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Effect of Water Saturation in Soil Organic Matter on the Partition of Organic Compounds

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■ The sorption of benzene, trichloroethylene, and carbon tetrachloride at room temperature from water solution and from vapor on two high-organic-content soils (peat and muck) was determined in order to evaluate the effect of water saturation on the solute partition in soil organic matter (SOM). The uptake of water vapor was similarly determined to define the amounts of water in the saturated soil samples. In such high-organic-content soils the organic vapor sorption and the respective solute sorption from water exhibit linear isotherms over a wide range of relative concentrations. This observation, along with the low BET surface areas of the samples, suggests that partition in the SOM of the samples is the dominant process in the uptake of these liquids. A comparison of the sorption from water solution and from vapor phase shows that water saturation reduces the sorption (partition) efficiency of SOM by ~42%; the saturated water content is ~38% by weight of dry SOM. This reduction is relatively small when compared with the almost complete suppression by water of organic compound adsorption on soil minerals. While the effect of water saturation on solute uptake by SOM is much expected in terms of solute partition in SOM, the influence of water on the solubility behavior of polar SOM can be explained only qualitatively by regular solution theory. The results suggest that the major effect of water in a drying-wetting cycle on the organic compound uptake by normal low-organic-content soils (and the associated compound's activity) is the suppression of adsorption by minerals rather than the mitigation of the partition effect in SOM.

Introduction

Earlier studies give an extensive account of the mechanism(s) for sorption of (nonionic) organic compounds by soil (1-14), in which the soil organic matter (SOM) is identified as a partition medium and the mineral matter as a conventional adsorbent. The moisture content in soil influences the extent of organic adsorption by minerals as a result of the strong competitive adsorption of water on polar minerals (4, 5). For water-saturated soils, the sorption of nonionic compounds occurs mainly by partition into SOM because of the suppression by water of organic adsorption on minerals. This model accounts for the linearity of the organic solute uptake from water by soils and other distinctive effects that are commonly found in the partition of solutes from water into an organic phase. The markedly greater uptake of organic compounds by dry and subsaturated soils and the isotherm nonlinearity are attributed to mineral adsorption, which predominates over the simultaneous uptake by partition in SOM.

On the premise of solute partition in SOM, one may expect the partition efficiency of SOM to depend on factors that influence its solvency. The difference in SOM composition (i.e., the medium polarity), for example, has an immediate impact on solute partition coefficients between SOM and water (15). Another important factor that influences the partition (solubility) of organic compounds in SOM is the saturation water content, as it would also alter the SOM polarity. The significance of this effect has not been investigated in previous studies, and this infor-

mation is needed to better define the partition uptake of organic compounds by SOM during a drying-wetting cycle and the associated change in the activity of sorbed compounds in soil.

In attempting to study the effect of water on solute partition in SOM, one has either to account for the adsorptive contribution by dry soil minerals or to select a system in which the mineral adsorption can be minimized or suppressed. Since the partition contribution of SOM to total uptake by ordinary (low-organic-content) dry soils would be very small in magnitude relative to mineral adsorption, separate and highly accurate mineral adsorption data are required to provide a reliable estimate of the partition effect with dry SOM, whereas the corresponding partition with the water-saturated SOM can be readily determined because mineral adsorption would be nearly completely swamped out by water. The difficulty in this case lies in obtaining accurate mineral adsorption data for the soil used. To overcome this problem, it is advantageous to obtain and compare the sorption data of selected compounds sorbed by high-organic-content soils from vapor phase and from aqueous solution, in which the (small) adsorptive contribution of minerals to soil uptake can be largely suppressed. Although the use of some extracted, high-purity organic constituents of soils (such as humic acids) may provide useful inputs for this purpose, the solubility of such samples in water and their lack of full representation in the intact SOM would make the evaluation less meaningful and straightforward.

In this study, we investigated the effect of water saturation on solute partition in SOM by obtaining the sorption data of three volatile organic liquids (benzene, carbon tetrachloride, and trichloroethylene) on two high-organic-content soils (Florida peat and Michigan muck) from aqueous and vapor phases. The peat and muck are those used in a previous study (15), in which the uptake of benzene and carbon tetrachloride from water by this peat organic matter is found to be reasonably representative of the uptake by SOM of other mineral soils. The vapor sorption data with peat and muck in this study show evidence that the adsorptive effect of minerals is practically insignificant relative to partition in SOM of the samples, which should make the comparison relatively unambiguous. (In aqueous systems, as mentioned, water effectively suppresses the mineral adsorption and there would be little concern about the mineral adsorption effect.) The noted difference in elemental composition between the peat and muck samples (15) is useful for determining the sensitivity of organic vapor partition in SOM in relation to water saturation. Isotherms for the uptake of water vapor by the respective samples were also obtained in order to assess the extent of water saturation in SOM and consequently its effect on SOM composition and polarity.

