

# Deviations from Sorption Linearity on Soils of Polar and Nonpolar Organic Compounds at Low Relative Concentrations

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A series of single-solute and binary-solute sorption data have been obtained on representative samples of polar compounds (substituted ureas and phenolic compounds) and of nonpolar compounds (e.g., EDB and TCE) on a peat soil and a mineral (Woodburn) soil; the data extend to low relative solute concentrations ( $C_e/S_w$ ). At relatively low  $C_e/S_w$ , both the nonpolar and the polar solutes exhibit nonlinear sorption. The sorption nonlinearity approaches apparent saturation at about  $C_e/S_w = 0.010$ – $0.015$  for the nonpolar solutes and at about  $C_e/S_w = 0.10$ – $0.13$  for the polar solutes; above these  $C_e/S_w$  regions, the isotherms are practically linear. The nonlinear sorption capacities are greater for polar solutes than for nonpolar solutes and the peat soil shows a greater effect than the Woodburn soil. The small nonlinear sorption capacity for a nonpolar solute is suppressed indiscriminately by either a nonpolar or a polar cosolute at relatively low  $C_e/S_w$  of the cosolute. By contrast, the abilities of different cosolutes to suppress the nonlinear capacity of a nominal polar solute differ drastically. For polar solutes, a nonpolar cosolute exhibits a limited suppression even at high cosolute  $C_e/S_w$ ; effective suppression occurs when the cosolute is relatively polar and at various  $C_e/S_w$ . These differences suggest that more than a single mechanism is required to account for the nonlinear sorption of both nonpolar and polar compounds at low  $C_e/S_w$ . Mechanistic processes consistent with these observations and with soil surface areas are discussed along with other suggested models. Some important consequences of the nonlinear competitive sorption to the behavior of contaminants in natural systems are discussed.

## Introduction

In studies of the sorption of nonionic organic compounds by soil (or sediment), the soil organic matter (SOM) has been recognized to behave mainly as a partition medium (1–5) and the soil mineral matter as an adsorbent (6, 7). For low-polarity contaminants (solutes) in soil–water systems, the strong suppression by water of solute adsorption on soil minerals leads to a relatively linear solute uptake by soil over a wide range of solute concentrations ( $C_e$ ) relative to solute solubility in water ( $S_w$ ). Such isotherm linearity is most evident for nonpolar solutes at moderate to high relative concentrations ( $C_e/S_w$ ); for example, the isotherm linearity

for benzene on a Woodburn soil ranges from about  $10^{-2}$  to near 1 in  $C_e/S_w$  (3). Young and Weber (8) found that the sorption of a nonpolar solute (phenanthrene) on some soils and shales exhibits a significant nonlinearity with a concave-downward shape at low concentrations. Spurlock and Biggar (9) observed nonlinear sorption of relatively polar substituted ureas on soils at low concentrations, with the nonlinear sorption coefficient increasing with decreasing solute concentration. Deviations from sorption linearity at low concentrations were also reported by Xing et al. (10) for some polar pesticides (triazines) and, to a lesser extent, for a relatively nonpolar compound (trichloroethylene) (TCE) on selected soil and organic-matter samples.

It is of practical interest to deliberate on the cause of such nonlinear sorption for organic solutes at low relative concentrations, since the levels of a wide variety of relatively soluble organic contaminants in natural waters would normally fall into this range. Although the nonlinear sorption of some polar solutes at low  $C_e/S_w$  on low-organic-content soils and minerals (e.g., SOM < 0.1–0.2%) could result from the unsuppressed adsorption on certain clay fractions of the samples (11–13), the effect as noted for polar and nonpolar solutes on soils with high SOM contents suggests the occurrence of a strong non-partition effect (e.g., adsorption or specific interaction) of solutes with either a small amount of active SOM groups or a small amount of nonmineral soil fraction.

A number of conceptual models have been postulated to account for the nonlinear solute sorption on soils of significant SOM contents: (i) the different equilibrium rates of the solute with the assumed two structural entities of the SOM, one in a rubbery state and the other in a glassy state (8, 14); (ii) the presence of a small amount of high-surface-area carbonaceous material (HSACM) (such as charcoal) that exhibits a greater nonlinear adsorption at low relative concentrations than the linear partition to SOM (15); (iii) the availability of different sets of “internal holes” (or internal pores) in SOM for adsorption of solutes of different classes and polarities when the SOM is water-saturated (10, 16, 17); and (iv) the occurrence of specific interactions between polar solutes and limited active sites in SOM in addition to solute partition to SOM, the former effect approaching saturation at lower solute concentrations (9). The relative powers of these models to accommodate a wide variety of sorption data have yet to be tested on more critical experimental data.

