

Sorption of Selected Organic Compounds from Water to a Peat Soil and Its Humic-Acid and Humin Fractions: Potential Sources of the Sorption Nonlinearity

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The sorption isotherms of ethylene dibromide (EDB), diuron (DUN), and 3,5-dichlorophenol (DCP) from water on the humic acid and humin fractions of a peat soil and on the humic-acid of a muck soil have been measured. The data were compared with those of the solutes with the whole peat from which the humic-acid (HA) and humin (HM) fractions were derived and on which the sorption of the solutes exhibited varying extents of nonlinear capacities at low relative concentrations (C_e/S_w). The HA fraction as prepared by the density-fractionated method is relatively pure and presumably free of high-surface-area carbonaceous material (HSACM) that is considered to be responsible for the observed nonlinear sorption for nonpolar solutes (e.g., EDB) on the peat; conversely, the base-insoluble HM fraction as prepared is presumed to be enriched with HSACM, as manifested by the greatly higher BET-(N₂) surface area than that of the whole peat. The sorption of EDB on HA exhibits no visible nonlinear effect, whereas the sorption on HM shows an enhanced nonlinearity over that on the whole peat. The sorption of polar DUN and DCP on HA and HM display nonlinear effects comparable with those on the whole peat; the effects are much more significant than those with nonpolar EDB. These results conform to the hypothesis that adsorption onto a small amount of strongly adsorbing HSACM is largely responsible for the nonlinear sorption of nonpolar solutes on soils and that additional specific interactions with the active groups of soil organic matter are responsible for the generally higher nonlinear sorption of the polar solutes.

Introduction

It is well established that the soil/sediment organic matter (SOM) acts primarily as a partition medium (1–5) and the mineral matter as an adsorbent in the sorption of nonionic organic compounds (6–8). In aqueous solution, the soil/sediment sorption of low-polarity organic solutes usually occurs mainly by partition into SOM, unless the SOM content

is very low, because the adsorption on mineral matter is strongly suppressed by the competitive adsorption of water (3, 6, 7). In such cases, the solute sorption isotherm is largely linear over a wide range of relative concentrations (C_e/S_w) (1–7), where C_e is the equilibrium concentration and S_w is the water solubility of the solute. It has recently been illustrated, however, that the sorption of both nonpolar and polar compounds, as single solutes in water, to some soils or natural solids displays varying extents of a nonlinear sorption (of a concave-downward shape) at low C_e/S_w even when the SOM content is significant (9–16); the nonlinear uptake of a solute at low C_e/S_w may be depressed to different extents by other solutes (i.e., cosolutes) in multiple-solute systems (9, 15, 16). Notable nonlinear effects found in an earlier study (16) include the following: (i) the smaller nonlinear range and nonlinear capacity for nonpolar solutes; (ii) the relatively polarity-independent suppression of the nonlinear sorption of a nonpolar solute by a cosolute; (iii) the highly polarity-dependent suppression of the nonlinear sorption of a polar solute by a cosolute; and (iv) the inadequacy of the BET-(N₂) surface area to account for the nonlinear capacity of a highly polar solute.

Several hypotheses have been proposed to account for the nonlinear solute sorption at low C_e/S_w on soils or natural solids having a significant SOM content. The glassy-rubbery SOM model of Weber and co-workers (11–13) considers the sorption of nonionic solutes to natural solids to be a composite of a linear partition to the rubbery portion of the SOM and a nonlinear uptake (or adsorption) to the glassy portion of the SOM. The model offers no specific accounts of the different nonlinear effects for polar and nonpolar solutes nor of the specific surface properties of the assumed glassy SOM. The internal-hole model of Pignatello and co-workers (14, 15) postulates the occurrence of a solute-specific adsorption into SOM internal holes in conjunction with a linear solute partition to the SOM matrix; the internal holes (or their “surface areas”) are considered to be inaccessible to inert gases (e.g., N₂) and therefore cannot be verified by conventional characterization methods. To reconcile the multiple nonlinear effects mentioned earlier, Chiou and Kile (16) postulated that the nonlinear sorption of nonpolar solutes on soils/sediments results from adsorption on a small amount of a high-surface-area carbonaceous material (HSACM), such as a charcoal-like substance or soot (16, 17); the more enhanced nonlinear effect for polar solutes is ascribed to their specific interactions with active SOM groups, as suggested by Spurlock and Biggar (10), in addition to adsorption on HSACM. For both polar and nonpolar solutes, partition into SOM is considered to predominate the soil/sediment sorption at moderate to high C_e/S_w . The HSACM hypothesis is compatible with the well-known occurrence of trace charcoal-like substance or soot, which results from biomass or fuel burning, in many soils/sediments and natural solids (18–20).