Experimental Section

The peat and muck samples were from the same batch as used in a previous study (15). The elemental compositions of the two samples and their BET (N_2) surface areas are given in Table I. The peat is the reference sample of

Table I. Surface Areas and Percent Elemental Contents of Organic Matter Samples on a Moisture-Free, Ash-Free Basis

material	surf area, m ² /g	C	H	O	N	S	ash
peat	1.5	57.1	4.49	33.9	3.60	0.65	13.6
muck	0.8	53.1	4.90	37.5	3.77	0.48	18.5

the International Humic Substances Society, collected from Everglades, FL, and the muck sample was obtained from the Michigan State University Muck Research Farm, Lainsburg, MI. The field samples were prepared to pass an 80-mesh sieve and then uniformly mixed for sorption experiments. Benzene, carbon tetrachloride (CT), and trichloroethylene (TCE) were all 99+ % spectrophotometric grade from Aldrich Chemical Co. and were used without further purification.

The procedures for sorption experiments in water solutions have been described in earlier works (2, 4, 15). Briefly, the ratios of peat or muck sample to water were selected to give more than 50% of solute uptake by the sample. Samples were prepared in duplicate in 25-mL screw-capped Corex centrifuge tubes, filled to minimal headspace with water containing 0.005 M CaCl₂. Known volumes of neat organic liquids (i.e., the test solutes) were injected into the tubes by microsyringe. The samples were equilibrated for 3–5 days on a rotary mixer at room temperature. After equilibration, the aqueous and solid phases were separated by centrifugation at 2990g. The aqueous phases were extracted by hexane and the solid phases by a 1:4 acetone–hexane solvent mixture; these extracts were analyzed by a gas chromatograph. The solute uptake by the solid sample was corrected for the amount of residual water. The amount of solute uptake per unit weight of the sample (Q) was plotted against the equilibrium concentration in water (C_e) to establish the isotherm.

A static vapor equilibrium system was used to determine the vapor sorption by peat and muck samples. A more detailed description of the apparatus and procedures is given elsewhere (8). Briefly, the test liquid was purified by vacuum distillation to remove residual air before introduction of its vapor into the sorption chamber in which a Cahn electrical microbalance was situated. The peat or muck sample was suspended from the microbalance in a small glass container, and the sample weight was tared with a metal calibration weight. The sample was baked at 90 °C for 10–12 h and then cooled to room temperature for 6–8 h under vacuum ($\sim 10^{-6}$ Torr) to remove moisture and to determine its “dry” weight before initiation of the vapor sorption experiment. A change in sample weight resulting from vapor sorption was recorded as an electrical signal from the balance and was displayed on a strip chart recorder. The partial pressure of the vapor was monitored by the Baratron pressure gauge. 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.

In typical sorption experiments, the peat or muck sample in amounts of 100–120 mg was first outgassed according to the described condition. When the sample reached a constant “dry” weight, the sorption chamber was isolated from the vacuum pump and the vapor of an organic liquid or water was then introduced into the sorption chamber for equilibrium. The increase in sample mass and the corresponding vapor partial pressure at the point of equilibrium were registered accordingly. The state of sorption equilibrium was signified by a constant sample weight and a constant vapor partial pressure.

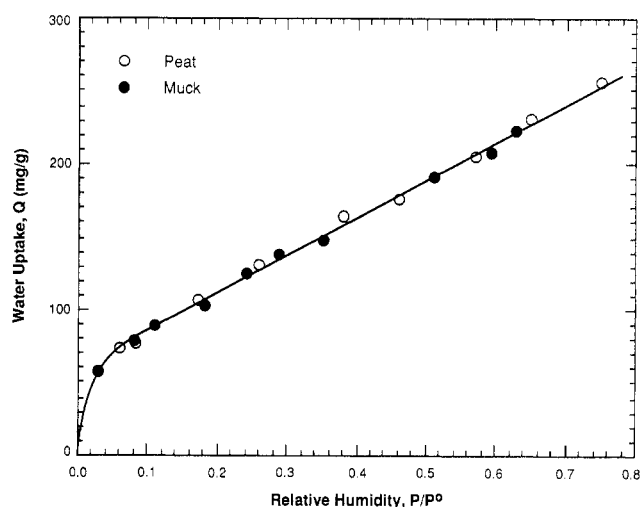


Figure 1. Uptake of water vapor by peat and muck samples as a function of relative humidity.