The sorption data on some reference samples (a soil, peat, and soil humic acid) from Xing et al. (10) indicate that the nonlinear sorption tends to be more pronounced for polar solutes (e.g., atrazine and prometon) than for low-polarity solutes (e.g., TCE), the data being based on their Freundlich plots. On the soil (a Cheshire fine sandy loam) used by Xing et al. (10), TCE exhibits essentially no nonlinearity, with TCE concentrations ranging from  $<0.1$  mg/L ( $<10^{-4}$  in  $C_e/S_w$ ) to  $>100$  mg/L ( $>10^{-1}$  in  $C_e/S_w$ ) (B. Xing, personal communication). By comparison, the sorption of phenanthrene on some soils and shales reported by Young and Weber (8) exhibits significant nonlinearity at low concentrations. It thus appears that the extent of nonlinear sorption for nonpolar solutes tends to depend on the soil source and appears to be smaller in magnitude relative to that for polar solutes. In addition, the finding that in binary-solute systems (10) a coexisting polar solute (prometon) strongly suppresses the nonlinear sorption of the nominal polar solute (atrazine) while a coexisting nonpolar solute (TCE) exerts only a small effect suggests that different mechanistic processes are operative for the nonlinear sorption of polar and of nonpolar solutes.

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**TABLE 1. Physico-Chemical Properties of the Organic Compounds Used in Sorption Experiments**

compound	abbreviation	$S_w$ (mg/L)	$\log K_{ow}$	$pK_a$
phenol	PHL	87 000 <sup>a</sup>	1.46 <sup>b</sup>	9.89 <sup>c</sup>
3,5-dichlorophenol	DCP	8050 <sup>d</sup>	3.23 <sup>e</sup>	7.85 <sup>e</sup>
monuron	MON	275 <sup>f</sup>	1.98 <sup>g</sup>	< -1 <sup>h</sup>
diuron	DUN	38 <sup>f</sup>	2.68 <sup>g</sup>	< -1 <sup>h</sup>
ethylene dibromide	EDB	3520 <sup>i</sup>	1.99 <sup>j</sup>	
trichloroethylene	TCE	1100 <sup>k</sup>	2.53 <sup>k</sup>	
lindane	LND	7.8 <sup>l</sup>	3.75 <sup>l</sup>	

<sup>a</sup> Reference 18. <sup>b</sup> Reference 19. <sup>c</sup> Reference 20. <sup>d</sup> Reference 21. <sup>e</sup> Assumed to be the same as the values for 2,4-dichlorophenol from ref 22. <sup>f</sup> Reference 9. <sup>g</sup> Reference 23. <sup>h</sup> As cited in ref 9. <sup>i</sup> Reference 1. <sup>j</sup> Reference 24. <sup>k</sup> As cited in ref 25. <sup>l</sup> As cited in ref 26.

This study presents additional relevant data of some polar and nonpolar solutes on soils to further investigate the mechanisms of nonlinear sorption on soils. To prevent complications from the interaction of polar solutes with minerals, most of the sorption data have been obtained on a peat soil ( $f_{om} = 0.86$ ), with supplemental data on a mineral soil ( $f_{om} = 0.020$ ). Polar solutes from two chemical classes (phenols and substituted ureas) and three low-polarity solutes (ethylene dibromide, TCE, and lindane) were used in sorption experiments for assessing their relative nonlinear sorption effects. In addition to single-solute isotherms, the isotherms of nominal solutes in binary-solute systems were also determined, with the competing solutes (cosolutes) from either the same class or a different class. The data from these studies examine the competitive sorption of polar solutes both between and within chemical classes, since the earlier binary-solute studies were confined mainly to solutes from the same or similar class (10). This information is essential to assessment of the effect of various cosolutes on the behavior of a given solute (contaminant) in natural systems. A comparison of single-solute and binary-solute isotherms enables one to separate the relative effects of linear partition to SOM and nonlinear sorption to soil.