Although the complete isolation of small amounts of HSACM (e.g., a charcoal-like substance) from ordinary soils/sediments for sorption studies is extremely difficult because of the small HSACM mass and the lack of effective isolation techniques, microscopic identification of a charcoal-like substance (e.g., fusinite) in natural solids and illustration of the associated impact on the sorption behavior of the natural solids has been presented in a recent work by Grathwohl and co-workers (21). As shown by these authors, the low-concentration sorption isotherms of a nonpolar compound (phenanthrene) on natural solids (limestone and sandstone grains) exhibit the greatest nonlinear sorption and the highest

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organic-carbon-normalized Freundlich coefficients with solids where the particle organic matter comprises predominantly charcoal particles and reworked vitrinite. As expected, the solid grains (geosorbents) containing charcoal particles show increased amounts of microporosity (22). The mineral matter of these geosorbents contributes little to phenanthrene adsorption because of the adsorptive competition of water (21).

Another independent support of the HSACM hypothesis for nonpolar solutes is given by Xia and Ball (23). Recognizing that the Polanyi-Manes adsorption potential theory (24) is most appropriate for accounting for solute pore-filling adsorption on the HSACM, the authors applied it to analyze the nonlinear sorption fractions of nine relatively nonpolar single solutes on an aquitard material. A plot of the "adsorbed solute volume" vs the solute adsorption potential per unit molar volume for all liquid solutes yields essentially a single correlation curve and thus about the same limiting adsorption volume. A similar plot for the solid solutes shows reduced adsorption capacities and limiting adsorption volumes, due supposedly to a less efficient packing for solid adsorbates within the porous adsorbent structure. These unique characteristics, which are well recognized for adsorption of organic compounds onto activated carbon (24), are intrinsically consistent with the expected effect of HSACM in a natural solid on the behavior of liquid and solid solutes.

Since the charcoal-like material or soot (HSACM) in soil is not an intrinsic component or a structural segment of the soil humic material, it may in principle be removed by appropriate means from the soil, although its complete isolation is very difficult for reasons as mentioned before. In this study, relatively pure, HSACM-free humic acids (HAs) from a peat soil and a muck soil and a presumably HSACM-enriched humin (HM) fraction from the peat soil were prepared for further evaluation of the solute sorption behavior. The same peat soil was used earlier as the sorbent (16), with which both polar and nonpolar solutes exhibited a sorption nonlinearity at low C_e/S_w . The much smaller nonlinear sorption occurring at relatively low C_e/S_w for nonpolar solutes with the peat soil was attributed to adsorption on a small amount of HSACM in the soil, concurrent with solute partition into SOM.

According to the HSACM and specific-interaction (SI) hypothesis, hereafter referred to as the HSACM-SI model, the sorption of a nonpolar solute on HSACM-free HA is expected to exhibit greatly reduced nonlinearity from low to high C_e/S_w , while the sorption of a polar solute on the same HA should remain nonlinear at low C_e/S_w because of the presumed additional solute-SOM specific interaction. Further, the sorption of all solutes (nonpolar and polar) to HSACM-enriched HM is expected to exhibit either an enhanced or a comparable nonlinear uptake at low C_e/S_w relative to that exhibited by the peat soil from which HA and HM are prepared. In this study, the intended sorption data of selected nonpolar and polar solutes on relatively pure HA and HSACM-enriched HM are presented and compared with the corresponding data of the solutes with the original peat soil to further evaluate the relative merits of the current nonlinear-sorption models.