For the organic-matter-rich peat and muck sample used, the equilibrium normally took 3–4 days, due to the slow rate of organic vapor partition (diffusion) into the network of intact soil organic matter. As a result, the completion of an isotherm run with the peat or muck sample usually required more than 2–3 weeks. Because of this extended time span, together with the strong uptake of water by the sample (as shown later), the organic vapor uptake by the sample had to be corrected for the sorption of residual moisture that resulted from desorption of sorbed water from the glass walls and other parts of the apparatus during the equilibration period. To account for this residual moisture effect, blank tests were conducted to monitor the weight gain of desorbed moisture by peat and muck samples inside the vacuum chamber over a span of ~ 1 week after the sample was outgassed under vacuum by the same procedure. Fresh peat and muck samples were used in blank runs following the sorption experiments of selected organic compounds. In general, the weight gain by blank samples usually approached an asymptotic value after 3 days of exposure in the sorption chamber, which corresponded to 6–10 mg of moisture uptake per gram of the sample. This weight increase was subsequently deducted from the total weight gain for each equilibrium point in establishing isotherms for the organic vapor sorption. The isotherm was plotted as the amount of vapor uptake per gram of dry sample (Q) vs the relative pressure of the vapor (P/P°), where P is the equilibrium partial pressure and P° is the saturation vapor pressure.

Results and Discussion

To determine the effect of water saturation on the partition of organic compounds in soil organic matter, we first consider the amount of water uptake by the selected peat and muck samples. The isotherms of water vapor uptake by (initially) dry peat and muck samples at room temperature (24 ± 1 °C) are shown in Figure 1. For both the peat and muck studied, the saturation water capacity (i.e., Q° at $P/P^\circ = 1$) is ~ 320 mg/g of the sample. This rather high capacity is attributed primarily to solubility of water (a highly polar solvent) in the polar polymeric material of SOM, in which the segments of the organic network are presumably not intensively cross-linked. The Q° value of water uptake normalized for SOM content (Q°_{om}) is ~ 370 mg/g with peat and 390 mg/g with muck; this gives the volume fractions of water in water-saturated SOM of peat and muck as 0.33 and 0.34, respectively, by assuming the dry SOM density to be 1.3 g/cm³. Table I

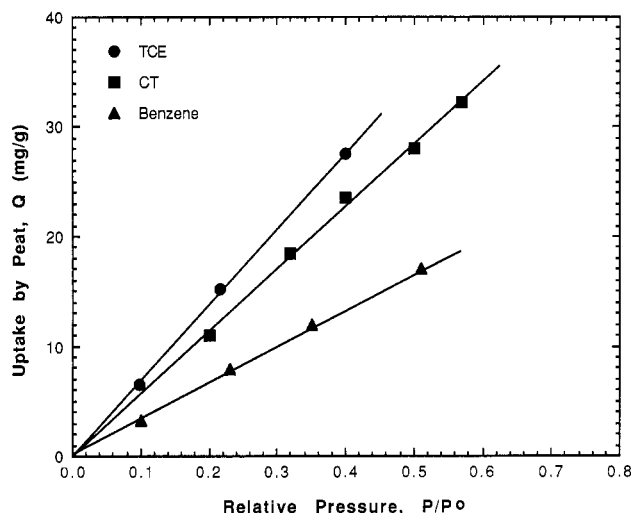


Figure 2. Uptake of vapors of trichloroethylene, carbon tetrachloride, and benzene on peat as a function of relative pressure.

shows the elemental compositions and BET (N_2) surface areas of peat and muck; the polar nature of these sorbent materials is evidenced by the high oxygen and nitrogen contents.