## Experimental Section

**Materials.** Phenol (PHL) (with a purity of 99+%), 3,5-dichlorophenol (DCP) (99%), diuron (DUN) (96%), monuron (MON) (99%), ethylene dibromide (EDB), (99+ %), trichloroethylene (TCE) (99+%), and lindane (LND) (97%), representing different chemical classes, were purchased from Aldrich Chemical Co. and used as received. In sorption experiments, these compounds were used either as nominal solutes or as competing solutes (cosolutes) in a series of single-solute and binary-solute sorption experiments on two soils, a high-organic-content peat and a mineral (Woodburn) soil. The physicochemical properties of these compounds at room temperature are listed in Table 1. The peat soil is the reference sample of the International Humic Substances Society (IHSS), collected from Everglades, FL; the sample used is from the same batch as reported earlier (4). The soil has a BET ( $N_2$ ) surface area of  $1.4 \pm 0.1 \text{ m}^2/\text{g}$  and an organic-carbon content of 49.3% by weight as determined by a high-temperature combustion method (4, 27). Woodburn soil is from the batch used in Kile et al. (5), which is similar in particle size distribution and organic matter content to the batch used in Chiou et al. (3), both being collected from Corvallis, OR. The Woodburn soil has a BET ( $N_2$ ) surface area of  $11.2 \text{ m}^2/\text{g}$  and an organic-carbon content of 1.26% by a high-temperature combustion method. The soil samples were ground to pass an 80-mesh sieve, oven-dried overnight at 90 °C, and uniformly mixed.

**Sorption Experiments.** The procedures for sorption equilibration of single-solute systems have been described

in earlier reports (3–5). A total of 1–5 g of soil was added to 25 mL screw-capped Corex centrifuge tubes, and filled to minimal head spaces with 0.005 M  $\text{CaCl}_2$  water solutions to which different amounts of solutes (sorbates) had been added. The samples were equilibrated for 2–4 days on a rotary mixer at room temperature ( $24 \pm 1$  °C). After equilibration, water and solid phases were separated by centrifugation at 2990g. The water solution pH was between 4.9 and 5.1 for all the soil–water systems tested. At this pH range, the substituted ureas and phenolic compounds studied remain undissociated. The water phase was extracted either by *n*-hexane for EDB, TCE, and DCP as the principal solutes or by dichloromethane (DCM) for DUN and MON as the principal solutes. The solid phases in all systems were extracted by a 1:4 acetone-*n*-hexane mixture (5). Both water-phase and solid-phase extracts were analyzed for solutes by a gas chromatograph. The uptake of solute by soil was corrected for the amount in residual water.

To assess the effect of pH on solute sorption, the DCP sorption on peat was measured at a controlled pH of 2.0 by use of HCl. The resulting DCP isotherm was essentially the same as that without pH adjustment. To ensure that no significant solute biodegradation occurred to affect the isotherm, the DCP isotherm was run with the addition of 400 mg/L initial concentration of  $\text{NaN}_3$ . Again, no significant change in the DCP isotherm data was noticed.

The procedures for binary-solute experiments were the same as described except that a fixed amount of a cosolute (i.e., the competing solute) was added to soil–water slurries that contained different amounts of nominal solutes. The amount of cosolute in some experiments was adjusted to determine its influence on the sorption of nominal solutes. The cosolute concentration at equilibrium in water, rather than the initial concentration (10, 17), was analyzed to describe the competitive power of the cosolute. In all binary-solute experiments, the cosolute concentrations measured at various concentrations of a nominal solute were relatively constant, varying by no more than 10% of the stated value, except for the pair of DCP (solute) and MON (cosolute) on peat, where the MON concentration increased greatly with increasing DCP concentration; the observed range of MON concentrations was given. DCM was the solvent used to extract the water phase with DUN and MON as the nominal solutes and with DCP as the nominal solute when PHL was the cosolute. For the remaining binary-solute systems, *n*-hexane was used to extract the water phase. The solid-phase extraction was all done by use of 1:4 acetone-*n*-hexane mixtures. For both single-solute and binary-solute systems, the total mass recoveries of nominal solutes were greater than 90%.

In addition to those cosolutes used in the reported binary-solute studies, methanol was also used as a cosolute, with an initial concentration of 10 000 mg/L, for the sorption of DCP as the nominal solute. The resulting DCP isotherm showed no significant effect of methanol (data not shown).