Experimental Section

Materials. The test organic compounds, ethylene dibromide (EDB) (99+% in purity), diuron (DUN) (96%), and 3,5-dichlorophenol (DCP) (99%), were purchased from Aldrich Chemical Co. and used as received. The physicochemical properties of these compounds are presented in the earlier study (16); the water solubilities at room temperature are as follows: 3520 mg/L (EDB), 38 mg/L (DUN), and 8050 mg/L (DCP). The solid samples (i.e., sorbents) include the following: a peat soil, the humic acid (HA), and humin (HM)

TABLE 1. BET-(N₂) Surface Areas (SA) and Percents of Organic Carbon (OC) of the Sorbents

sorbent	OC (%)	SA (m ² /g)	sorbent	OC (%)	SA (m ² /g)
peat	49.3	1.4	muck HA	46.3	0.17
peat HA	47.3	0.16	HM	51.4	4.5

fractions derived from the same peat soil, and the HA derived from a muck soil. The peat soil is the reference sample of the International Humic Substances Society (IHSS), collected from Everglades, FL. The muck soil is from the Michigan State University Muck Research Farm, Lainsburg, MI. The earlier study with this peat soil suggests that a small amount of HSACM is contained in the soil, as inferred by the small but distinct nonlinear sorption of nonpolar solutes at relatively low C_e/S_w , the compliance of the nonlinear-sorption capacities with the surface adsorption capacity of the soil, according to the measured BET-(N₂) surface area, and the general adsorptive competition between the solutes (16). The HA and HM fractions were prepared by the procedures described below with the intention that the resulting HA sample would be largely free of HSACM, while the HM sample would be enriched with HSACM relative to that in the soil. The BET-(N₂) surface areas and the organic carbon contents of the peat soil, HA, and HM samples are given in Table 1. The samples were ground to pass an 80-mesh sieve, uniformly mixed, and oven-dried overnight at 90 °C prior to the sorption experiment.

Sample Preparation. Relatively pure HAs were extracted from the Florida peat soil and Michigan muck soil according to the procedures recommended by IHSS. To each of six 250-mL glass centrifuge bottles, 20 g of the peat or muck soil was added, and each bottle was filled with 200 mL of distilled water. The pH of the soil suspensions was then adjusted to 1–2 with 1 M HCl. After shaking for 1 h, the suspensions were centrifuged (at 6555g, 30 min) and the supernatants decanted. The solids were then neutralized by 1 M NaOH to pH 7, and 200 mL of 0.1 M NaOH was added to resuspend the solids under a N₂ stream. The suspensions were immediately sealed, shaken overnight, and centrifuged. The supernatants were decanted, acidified with 6 M HCl to pH 1, and allowed to sit for 24 h before the humic acid (HA) and fulvic acid (FA) fractions were separated by centrifugation.

The precipitated HA fraction was then redissolved in a minimum amount of 0.1 M KOH under N₂, to which KCl was added to give approximately 0.3 M for K⁺. The HA solution was again centrifuged to remove the suspended solids. This dissolution-precipitation procedure was repeated three times. It was assumed that the HSACM particles associated with the peat or muck soil were relatively resistant to acidic or alkaline solution and had densities greater than that of the solution so that they would precipitate upon centrifugation. The HA solution was then acidified and transferred to a dialysis bag having a molecular cutoff of 12 000–14 000 Daltons; it was dialyzed with distilled water until the test for Cl[−] in water with AgNO₃ turned negative. The dialysis step also removed the residual FA in HA. The solid HA was obtained by air-drying the HA solution at room temperature in a fume hood. The HA samples from replicate experiments were combined and uniformly mixed.