The shape of the isotherms and the measured capacity for water on peat and muck closely resemble the findings of the water uptake by a high-purity soil humic acid in an earlier study (8). The isotherms show a noticeable curvature in the region of $P/P^\circ = 0-0.1$, which is followed by an essentially linear rise to $P/P^\circ = 0.8$. In light of the similarity in water uptake and isotherm shape between these samples and the small measured BET surface areas of the sorbent materials, the amount of water uptake by adsorption on ash (minerals) should be largely insignificant; presumably this mineral fraction is deeply enclosed by the organic component of the samples. That the isotherm curvature at low P/P° is unlikely caused by water adsorption on the mineral or organic fraction of the sample can be ascribed to the fact that a sample surface area of $<2.0 \text{ m}^2/\text{g}$ would correspond to $<1.0 \text{ mg/g}$ monolayer adsorption of water, which is far too small to account for the water uptake at low P/P° . A similar effect has been found for water uptake by some polar polymeric substances. For example, the moisture uptake by cellulose at $P/P^\circ = 0-0.8$, as shown by Hermans (16), exhibits a sorption capacity and isotherm shape comparable with the present system; these results are attributed to dissolution of water in the (three-dimensional) amorphous cellulose network by hydrate formation (16). The high water uptake by the SOM of peat and muck at low P/P° can thus be explained by water hydration with specific polar groups of (amorphous) SOM throughout the organic polymer network, which may be considered as a special type of solubility. At higher P/P° (where the water uptake is linear), water presumably dissolves in the hydrated organic matter network. Therefore, whereas linear isotherms for single-solute systems would imply a partition interaction (solubility), the partition effect may result in nonlinear isotherms (as for water) at conditions under which the intermolecular forces leading to solute solubility vary with the solute concentration.

We now consider the vapor uptake of selected organic liquids by "dry" peat and muck. Figure 2 shows isotherms for the vapor uptake of benzene, CT, and TCE by the peat sample at room temperature. The respective isotherms of benzene and CT with muck are presented in Figure 3. All isotherms obtained with both peat and muck are highly linear, with relative pressures (P/P°) extended to more

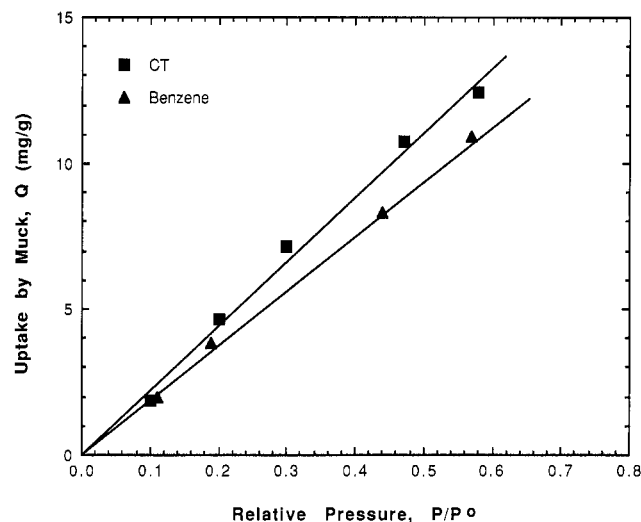


Figure 3. Uptake of vapors of carbon tetrachloride and benzene on muck as a function of relative pressure.

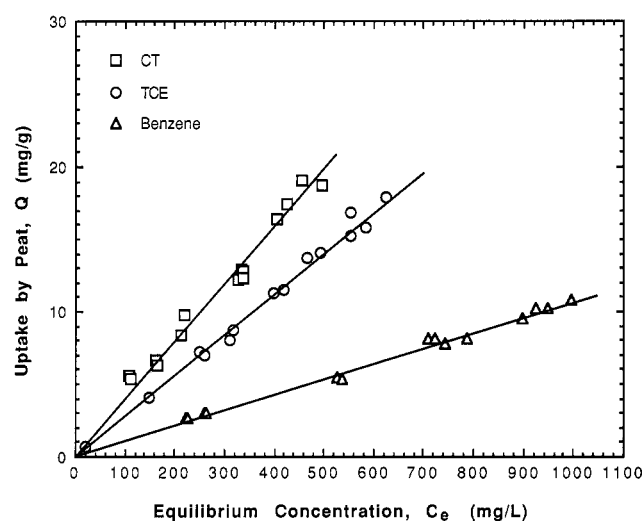


Figure 4. Uptake of carbon tetrachloride, trichloroethylene, and benzene from water on peat as a function of equilibrium concentration.

