere (*6, 10*). Briefly, sorbed weights were determined at different pressures by suspending the sample (peat) in a glass container from a Cahn electrical microbalance in a static chamber in which the equilibrium pressures were measured by a Baratron pressure gauge. The temperature of the sorption chamber was controlled by laboratory air maintained at 24 ± 1 °C. Samples of 90–180 mg were typically used. The state of sorption equilibrium was signified by a constant sample weight and a constant vapor partial pressure. Before the vapor sorption was initiated, the sample was heated at 90 °C for 10–12 h and then cooled to room temperature for 6–8 h under vacuum to remove moisture and to determine the "dry" weight of the sample. The test liquid was purified by vacuum distillation to remove residual air and volatile impurities before the introduction of its vapor to the sorption chamber. All control valves of the sorption apparatus were Teflon or stainless steel with Viton O-ring seals. The vacuum system was free of oil and grease.

The time of vapor sorption equilibrium with dry peat is usually very long, especially for vapors of polar liquids, which can extend to more than 3–4 weeks when the peat is allowed to equilibrate with a given dose of the vapor. To accelerate the vapor equilibrium with peat, a relatively high partial pressure of the test liquid was initially introduced to the peat sample to enhance the rate of sorption during the first week. The partial pressure of vapor in the sorption chamber was then gradually reduced such that no significant desorption of the vapor from peat occurred. This was done slowly in a stepwise manner until the point that a further reduction in vapor partial pressure would cause a desorption (*10*). This procedure shortened the equilibrium time to 2–3 weeks. Since the organic vapor uptake by peat is essentially linear, reflecting the predominance of vapor partition (*10*), determination of the approximate partition capacity of the liquid is achieved by extrapolating the slope of the isotherm at low relative pressures to the point of saturation ($P/P° = 1$), where P is the partial pressure and $P°$ is the saturation pressure of the liquid at the system temperature. The $P°$ values of organic liquids are obtained from the literature (*18*). In this study, sorption data were determined with $P/P°$ up to about 0.3 for most vapors, since a long experimental time would be needed to extend the range of the isotherm that is not critically required.

Because of long equilibrium times for organic vapors with the peat sample, the amount of vapor uptake by the sample had to be corrected for the sorption of residual moisture that resulted from the desorption of water vapor from the glass walls and other parts of the apparatus during the equilibration period. Blank tests using fresh peat were conducted to evaluate the weight gain by the peat of the moisture desorbed from the sorption chamber after the sample was outgassed under vacuum by the same procedure. This was done following the completion of the vapor-
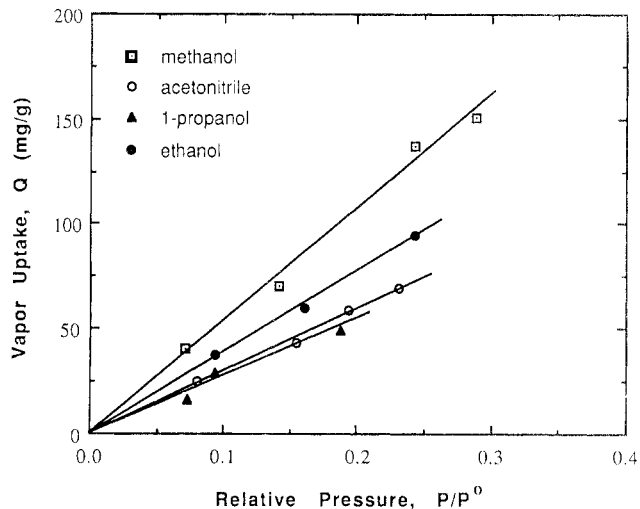