The HSACM-enriched HM fraction was prepared from the Florida peat soil. To each of six 250-mL polyethylene bottles was added 50 g of the peat, and each bottle was filled with about 200 mL of 0.1 M NaOH solution. The suspensions were equilibrated overnight. Upon centrifugation of the suspensions (at 3323g, 30 min), the supernatants were decanted off, refilled with 200 mL of fresh 0.1 M NaOH solution, and allowed to reequilibrate with the remaining peat. This dissolution-precipitation cycle was repeated about

50 times so that the HSACM content of the undissolved solid peat (i.e., the designated HM fraction) could be greatly enriched. After this exhaustive sample treatment, the mass of the HM fraction (i.e., the residual solid) corresponded to about 10% of the starting peat. The resulting HM was rinsed by deionized water to remove its alkalinity and then air-dried. The HM samples from replicate experiments were combined and uniformly mixed.

Sorption Experiments. The procedures for sorption equilibration consisted of adding either 0.3–0.5 g of HA (or HM) or 1.0 g of whole peat to 25-mL screw-capped Corex centrifuge tubes with 0.005 M CaCl₂ water solutions to which different amounts of test solutes were added. With whole peat as the sorbent, the solution pH was 4.9–5.1, and no pH adjustment was made (16). When HA and HM were used as the sorbents, the solution pH was maintained at 4.5–5.0 by use of 0.1 M HCl. Over this pH range, DUN and DCP remained undissociated (16). The dissolved organic carbon (DOC) concentrations in water were 16, 30, 43, and 178 mg/L, when HM, peat HA, muck HA, and whole peat were used respectively as the sorbents. The samples were equilibrated for 2–3 days on a rotary mixer at room temperature (24 ± 1 °C). After equilibration, the solid and solution phases were separated by centrifugation (2990g, 1 h). EDB and DCP in water were extracted by hexane and DUN by dichloromethane. All solutes with solid phases were extracted by use of 1:4 acetone–hexane solvent mixtures. These extracts were analyzed for the solute by gas chromatography. Mass recoveries were 90–100% for EDB, 75–100% for DUN, and 80–100% for DCP, with values > 90% for EDB and DCP and > 80% for DUN in most experiments. The solute uptake by a sorbent was corrected for the amount in residual water with the sorbent phase. At the stated DOC levels in water, no significant solubility enhancement of the solutes by DOC was expected (25), and no correction was made for the loss of the sorbent by dissolution in water when calculating the solute uptake by the sorbent. The sorption data of EDB, DUN, and DCP on whole peat were reported earlier (16) and are reproduced in this study.

Results and Discussion

The sorption isotherms of nonpolar ethylene dibromide (EDB) from water to the two HA sorbents are presented in Figure 1(a), in which the EDB uptake by the sorbent (mg/g) is plotted against the EDB relative concentration in water (C_e/S_w). The corresponding isotherms for EDB on whole peat and peat-derived HM are shown in Figure 1(b). The EDB isotherms on both HAs exhibit virtually no visible nonlinearity from low to high C_e/S_w ; the high linearity is indicative of solute partition into SOM being the dominant sorption mechanism. In contrast, the EDB isotherms on whole peat and (peat-derived) HM display a noticeable nonlinearity at low C_e/S_w . The apparent nonlinear capacity (Q_{ans}) of EDB with HM, i.e., the value extrapolated from the upper linear isotherm to the ordinate axis, is much greater than with whole peat; the extent of EDB sorption nonlinearity at low C_e/S_w , as characterized by the Freundlich n exponent in Table 2, is also somewhat higher with HM than with whole peat. The increased linearity at moderate to high C_e/S_w reflects dominance of the solute uptake by partition into SOM. The partition capacities of EDB on the two HAs are practically equal. The uptake capacity of EDB on whole peat at all but low C_e/S_w is also about the same as that on peat HA.