than 0.5. This linearity is consistent with the known partition effect of nonionic organic compounds in (water-saturated) SOM. As noted, the sorption (partition) capacities for vapors of the selected organic liquids are considerably smaller than for water, which can be ascribed to the disparity in polarity between these low-polarity liquids and the relatively polar SOM. A similar effect has been noted in the uptake of water vapor in comparison with other relatively nonpolar vapors by soil humic acid (8). The organic vapor uptake by the present peat is about the same as that by soil humic acid (8). The isotherm linearity to high P/P° for the vapors, as shown in Figures 2 and 3, suggests that only one type of molecular force is primarily responsible for their partition in the organic matter sample. In view of the low polarity of the organic liquids studied, the London forces are most likely the dominating forces for solute solubility. In spite of the much lower limiting uptake capacity for these organic liquids relative to that of water (i.e., the Q° value at $P/P^\circ = 1$), the observed value is still orders of magnitude greater than can be accounted for by surface adsorption on the small surface areas of the sorbents.

We consider next the sorption of these three organic liquids from water by the same peat and muck. The data for benzene, CT, and TCE with peat at room temperature are given in Figure 4, and the corresponding data for

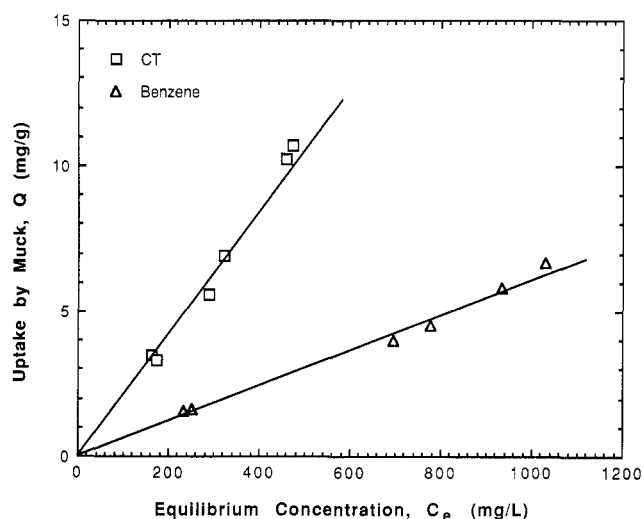


Figure 5. Uptake of carbon tetrachloride and benzene from water on muck as a function of equilibrium concentration.

Table II. Sorption Coefficients (K_{om}) from Water Normalized for the Organic Matter Content of the Sorbent for Benzene, Trichloroethylene, and Carbon Tetrachloride and Respective Molar Volumes (V_i) and Octanol-Water Partition Coefficients (K_{ow})

compd	K_{om}		V_i , mL/mol	K_{ow}^a
	peat	muck		
benzene	12.5	7.67	89.2	135
TCE	33.1	nd ^b	89.7	407
CT	44.6	27.8	96.9	676

^a Values for benzene and CT from ref 18; value for TCE from ref 19. ^b nd, not determined.

benzene and CT with muck are shown in Figure 5. Again, the isotherms are all highly linear, with the equilibrium concentrations (C_e) extended to more than 50% solute solubility in water (S_w), and these results are in keeping with solute partition in the SOM of peat and muck samples. The partition coefficients of these solutes between SOM and water (i.e., the K_{om} values) are obtained by normalizing the sorption coefficients for the organic content of peat and muck (i.e., by correcting for the ash content of the dry sample); results are given in Table II. On each soil sample, the log K_{om} values of the solutes are inversely related to the solutes' log molar solubilities in water, based on reported values of 1780, 1100, and 800 mg/L for benzene, TCE, and CT, respectively (17). Similarly, the log K_{om} values correlate linearly with the respective log K_{ow} (octanol-water) values (Table II). For each solute, the greater K_{om} value with peat than with muck is consistent with the effect of polar group content of these samples on solute partition, as discussed in more detail in the earlier work (15).