## Results

**Single-Solute Systems.** Typical single-solute sorption isotherms of TCE, EDB, DUN, and DCP at room temperature ( $24 \pm 1$  °C) on peat soil are shown in Figures 1–4 and on Woodburn soil in Figures 5 and 6. The isotherms are plotted on a linear scale of the solute uptake per unit mass of soil ( $Q$ ) against the relative concentration of the solute in water ( $C_e/S_w$ ) to enable a better distinction of individual solute behaviors. Unique characteristics are found between the solutes. In all cases, the isotherms display nonlinearity with concave-downward curvatures at low  $C_e/S_w$  but exhibit a practically linear shape at moderate to high  $C_e/S_w$ . The nonlinear effects are relatively more visible for the polar solutes (e.g., DCP and DUN) than for the nonpolar solutes

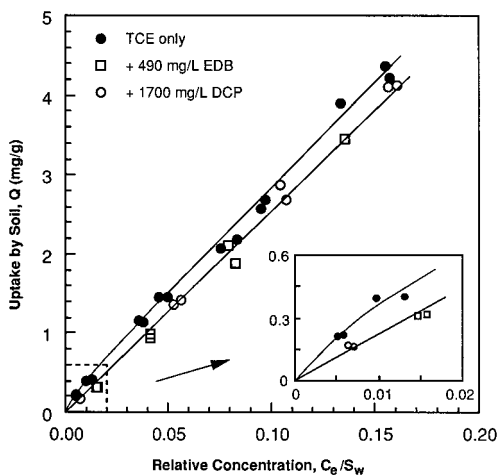


FIGURE 1. Sorption isotherms of TCE alone on peat soil and with EDB and DCP as cosolutes at specified concentrations.

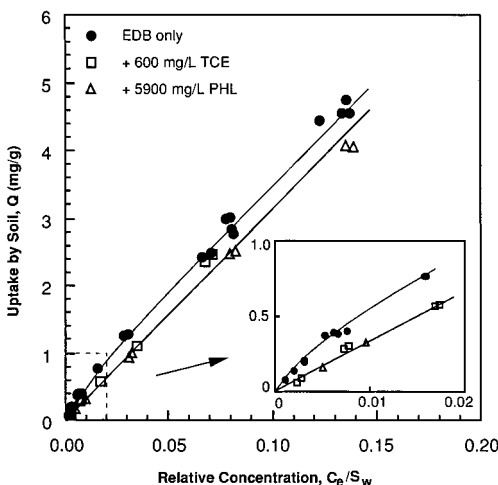


FIGURE 2. Sorption isotherms of EDB alone on peat soil and with TCE and PHL as cosolutes at specified concentrations.

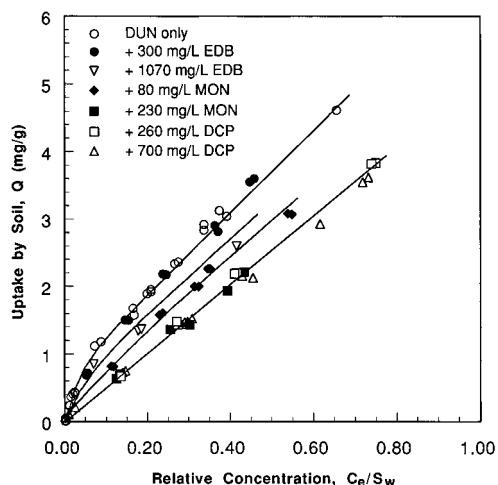


FIGURE 3. Sorption isotherms of DUN alone on peat soil and with EDB, MON, and DCP as cosolutes at specified concentrations.

(e.g., EDB and TCE). Such an overall isotherm shape bears no resemblance with any of conventional adsorption shapes. Moreover, whereas the apparent nonlinear capacities, as measured by the extrapolated intercepts of the upper linear isotherms, are about the same for the nonpolar solutes, they vary significantly among the polar solutes both on peat soil and on Woodburn soil. The apparent nonlinear capacities,

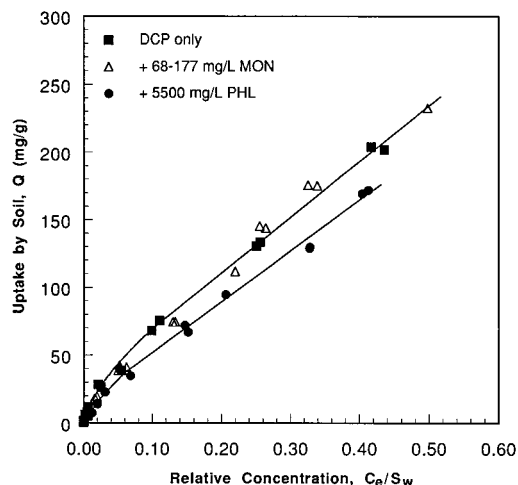


FIGURE 4. Sorption isotherms of DCP alone on peat soil and with MON and PHL as cosolutes at specified concentrations.