The sorption isotherms of moderately polar diuron (DUN) on the same four sorbents are illustrated in Figure 2, in which the sorption on HM exhibits the highest uptake and nonlinear capacity relative to the sorption on other sorbents studied. The DUN uptake capacities on the two HAs are comparable in magnitude, being slightly lower than that on the whole peat. The sorption isotherms of more polar 3,5-dichlorophe-

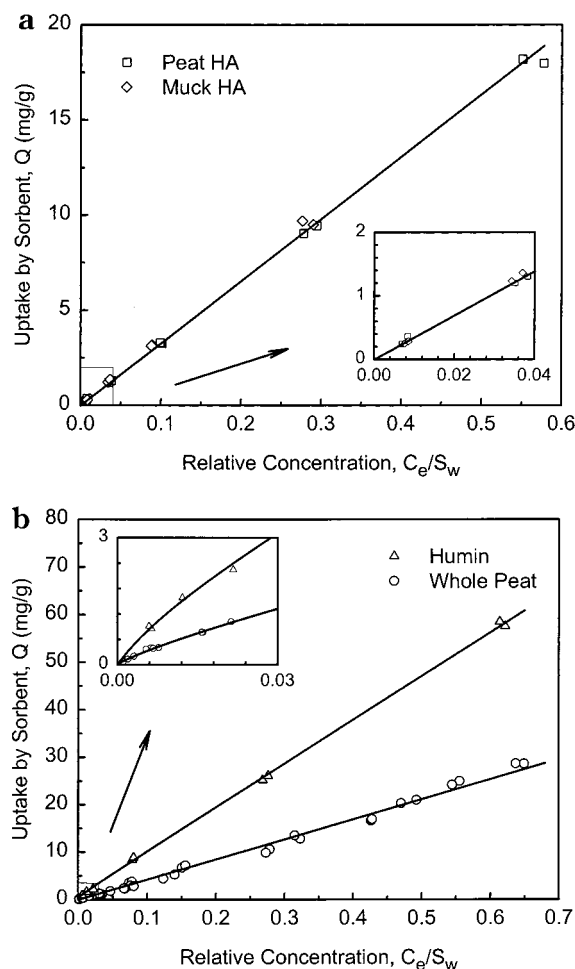


FIGURE 1. (a) Sorption isotherms of EDB from water on peat HA and muck HA. (b) Sorption isotherms of EDB from water on whole peat and peat humin.

TABLE 2. Apparent Nonlinear Saturation Capacities (Q_{ans}), Nonlinear Saturation Points [$(C_e/S_w)_{ans}$], and Freundlich Exponents (n) for the Sorption of Selected Solutes on Sorbents

solute/sorbent	Q_{ans} (mg/g)	$(C_e/S_w)_{ans}$	n_1^a	n_2^a
EDB/peat ^b	0.18	0.010	0.91	0.99
EDB/peat HA	~0	~0	1.00	1.00
EDB/muck HA	~0	~0	1.00	1.00
EDB/HM	0.50	0.018	0.88	1.00
DUN/peat ^b	0.60	0.10	0.63	1.00
DUN/peat HA	0.40	0.12	0.72	0.99
DUN/muck HA	0.50	0.10	0.72	0.99
DUN/HM	2.0	0.17	0.51	0.94
DCP/peat ^b	25	0.12	0.56	0.98
DCP/peat HA	16	0.10	0.61	1.00
DCP/muck HA	16	0.12	0.61	1.00
DCP/HM	45	0.13	0.41	1.00

^a n_1 is the best-fit n exponent at $P \leq 0.05$ in Freundlich plot, $Q = K(C_e/S_w)^n$, for the sorption data within the stated nonlinear range, i.e., at $C_e/S_w \leq (C_e/S_w)_{ans}$; n_2 is the corresponding best-fit n value at $P \leq 0.05$ for the sorption data at $C_e/S_w \geq (C_e/S_w)_{ans}$. ^b The data on peat are taken from ref 16.