To determine the influence of water saturation on the organic compound partition in SOM, we first normalized the aqueous isotherms from the conventional form of Q vs C_e to the form of Q vs C_e/S_w . The normalized aqueous isotherms can then be superimposed on the (normalized) vapor-phase isotherms (Q vs P/P°) for comparison, since $C_e/S_w = P/P^\circ$ for a sparingly soluble liquid at vapor-liquid equilibrium. The requisite plots are given in Figure 6 for benzene and CT on peat (the TCE plot is not shown to ease the congestion of the data). The respective plots for benzene and CT on muck are shown in Figure 7. The extrapolated Q values at $P/P^\circ = 1$ or $C_e/S_w = 1$ (designated as Q°) and subsequent normalization of Q° to SOM content of the samples define the solutes' solubilities in

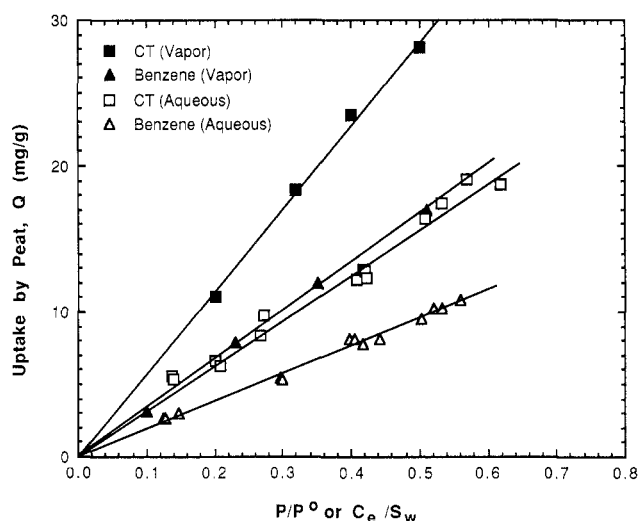


Figure 6. Comparison of uptakes of carbon tetrachloride and benzene from vapor phase (Q vs P/P°) and from water (Q vs C_e/S_w) on peat.

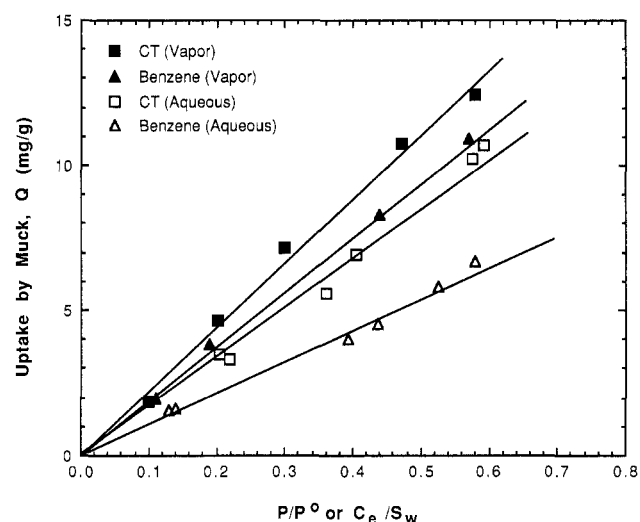


Figure 7. Comparison of uptakes of carbon tetrachloride and benzene from vapor phase (Q vs P/P°) and from water (Q vs C_e/S_w) on muck.

Table III. Partition Capacities Normalized for the Organic Matter Content of the Sorbent (Q_{om}°) and Volume-Fraction Solubilities (ϕ°) of Benzene, Trichloroethylene, and Carbon Tetrachloride

compd	SOM	aqueous		vapor	
		Q_{om}° , mg/g	ϕ°	Q_{om}° , mg/g	ϕ°
benzene	peat	22.0	0.0291	38.9	0.0541
TCE	peat	36.4	0.0290	80.0	0.0667
CT	peat	35.6	0.0261	65.9	0.0510
benzene	muck	13.7	0.0189	23.4	0.0339
CT	muck	22.2	0.0165	30.7	0.0244

SOM of dry and water-saturated samples (Q_{om}°). The Q_{om}° values of selected organic liquids with SOM of peat and muck are given in Table III.

Comparison of the isotherms for dry and water-saturated samples illustrates that water saturation reduces the partition efficiency of the organic matter in peat (on a dry basis) by 44% for benzene, 55% for TCE, and 46% for CT; the decrease in partition efficiency by water of the organic matter in muck is 41% for benzene and 28% for CT. The smaller effect of water on the organic partition in SOM of muck may reflect a smaller change in medium polarity of muck SOM (than that of peat SOM) by water saturation since the intrinsic SOM of muck has a larger polar group content (Table I). Despite a significant difference in the

extent of partition reduction by water for compounds in SOM of peat and muck, the magnitude of this reduction (by an average of 42% for peat and muck) is small in comparison with the nearly complete suppression by water saturation of adsorption of organic compounds on the mineral matter in soil (4, 5). The small effect of water on organic uptake by SOM is what one would expect for the change in the solvency of polar SOM by moderate amounts of water.