Figure 1. Vapor sorption isotherms of methanol, ethanol, 1-propanol, and acetonitrile at room temperature on peat.
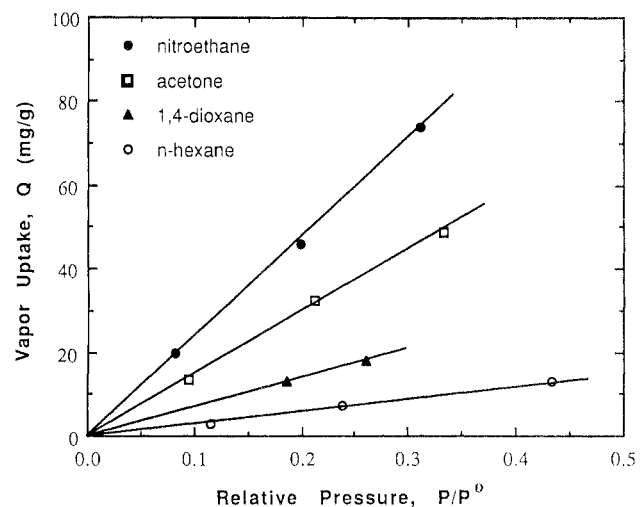

Figure 2. Vapor sorption isotherms of nitroethane, acetone, 1,4-dioxane, and hexane at room temperature on peat.

isotherm measurement. The moisture gain by the peat approached a relatively constant value at about 6 ± 2 mg/g of the dry sample after 3–4 days of exposure. This weight was subsequently deducted from the total sorbed weight for each organic vapor equilibrium point. In general, this moisture correction is insignificant for polar organic vapors which sorb markedly on peat, but it is significant for low-polarity vapors which sorb weakly. Because of some variation of this moisture uptake by peat from one experiment to another, the isotherm data of low-polarity vapors are less accurate than those of polar vapors, the estimated uncertainty being as high as 20%.

Results and Discussion

The sorption isotherms plotted as milligrams of vapor uptake per gram of dry peat (*Q*) against the relative pressure (*P/P°*) of the liquid for methanol, ethanol, propanol, and acetonitrile at room temperature (24 ± 1 °C) are shown in Figure 1; the corresponding isotherms for acetone, nitroethane, 1,4-dioxane, and *n*-hexane are given in Figure 2. The linearity of the isotherms reflects the dominant effect of vapor partition into the organic fraction of the peat, as illustrated previously for trichloroethylene (TCE), carbon tetrachloride (CT), benzene (*10*), and ethylene glycol monoethyl ether (EGME) (*17*) on the

Table 1. Partition Capacities (Q°_{om}) and Volume Fraction Solubilities (ϕ°) of Liquids in Peat Organic Matter

liquid	Q°_{om} (mg/g)	ϕ°	liquid	Q°_{om} (mg/g)	ϕ°
n-hexane	28.2	0.053	acetone	171	0.22
carbon tetrachloride	65.9[a]	0.051[a]	nitroethane	272	0.25
benzene	38.9[a]	0.054[a]	acetonitrile	344	0.36
trichloroethylene	80.0[a]	0.067[a]	1-propanol	313	0.34
1,4-dioxane	80.2	0.092	ethanol	396	0.40
ethylene glycol	190[b]	0.21[b]	methanol	620	0.51
monoethyl ether			water	370[a]	0.33[a]

[a] Value from ref 10. [b] Value from ref 17.

same sample. As may be noticed, the sorption capacities of the polar vapors (e.g., methanol, ethanol, and acetonitrile) are considerably greater than those of vapors of low polarity, such as CT, TCE, and n-hexane, in keeping with the expectation that polar liquids dissolve more effectively in the relatively polar SOM phase. Because the peat has a low mineral content and a low surface area (1.3–1.5 m²/g) (10, 17), the contribution by surface adsorption to observed vapor uptake would be inconsequential (less than 1 mg/g of peat at monolayer capacity).

Linear extrapolation of the isotherms to $P/P^{\circ} = 1$ gives the limiting capacities or solubilities (Q°) of the liquids in peat. Since the mineral adsorption effect is minimal, the solubilities in the organic fraction of peat (Q°_{om}) are obtained by normalizing Q° to the organic content of the peat. For liquids exhibiting high solubilities in peat, this extrapolation could underestimate experimental solubilities because their isotherms would likely be type-III when extended to high P/P°, in reflection of the significant change in composition of SOM with the incorporation of large amounts of liquids (19). In calculations of the solubility parameter(s) for SOM (δ_m) from the extrapolated Q°_{om} values (shown later), the resulting δ_m value(s) would be representative of relatively pure SOM. The calculated Q°_{om} values for organic liquids from this study and other organic liquids and water from a previous study (10) are presented in Table 1. Since the solubility of liquids in an amorphous polymer or a macromolecular substance can be better appreciated in terms of volume fractions (10), the volume fraction solubilities in organic matter (ϕ°) are calculated from the values of Q°_{om} using the densities of liquids and an assumed dry SOM density of 1.3 g/mL (10). The results are also presented in Table 1.