nol (DCP) on the four sorbents are shown in Figure 3. Again, the sorption on HM exhibits the highest capacity and nonlinear effect, and the sorption isotherms with whole peat, peat HA, and muck HA are relatively comparable. The apparent nonlinear capacities and the apparent nonlinear saturation points, $(C_e/S_w)_{ans}$, determined manually as described earlier (16), for the studied solutes on all sorbent

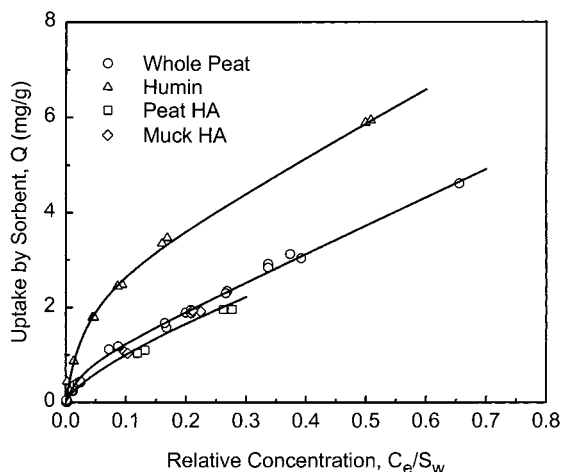


FIGURE 2. Sorption isotherms of DUN from water on whole peat, peat HA, muck HA, and peat humin.

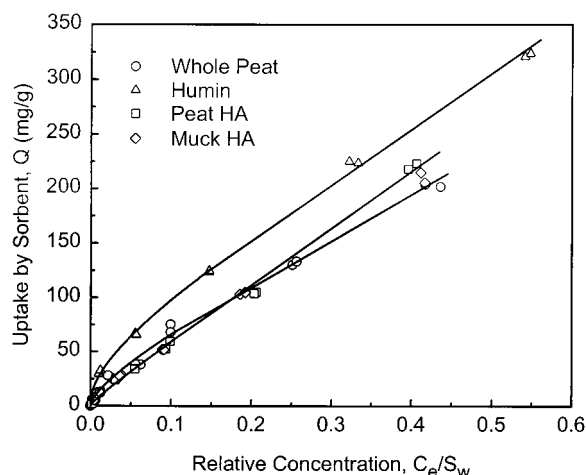


FIGURE 3. Sorption isotherms of DCP from water on whole peat, peat HA, muck HA, and peat humin.

samples are given in Table 2. These values are only semi-quantitative because the transition points between nonlinear and linear sorption ranges are usually, and as expected, not sharp (16, 23). As noted graphically in Figures 1–3 and with the Freundlich n exponents in Table 2, the sorption isotherms at $C_e/S_w > (C_e/S_w)_{\text{ans}}$ are essentially linear.

Consider first the sorption data of EDB. As shown in Table 1, the peat HA exhibits a much lower BET-(N_2) surface area than the original peat ($0.16 \text{ m}^2/\text{g}$ vs $1.4 \text{ m}^2/\text{g}$), due presumably to the removal of HSACM from the peat when the HA was prepared by density-fractionation. In the earlier study with the peat (16), the observed sorption nonlinearity at low C_e/S_w for nonpolar solutes (e.g., EDB) was ascribed to adsorption on a small amount of strongly adsorbing HSACM, concurrent with solute partition into SOM. The absence of a nonlinear sorption at low C_e/S_w with density-fractionated HA is consistent with that hypothesis. The base-insoluble HM fraction prepared from the peat contains presumably a greater proportion of HSACM per unit mass than the original peat, as manifested by the approximately 3-fold higher BET-(N_2) surface area of the HM ($4.5 \text{ m}^2/\text{g}$ vs $1.4 \text{ m}^2/\text{g}$). The comparable organic-carbon contents with HM and whole peat (Table 1) suggest that the increased surface area of HM over that of the whole peat is not related to the mineral or ash content of the sample. As noted in Table 2, the nonlinear capacity of EDB on HM (about 0.50 mg/g) is approximately three times the capacity on the peat (0.18 mg/g), again consistent with the HSACM hypothesis. In all cases, the BET-(N_2) surface areas of the sorbents are sufficient to account for the EDB