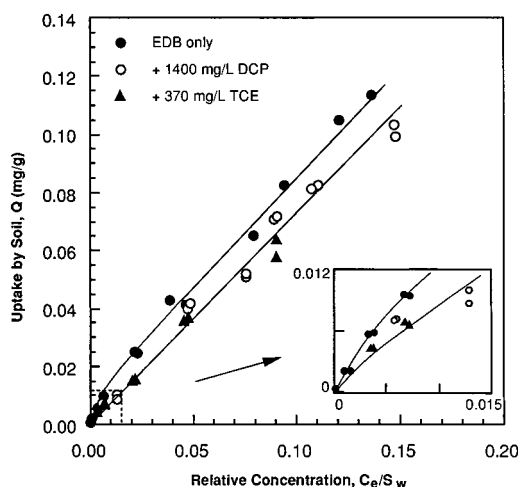


FIGURE 5. Sorption isotherms of EDB alone on Woodburn soil and with TCE and DCP as cosolutes at specified concentrations.

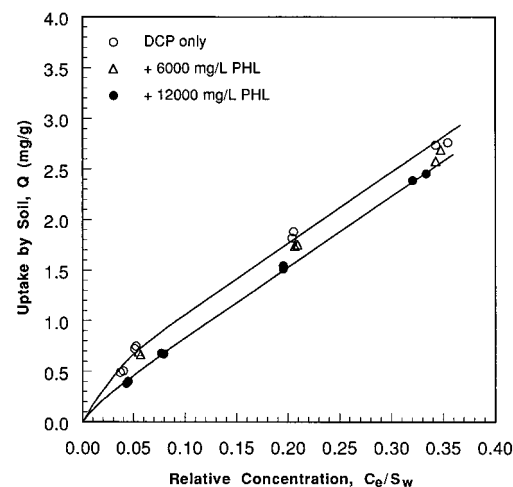


FIGURE 6. Sorption isotherms of DCP alone on Woodburn soil and with PHL as the cosolute at specified concentrations.

the approximate  $C_e/S_w$  values at which these nonlinear capacities approach apparent saturation, and the organic-carbon-normalized partition coefficients for the linear sections of the isotherms are presented in Table 2.

DCP exhibits the highest nonlinear capacity, and DUN/MON and EDB/TCE exhibit progressively lower nonlinear

TABLE 2. The Apparent Nonlinear Saturation Capacities ( $Q_{ans}$ ), the Apparent Nonlinear Saturation Points [ $(C_e/S_w)_{ans}$ ], and the Organic-Carbon-Normalized Linear Partition Coefficients ( $K_{oc}$ ) of the Solutes on Studied Soils

sorption system	$Q_{ans}(\text{mg/g})$	$(C_e/S_w)_{ans}$	$\log K_{oc}$
TCE/peat	0.15	0.012	1.69
EDB/peat	0.18	0.010	1.28
DUN/peat	0.60	0.10	2.43
MON/peat	0.82	0.13	1.45
DCP/peat	25	0.12	2.03
EDB/Woodburn	<0.008	0.015	1.23
LND/Woodburn	<0.005	0.010	2.92
DCP/Woodburn	0.38	0.080	1.87

capacities on either soil. On peat soil (Figures 1–4), the apparent nonlinear capacity is about 0.15 mg/g for TCE, 0.18 mg/g for EDB, 0.60 mg/g for DUN, 0.82 mg/g for MON, and 25 mg/g for DCP. The corresponding nonlinear capacity on Woodburn soil is <0.008 mg/g for EDB, <0.005 mg/g for LND, and about 0.38 mg/g for DCP (Figures 5 and 6). The nonlinear capacity approaches apparent saturation at about 0.010–0.015 in  $C_e/S_w$  for EDB, TCE, and LND and at about 0.10–0.13 in  $C_e/S_w$  for DCP, MON, and DUN on both soils. The present MON and DUN isotherm shapes resemble closely the ones reported by Hance (28) when Hance's data in log scales are converted into linear scales.