We now examine liquid solubilities in peat SOM in relation to liquid solubility parameters. While the single solubility parameters (δ), as determined from the cohesive energy densities of the liquids, have been used with success in analyzing the solubilities of components in nonpolar solutions, they do not properly account for the solubility data in polar systems because of the specificity of intermolecular interactions involving polar functional groups (20). In such polar systems, as for liquids in SOM, the solubility data are more effectively correlated by a combination of all molecular interactions, i.e., dispersion force, polar interaction, and hydrogen-bonding; the significance of each contribution depends on specific functional groups in liquids and in SOM. Empirically determined component solubility parameters for dispersion (δ_d), polar interaction (δ_p), and hydrogen-bonding (δ_h) of common liquids have been established (21), in which

$$\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

Table 2. Values of One-Component Solubility Parameters (δ), Total Solubility Parameters (δ_o), and Component Solubility Parameters for Dispersion (δ_d), Polar Interaction (δ_p), and Hydrogen Bonding (δ_h) of Selected Liquids[a]

liquid	δ	δ_o	δ_d	δ_p	δ_h
n-hexane	7.3	7.3	7.3	0	0
carbon tetrachloride	8.6	8.7	8.7	0	0.3
trichloroethylene	9.2	9.3	8.8	1.5	2.6
benzene	9.2	9.1	9.0	0	1.0
1,4-dioxane	10.0	10.0	9.3	0.9	3.6
ethylene glycol monoethyl ether	10.5	11.5	7.9	4.5	7.0
acetone	9.9	9.8	7.6	5.1	3.4
nitroethane	11.1	11.1	7.8	7.6	2.2
acetonitrile	11.9	12.0	7.5	8.8	3.0
1-propanol	11.9	12.0	7.8	3.3	8.5
ethanol	12.7	13.0	7.7	4.3	9.5
methanol	14.5	14.5	7.4	6.0	10.9
water	23.4[b]	23.4[b]	7.6[b]	7.8[b]	20.7[b]

[a] All solubility parameters are in units of $cal^{1/2}$ $cm^{-3/2}$ and taken from the compilation of Barton (21). [b] Value uncertain.
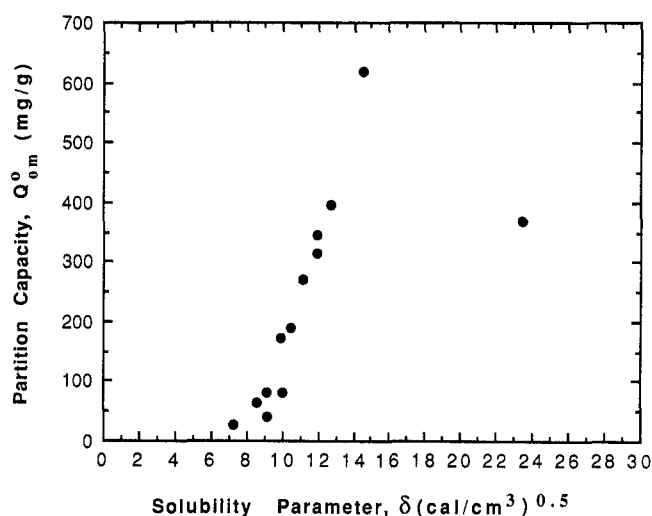

Figure 3. Partition capacities of organic liquids and water in peat organic matter (Q°_{om}) plotted against their single solubility parameter values (δ). (The data for water is included to show the trend of the plot, although the δ value for water, 23.4, is uncertain.)

where δ_o is the total solubility parameter of the liquid. This empirical δ_o has about the same magnitude as the single solubility parameter of the liquid (δ), which is defined earlier. A list of δ, δ_o, δ_d, δ_p, and δ_h for the liquids studied, taken from the compilation of Barton (21), is given in Table 2.