nonlinear capacities, in which $1 \text{ m}^2/\text{g}$ of a porous carbonaceous material corresponds to about 0.25 mg/g of an adsorbate with a density (ρ) of 1 g/mL at the point of the monolayer adsorption, which occurs at relatively low C_e/S_w (16); for adsorbates with $\rho \neq 1 \text{ g/mL}$, the adsorbed mass is adjusted approximately by a factor of $\rho^{2/3}$. The much higher EDB linear uptake on HM than on other sorbents at moderate to high C_e/S_w suggests that the organic medium of HM is less polar than that of the peat or peat-derived HA. The partition of nonpolar solutes to organic media is known to be sensitive to the polarity of the medium (26).

The nonlinear capacity of DUN on the peat is about 0.60 mg/g (16), which is considered to result both from its specific interaction with active SOM groups and from its adsorption on a small amount of HSACM. On this basis, the nonlinear capacity of DUN on peat HA is expected to be only slightly lower than that on the peat, since the partition uptakes by these two samples should be about the same based on the EDB partition data. The observed value (about 0.40 mg/g) is consistent with the estimation. Conversely, the nonlinear capacity of DUN on HM is expected to be greater than that on the peat because HM has a much higher surface area (and presumably more HSACM), if the active sites in peat and HM are not vastly different. The noted nonlinear capacity for DUN on HM (about 2.0 mg/g) agrees semiquantitatively with the expectation. The surface area of HM (or the HSACM contribution) is not sufficient to account for the nonlinear capacity of DUN on HM. The slope of the upper DUN-HM isotherm, which reflects the DUN partition effect, is similar to that of DUN on the peat (Figure 2). This indicates that the reduced HM medium polarity affects less significantly the partition uptake of a moderately polar solute (DUN) than that of a nonpolar solute (EDB).

The sorption of DCP on peat, HA, and HM exhibits trends similar to those observed for the DUN sorption. For relatively polar DCP, the nonlinear effect is considered to result predominantly from its specific interaction with active SOM groups (10, 16). Here the nonlinear capacity of DCP is about 25 mg/g with the peat, 16 mg/g with HA, and 45 mg/g with HM (Table 2). The disparate nonlinear capacities of DCP on these sorbents appear to reflect some changes in either the affinity or the abundance of the active-sites in HA and HM materials when prepared from the peat soil. It is also noted that the manual method for estimating the nonlinear capacity (and the nonlinear saturation point) is sensitive to minor data scattering. Nonetheless, the nonlinear capacities for DCP on all sorbents are far too high to be reconciled with the measured BET-(N_2) surface areas alone. This supports the view that solute-SOM specific interactions (or other not-surface-area related effects yet to be defined) predominate over the much weaker solute adsorption on a small amount of HSACM for the nonlinear sorption of relatively polar solutes. The presumed different sources for the nonlinear effects of polar and nonpolar solutes is further illustrated by their different nonlinear-sorption ranges, i.e., the observed $(C_e/S_w)_{\text{ans}}$ values are considerably greater for polar DCP and DUN than for nonpolar EDB (Table 2). As with the DUN sorption, the slope of the upper DCP-HM isotherm is comparable with that of DCP on the peat (Figure 3), suggesting that the polarity of the sorbent does not significantly affect the partition uptake of a relatively polar solute.