The effect of water saturation on solute partition in SOM is difficult to account for quantitatively from current solution theories, which deal effectively only with nonpolar solute-solvent systems; however, this effect can be described qualitatively by considering the influence of water saturation in a solvent on the molecular interaction forces between the solvent and solute. According to Flory (20), the solubility of a liquid solute in a (amorphous) polymer in which the molar volume of the liquid is negligibly small compared to that of polymer can be expressed as

$$\ln \phi^\circ + \phi_p + \chi \phi_p^2 = 0 \quad (1)$$

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 expressing the extent of molecular interaction between solute and polymer. The χ value is a sum of χ_s , the excess entropic contribution to solute-polymer interactions, and χ_h , the excess enthalpic contribution to solute-polymer interactions. To a good approximation, χ_s is only a function of the accessibility and flexibility of the chain segments in the polymer. For relatively nonpolar solutes in (polar) SOM, it has been shown that the contribution χ_s to χ is small relative to χ_h (10, 14).

According to Hildebrand (21), if the contribution to the incompatibility of a solute in a polymer, other than that of the size disparity, follows the regular solution theory, then χ_h can be reasonably correlated by the solubility parameters of solute and polymer. In this case

$$\chi_h = (V_i/RT)(\delta_i - \delta_p)^2 \quad (2)$$

where V_i is the molar volume of the solute, R is the gas constant, T is the absolute temperature, δ_i is the solubility parameter of the solute, and δ_p is the solubility parameter of the polymer. By eqs 1 and 2, the solubility of a solute in polymer decreases with increasing χ_h or with increasing $(\delta_i - \delta_p)^2$.

Because the δ of a substance usually increases with polarity, the δ_i values for relatively nonpolar compounds are therefore small and relatively constant compared to δ_p for the polar SOM. For instance, δ_i is 9.2 (cal/cm³)^{0.5} for benzene, 9.2 (cal/cm³)^{0.5} for TCE, and 8.6 (cal/cm³)^{0.5} for CT (22), whereas the δ_p for a water-saturated SOM was estimated to be ~13.0 (cal/cm³)^{0.5} in an earlier study (2). The fact that benzene, TCE, and CT partition more effectively in dry SOM of peat and muck than in respective water-saturated SOM suggests that δ_p for SOM increases with water saturation.

When computations are carried out for δ_p by substituting into eqs 1 and 2 the calculated ϕ° values in Table III, the solute molar volumes (V_i), and the assumption of $\chi_s = 0.25$ as assigned earlier (2), the average δ_p is 12.5 for dry peat SOM and 13.0 for the water-saturated peat SOM. Similarly, the average δ_p calculated for dry muck SOM is 12.9 and 13.3 upon water saturation. When ϕ° is calculated, the density of dry SOM is assumed to be 1.3 g/cm³ and that of water-saturated SOM to be 1.2 g/cm³, taking into account the solubility of water in SOM. The greater δ_p for water-saturated SOM (and hence the reduction in solute solubility in SOM by water saturation) can thus be at-

tributed to an increased medium polarity of SOM by water saturation, which makes it less favorable for solute partition. Since the δ_i values for nonpolar compounds are relatively comparable, one may expect according to eqs 1 and 2 that the volume fraction solubility (ϕ°) and the effect of water saturation on solute partition in a given SOM should be comparable for nonpolar liquids; for solid compounds, the solubility is corrected for the solid activity (8, 11). This expectation is largely consistent with the present findings.

For the solubility of nonpolar solutes in nonpolar solvent mixtures, Hildebrand (21) suggested that the solubility parameter of a binary solvent mixture can be approximated as

$$\delta_i^* = \phi_1 \delta_1 + \phi_2 \delta_2 \quad (3)$$

where ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2 and δ_1 and δ_2 are their respective solubility parameters as pure components. Unfortunately, eq 3 does not apply effectively for solvent mixtures containing polar components (especially, water) to render a reasonable prediction of δ_p^* for water-saturated SOM. Hence, when one substitutes into eq 3 the δ_p values for SOM in dry peat and muck (12.5 and 12.9, respectively), the suggested (but highly uncertain) solubility parameter for water (δ_w) of 23.4 (22), and the respective volume fractions of water and SOM (obtained from amounts of water saturation in SOM of peat and muck), the calculated δ_p^* for water-saturated SOM of peat and muck is ~16.0, which is nearly 3 units greater than the value calculated by use of eqs 1 and 2; i.e., it would grossly underestimate the observed solute solubility in the water-saturated SOM. In the present systems, eq 2 probably gives a better estimate of δ_p^* for water-saturated SOM than eq 3 in consideration of the ineffectiveness of eq 3 for polar solvents. While more complex treatments of the solubility parameters for polar substances exist, which separate δ into London, polar, and hydrogen-bonding interactions, the lack of definitive information on the relative contributions of these forces would make such an approach impractical for predicting the solute solubility in our systems.