The calculated Q°_{om} values (mg/g) of organic liquids and water are plotted against their respective δ values in Figure 3. The relation of ϕ° to δ is shown in Figure 4. As seen, the value of Q°_{om} or ϕ° is strongly a function of δ, which for these liquids correlate in turn with δ_o. Since the δ_d values are relatively constant for the liquids, the differences in their δ values reflect largely their polar (δ_p) and H-bonding (δ_h) contributions. For low-polarity hexane, CT, TCE, benzene, and 1,4-dioxane, where $\delta_d^2 \gg \delta_p^2 + \delta_h^2$, the solubilities are all very small, indicating that the nonpolar molecular interactions of liquids with SOM do not result in high solubility. On the other hand, polar liquids such as nitroethane, acetonitrile, C_1–C_3 alcohols, and water show greatly increased solubilities in which the contribution of polar interaction and H-bonding exceeds that of the dispersion forces (i.e., $\delta_p^2 + \delta_h^2 > \delta_d^2$). This finding is consistent with the polarity of SOM, which is
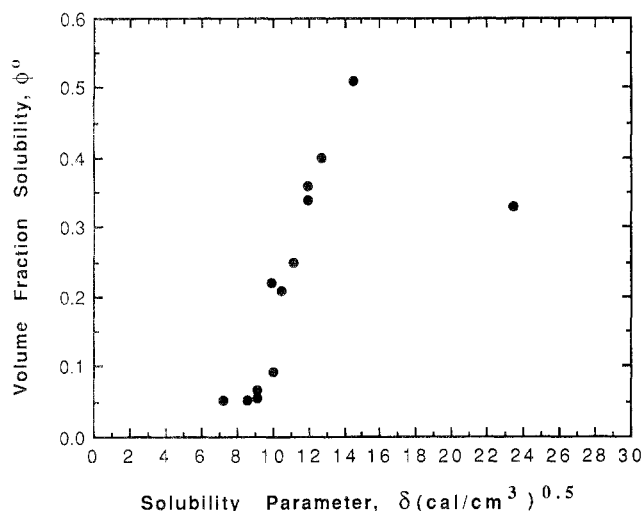
Figure 4. Volume fraction solubilities of organic liquids and water in peat organic matter (ϕ°) plotted against their single solubility parameter values (δ). (The data for water is included to show the trend of the plot.)
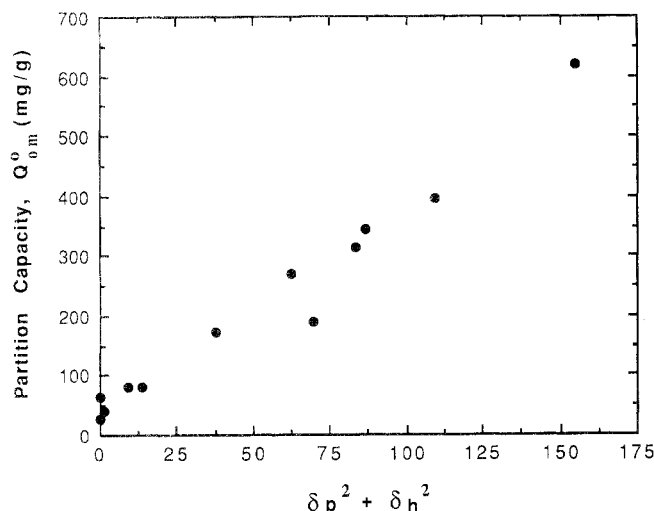

Figure 5. Plot of Q°_{om} versus $\delta_p{}^2 + \delta_h{}^2$ for organic liquids.

known to contain significant amounts of phenolic and carboxylic functional groups (22, 23), as reflected in its high oxygen content.