The nonlinear sorption characteristics of EDB, DUN, and DCP on the four sorbents, as illustrated, are intrinsically consistent with the expectations of the HSACM-SI model, in which the observed nonlinear capacities for nonpolar EDB are well related to the BET-(N_2) surface areas (or to the presumed amounts of HSACM) of the sorbents, whereas those for polar DUN and DCP call for additional specific interactions with SOM. The diversity of the data cannot be readily reconciled with the glassy-rubbery SOM model nor with the

internal-hole model without much additional *ad hoc* hypothesis. The glassy-rubbery SOM model, adapted originally for nonpolar solutes on natural solids, does not consider specifically the disparate nonlinear effects between polar and nonpolar solutes. The present sorption data with density-fractionated HA and base-insoluble HM would force this model to further assume that the availability or the effect of the glassy component in SOM depends also on the solute polarity; for nonpolar solutes, the glassy component (or its effect) exists in HM but not in HA, whereas for polar solutes it occurs in both HA and HM. To reconcile the present data, the internal-hole model would similarly have to further assume that the compound-specific internal holes accessible to nonpolar solutes are located only in HM, but those accessible to polar solutes exist in both HA and HM. It is difficult, however, to rationalize the inconsistent pictures on the source/availability of the glassy component or internal holes in SOM, since both polar and nonpolar solutes partition effectively into the organic-matter matrix of HA or HM and thus should have equal chances to gain access to the presumed glassy SOM or internal holes.

Given the sorption data from this and earlier studies (16, 23) and the illustrated properties and effect of charcoal-like substance in natural solids on sorption nonlinearity (21, 22), there is good evidence that adsorption on small amounts of HSACM in soils or natural solids is at least a significant contribution to the nonlinear effect of nonpolar compounds at low C_e/S_w . Although the available information at this time does not exclude the possibility of other nonlinear sources for nonpolar compounds, e.g., other materials in natural solids with carbon-like adsorptive properties, the HSACM model is currently supported by more experimental evidence. For the nonlinear effect of polar solutes, such as DCP on HA in this work, where the nonlinear capacity surpasses greatly the amount attributable to surface adsorption, the solute-SOM specific interaction, as suggested by Spurlock and Biggar (10), is a reasonable explanation to the greater nonlinear effect, although the mode of specific interaction remains to be substantiated. At this point, more efforts are needed to explore all possible nonlinear sources and causes for nonionic compounds with soils and natural solids.

In summary, the sorption data of EDB, DUN, and DCP on density-fractionated HA and base-insoluble HM fractions of a peat soil and the associated BET-(N₂) surface areas of the samples are analyzed together with the corresponding data of the solutes with the whole peat to test the merits of the various nonlinear-sorption models. The HA and HM fractions were prepared with intentions to deplete HSACM in HA and to enrich it in HM. Nonpolar EDB exhibits practically no nonlinear sorption with HA but shows an enhanced nonlinear sorption with HM relative to that with the whole peat; the observed nonlinear capacities relate closely to the BET-(N₂) surface areas of the samples. The sorption of polar DUN and DCP on respective samples shows much greater nonlinear effects; the observed nonlinear capacities are markedly higher than the values attributable to surface adsorption. The HSACM hypothesis effectively accounts for the sorption data of nonpolar solutes from this and earlier studies (16, 23) and is further supported by the observed effect of a charcoal-like substance in natural solids on the sorption nonlinearity (21). The enhanced nonlinear effect for polar solutes is attributed to additional solute-SOM specific interactions (SI). As noted here and before (16,

21, 23), the nonlinear sorption capacity for a nonpolar solute depends critically on the amount of presumed HSACM in a natural sorbent. With a small amount of HSACM in soils or natural solids, the nonlinearity is important only at low C_e/S_w (16, 23); moreover, it occurs mainly in single-solute systems, because it would be suppressed in a multiple-solute system by mutual adsorptive competition (15, 16). In natural systems, where multiple solutes are usually present, the nonlinear effect for nonpolar solutes could therefore be significantly attenuated. The nonlinear sorption for polar solutes is likely to be more environmentally significant, since it is more pronounced and largely independent of trace HSACM. Nonetheless, it would also be attenuated by cosolutes to an extent depending on system conditions.

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