In summary, this study shows that the effect of water saturation on the uptake of low-polarity solutes by SOM in soil is small in comparison with the suppressive effect of water on the adsorption by soil minerals. This effect is attributed to the higher polarity of the water-saturated SOM; it may be qualitatively expressed in terms of the change in solubility parameter of SOM according to regular solution theory. The effect of moisture at subsaturation in SOM is expected to be correspondingly lower than for water-saturated SOM, for the expected reduction in partition capacity is no more than 50%. For normal soils low in SOM content, the major effect of a drying-wetting cycle on the organic compound uptake would therefore be the marked suppressive effect of water for adsorption onto the exposed mineral fraction. Consequently, the chemical activity of low-polarity solutes in SOM is only moderately increased by water saturation; by contrast, the water saturation would greatly enhance the chemical activity of these solutes in soils low in SOM content by suppressing the mineral adsorption.

Acknowledgments

We thank Dr. Ronald L. Malcolm of the U.S. Geological Survey for the gift of peat sample and Dr. Stephen A. Boyd of Michigan State University for the gift of muck sample used in this work. We also thank Dr. Milton Manes, Professor Emeritus, Kent State University for valuable

discussion of and comments on the manuscript.

Registry No. TCE, 79-01-6; CT, 56-23-5; benzene, 71-43-2.

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Received for review August 27, 1991. Revised manuscript received December 20, 1991. Accepted December 30, 1991. The use of trade and product names in this article is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Deposition of S and NO_x Nitrogen to the Great Lakes Estimated with a Regional Deposition Model

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■ Atmospheric loading of anthropogenic S and NO_x N to the Great Lakes is estimated with a regional deposition model. Dry deposition calculations include the effects of the wet surface and the predominant seasonal atmospheric boundary-layer structure over the lakes, i.e., strong stability in spring and summer and strong instability in autumn and winter. Modeling results are generally consistent with objective analyses of observed deposition. Best agreement is shown for the lower lakes; the model appears to underestimate deposition to Lake Superior, particularly for S. The analyses themselves contain large uncertainties, especially for Lake Superior, because all monitoring is over land and dry deposition monitoring is also both sparse and indirect. Examination of S and N mass budgets for Lake Superior indicates that the atmospheric pathway plays an important role in total loading and that the atmospheric pathway is more important for N than for S. An examination of modeled and observed S deposition trends during the 1980s illustrates the difficulty in separating possible emission-related trends in deposition from meteorologically induced variability and uncertainties in modeling or analysis when the emission changes are relatively small.

Introduction

The Great Lakes, together with their land drainage areas, form a combined basin of approximately 7.5×10^5

km², with the lakes covering one-third of the area. Atmospheric deposition to the Great Lakes ecosystem is an issue of continuing concern (1), because wet or dry deposition directly to the lakes is believed to constitute the major input mechanism for many nutrients and toxic substances (2-4). Atmospheric deposition to the land basins and subsequent collection in runoff may be a significant additional input. Horizontal mixing within each lake reduces any gradient in cumulative deposition loading, particularly dry, that might otherwise occur downwind of sources near the shore; thus, integrated deposition across the various lakes and land basins should be the most useful measure of loading.

While deposition of heavy metals and toxic organic compounds is the most critical issue in atmospheric loading to the Great Lakes, monitoring data for those pollutants are generally insufficient for reliable estimation of atmospheric loading. An alternate approach is to estimate such loading with models; modeling has the important additional advantage of potential use with future emission scenarios. However, for most toxic substances, significant difficulties occur in determining model emissions input, in quantifying and parameterizing removal processes, and in verifying model output. In contrast, the intensive investigation of acidic deposition during the last decade has produced a wealth of observational data and regional deposition modeling studies for SO_x and NO_x. Thus, in this