The importance of polar interaction and H-bonding for liquid solubility in SOM is illustrated by the increased solubility from propanol and ethanol to methanol, which is accompanied by increasing $\delta_p{}^2 + \delta_h{}^2$. Since for these alcohols $\delta_h > \delta_p$, H-bonding with SOM appears to be a powerful promoter of liquid solubility. In support of this view, water shows a high solubility in SOM, despite that it has relatively small dispersion and polar component solubility parameters (although these values for water are relatively uncertain). From the moderately high solubility of acetonitrile, where $\delta_p{}^2 > \delta_d{}^2 \gg \delta_h{}^2$, one may infer that polar interaction also makes a significant contribution to liquid solubility in SOM. The significance of polar interaction is further illustrated by the higher solubility of acetone than of 1,4-dioxane, where the two liquids have about the same δ_o and δ_h values while acetone has a higher δ_p value. These data illustrate the importance of both polar interaction and H-bonding in enhancing solubility in SOM. As shown in Figures 5 and 6, the values of Q°_{om} and ϕ° of the liquids in SOM are well correlated with the values of $\delta_p{}^2 + \delta_h{}^2$, indicating the relative insignificance
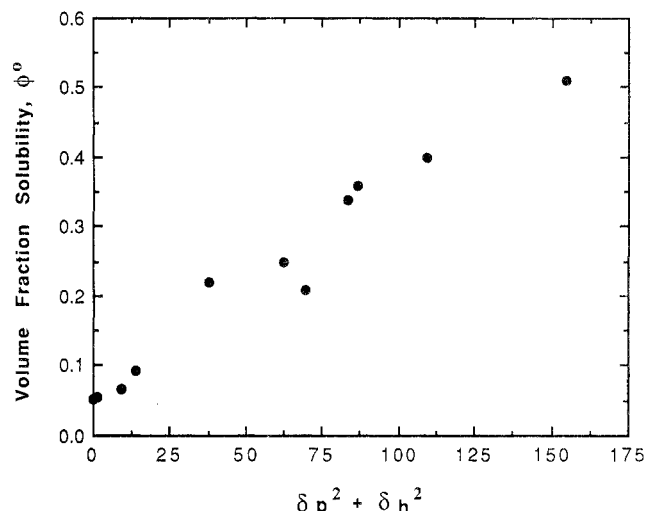

Figure 6. Plot of ϕ° versus $\delta_p{}^2 + \delta_h{}^2$ for organic liquids.

of London (dispersion) forces in effecting liquid solubility in polar SOM. The solubility data of water are not included in Figures 5 and 6 because of the uncertainty of its component solubility parameter values.

The solubility data suggest that the polar functional groups in SOM are responsible for the enhanced solubility of polar liquids in SOM through polar interaction and H-bonding. Hence, SOM should have a high cohesive energy density or solubility parameter(s). According to the polymer solution theory, one can estimate the solubility parameter of a polymer (SOM) from the observed volume fraction solubility of liquids. On the assumption that the molar volume of the solute liquid is negligibly small compared to that of polymer, this gives (24)

$$\ln \phi^\circ + \phi_p + \chi\phi_p{}^2 = 0 \qquad (2)$$

where ϕ° is the volume fraction solubility of the liquid, ϕ_p is the volume fraction of the polymer ($\phi_p = 1 - \phi^\circ$), and χ is the Flory interaction parameter, the sum of the excess entropic (χ_s) and excess enthalpic (χ_h) contribution to liquid–polymer interactions. To a good approximation, χ_s is only a function of the accessibility and flexibility of the polymer chain segments. For weakly cross-linked polymers, χ_s is about 0.25 (25), and this value has been assumed for SOM (2). It has been shown that χ_s is small relative to χ_h for organic compound in SOM (2, 12). If the contribution to the incompatibility of a liquid with polymer, other than that of the size disparity, follows the regular solution theory (20), then χ_h can be reasonably correlated by one-component solubility parameters of the liquid and polymer as

$$\chi_h = (V/RT)(\delta_m - \delta)^2 \qquad (3)$$

where V is the molar volume of the liquid, R is the gas constant, T is the absolute temperature, δ is the single solubility parameter of the liquid (instead of δ_o as defined in eq 1), and δ_m is the solubility parameter of the polymer (SOM). Using the liquid solubility data and eqs 2 and 3 along with the assumed density of 1.3 for dry SOM, the δ_m value for peat SOM may be calculated.

Because of specific intermolecular forces involving polar functional groups, which cannot be well handled by regular solutions (eq 3), the calculated δ_m value for peat SOM is not constant but depends on the polarity of liquid. Such

a result is usually found for polar amorphous polymers which exhibit different molecular interactions in promoting the solute solubility (21). The calculated δ_m for peat SOM increases proportionally with increasing solubility or polarity of the liquid. It has a value of 10.3 $(cal/cm^3)^{0.5}$ based on the volume fraction solubility of n-hexane; an average of 12.5 $(cal/cm^3)^{0.5}$ based on the solubilities of CT, TCE, and benzene; and a value of 17.2 $(cal/cm^3)^{0.5}$ based on the solubility of methanol. The spread of δ_m values for SOM shows the limitations of the model (eq 3) for interactions involving polar functional groups.

The preceding liquid solubility data with dry model SOM (peat) have important implications for the sorption behavior of polar and nonpolar compounds on water-saturated soils and sediments. In aqueous solution, the saturation of SOM by water may further affect the partition interaction of organic compounds, since the appreciable amount of water dissolved in SOM would increase the SOM polarity. For nonpolar solutes that are relatively insoluble in water, this water saturation would decrease their partition efficiency in wet SOM by making the SOM less compatible with the solutes. This expectation is in keeping with the reduced solubility of benzene, CT, and TCE in water-saturated SOM relative to dry SOM, the reduction being about 40–50% (10). On the other hand, for very polar compounds (such as small alcohols, ketones, and organic acids), which are more soluble in water than in SOM, their partition into water-saturated SOM would likely be enhanced. For moderately polar solutes, the effect of water saturation in SOM on solute partition efficiency should be less significant than for nonpolar solutes. Because of these expected discrepancies, the SOM–water partition coefficients (K_{om}) of compounds are influenced not only by their solubilities in water (S_w) but also significantly by their noncomparable solubilities in water-saturated SOM. In other words, the relation of K_{om} to S_w or K_{om} to K_{ow} is expected to vary considerably between polar and nonpolar classes of compounds.

Let us consider the values of K_{om} and K_{ow} for different classes of compounds. For a number of low-polarity compounds such as benzene, chlorobenzenes, alkylbenzenes, and PCBs, Chiou et al. (2) show that soil K_{om} values are lower than corresponding K_{ow} values by about 1 order of magnitude or greater. For example, the respective log K_{om} and log K_{ow} values are 1.26 and 2.13 for benzene, 1.98 and 3.15 for ethylbenzene, 2.70 and 4.02 for 1,2,4-trichlorobenzene, 3.89 and 5.10 for 2,4'-PCB, and 4.38 and 5.62 for 2,4,4'-PCB. Similar differences are found by Briggs (15) for naphthalene (log K_{om} = 2.38; log K_{ow} = 3.36), tetrachlorobenzene (3.25; 4.68), and hexachlorobenzene (4.25; 5.44). By contrast, according to Briggs (15), the soil K_{om} values are much more comparable with respective K_{ow} values for many classes of polar compounds and pesticides (e.g., substituted anilines, anilides, phenols, nitrobenzenes, dimethylureas, phenylureas, and alkyl-N-phenylcarbamates). To highlight the differences, the respective log K_{om} and log K_{ow} values for compounds from each of several classes are listed as follows: aniline (1.17; 0.90), m-toluidine (1.41; 1.42), and 3,4-dichloroaniline (2.05; 2.78); anilide (1.19; 1.16), 3-bromoanilide (1.77; 2.04), and 3,4-dichloroanilide (2.10; 2.54); phenol (1.48; 1.46) and 4-bromophenol (2.17; 2.59); nitrobenzene (1.70; 1.85), 4-bromonitrobenzene (2.18; 2.60), and 3-chloro-4-bromonitrobenzene (2.36; 3.25); fenuron (0.88; 0.96), monuron (1.46; 1.98), and diuron (1.97; 2.68); methyl-N-phenylcar-

bamate (1.49; 1.76), ethyl-N-phenylcarbamate (1.58; 2.26), and n-propyl-N-phenylcarbamate (1.82; 2.80); dimethoate (0.72; 0.79), diazinon (2.12; 3.11), and parathion (2.78; 3.93); and, for miscellaneous compounds, simazine (1.44; 1.51), aldicarb (1.39; 1.57), carbaryl (1.78; 2.32), and captan (2.06; 2.54).

It is clear from the above data that the K_{om} values of polar compounds are much closer to the respective K_{ow} values than for nonpolar compounds, in support of the view that polar interaction and H-bonding contribute markedly to their higher partition interactions with SOM in comparison with those of low-polarity compounds. For each class of compounds, the addition of any nonpolar groups (such as alkyl and halogen groups) to parent polar compounds leads to increased deviations between K_{om} and K_{ow}, and such deviations eventually approach those noted for low-polarity compounds when the polarity of the compound is largely swamped out by the nonpolar moieties of the molecule. The differences between K_{om} and K_{ow} for these compounds are attributable to the different sensitivities of SOM and octanol to the solute polarity. As a moderately polar solvent, octanol is nearly equally hospitable to both polar and nonpolar compounds (11), which makes K_{ow} almost a single function of S_w for different classes of compounds. On the other hand, the high polarity of SOM results in a more sensitive response to solute polarities; thus the relation of K_{om} to K_{ow} is more specific to the compound class. For example, the correlation equation reported by Chiou et al. (2), based on relatively nonpolar compounds (substituted benzenes and PCBs)

$$\log K_{om} = 0.904 \log K_{ow} - 0.779 \qquad (4)$$

is quite different in form from the correlation equation of Briggs (15), which is based primarily on polar pesticides, i.e.

$$\log K_{om} = 0.52 \log K_{ow} + 0.64 \qquad (5)$$

Thus, while eq 4 well predicts the K_{om} values for nonpolar compounds and eq 5 well predicts the K_{om} values for polar compounds, eq 4 predicts poorly the K_{om} values of polar compounds and eq 5 predicts poorly the K_{om} values of nonpolar compounds. The relation of K_{om} to S_w (in which the S_w for solid compounds is corrected for the melting-point effect) would show the same discrepancies. As a consequence, a polar compound would give a higher K_{om} than a nonpolar one if they have about equal K_{ow} and/or S_w. In this sense, octanol is not a sufficiently good general model for SOM.

Since polar compounds are relatively soluble in water and have log K_{ow} values usually much below 3, a large variability between K_{om} and K_{ow} is expected for compounds at log $K_{ow} \ll 3$, where the differences between K_{om} and K_{ow} should be greater for low-polarity compounds than for polar compounds, as demonstrated. At the high end of log K_{ow}, the K_{om} values of compounds will deviate farther from K_{ow}, and the deviation will be more of a monotonic function of K_{ow} or S_w. This point is exemplified by the log K_{om} and log K_{ow} data of some organophosphates (diazinon and parathion), higher chlorobenzenes, and PCBs. The enhanced K_{om} relative to K_{ow} values for polar compounds are a consequence of their enhanced solubilities in SOM, as illustrated by enhanced solubilities of polar liquids in peat. In the absence of this information, the higher K_{om} values for polar compounds could be mistakenly

ascribed to the increased adsorption of polar compounds on soil/sediment minerals. Therefore, attempts to deal with the weak mineral adsorption of solutes by soils and sediments in aqueous solution must simultaneously consider the polarity effect on solute partition in SOM.

In summary, the vapor partition into a model SOM (peat) shows a large disparity in the solubility of polar and nonpolar liquids. Polar interaction and H-bonding contribute powerfully to liquid solubility in SOM because of the polar nature of SOM, which is relatively incompatible with nonpolar solutes. The component solubility parameters of a solute provide a useful basis for assessing the relative molecular forces (dispersion, polar interaction, and H-bonding) operating between solute and SOM. A range of solubility parameters is found for SOM (δ_m = 10.3–17.2) from liquid solubility data, using a regular-solution model for polar amorphous polymers; if the model were accurate for SOM, δ_m should be a single value or nearly so. Because polar solutes tend to be compatible with octanol and SOM, the K_{om} values of polar compounds tend to be comparable with the respective K_{ow} values. Nonpolar solutes tend to be compatible with octanol and relatively incompatible with SOM. This effect prohibits accurate prediction of K_{om} from K_{ow} (or S_w), or from other molecular parameters, by a single correlation equation for both polar and nonpolar compounds. In this context, octanol is not a good general model for the organic medium of soil/sediment organic matter.

Acknowledgments

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