**Binary-Solute Systems.** The sorption isotherms of TCE, EDB, DUN, and DCP as nominal solutes with various polar and nonpolar cosolutes (competitors) on peat soil at fixed cosolute concentrations are shown in Figures 1–4. The isotherms for EDB and DCP as nominal solutes with other cosolutes at fixed concentrations on Woodburn soil are given in Figures 5 and 6. On either soil, the isotherms of nominal nonpolar solutes (e.g., TCE and EDB) in binary-solute systems exhibit significantly lower capacities than their respective single-solute isotherms only at relatively low  $C_e/S_w$  (mostly, <0.02) (Figures 1, 2, and 5). That is, with the uncertainties of the sorption data being about 10%, the slopes of the nominal solutes at high  $C_e/S_w$  in single-solute and binary-solute systems are not statistically different. At the applied cosolute concentrations, the TCE and EDB isotherms become relatively linear at low  $C_e/S_w$ . For example, the small nonlinear EDB capacities on both peat soil and Woodburn soil (Figures 2 and 5) are greatly suppressed by nonpolar TCE as the cosolute at 370 mg/L ( $C_e/S_w = 0.34$ ), by polar DCP at 1400 mg/L ( $C_e/S_w = 0.17$ ), and by polar PHL at 5900 mg/L ( $C_e/S_w = 0.068$ ). On the other hand, the nominal solute isotherms of the polar solutes vary considerably among the cosolute–soil systems.

As noted, the sorption of DCP on peat is largely unaffected by MON as the cosolute even with MON at as high as 177 mg/L ( $C_e/S_w = 0.64$ ) (Figure 4). However, when PHL is used as the cosolute at 5500 mg/L ( $C_e/S_w = 0.063$ ), it suppresses a fair amount of the DCP nonlinear capacity, although the suppression is not complete. The relative competitive powers of various cosolutes are exhibited most distinctly by the binary-solute DUN sorption isotherms (Figure 3). In this case, EDB as the cosolute imposes little effect on DUN sorption at the EDB concentration of 300 mg/L ( $C_e/S_w = 0.085$ ) while it exhibits a small depression of DUN sorption at the EDB concentration of 1070 mg/L ( $C_e/S_w = 0.30$ ); MON at 80 mg/L ( $C_e/S_w = 0.29$ ) exhibits a significant but incomplete suppression of the DUN nonlinear capacity; MON at 230 mg/L ( $C_e/S_w = 0.84$ ) and DCP at 260 mg/L and 700 mg/L ( $C_e/S_w = 0.032$  and 0.087, respectively) suppress most of the nonlinear capacity. In the latter case, the resultant DUN isotherms are relatively linear with slopes about equal to that of the upper linear DUN single-solute isotherm. The response of DCP to cosolute PHL on Woodburn soil (Figure

6) is similar to that of DCP on peat soil (Figure 4), in which PHL as the cosolute at 12 000 mg/L ( $C_e/S_w = 0.14$ ) erases most of the DCP nonlinear capacity.

The above results indicate that the nonlinear behavior of a nominal solute in binary-solute systems is influenced by both the cosolute type and concentration and that a polar cosolute (e.g., DCP) of one chemical class may effectively suppress the nonlinear sorption of a nominal polar solute of a different class (e.g., DUN). In this respect, phenolic compounds are more powerful sorbates and competitors than substituted ureas, which is consistent with their relative nonlinear sorption capacities. If the nominal solute is a polar compound, the suppression by various cosolutes occurs in a highly selective manner. Here, the large nonlinear capacities of polar solutes (e.g., DCP and DUN) are not strongly affected by nonpolar cosolutes at relatively low  $C_e/S_w$ . A large suppression occurs if the cosolute is of high polarity even at relatively low  $C_e/S_w$ , as illustrated by DCP on DUN (Figure 3). For the polar solutes studied, the relative suppressive power follows the order: PHL  $\geq$  DCP  $>$  MON  $>$  DUN, which is essentially the order of their  $S_w$  values. By contrast, the small nonlinear capacities of nonpolar solutes (e.g., EDB and TCE) are more effectively depressed by either polar or nonpolar cosolutes if the  $C_e/S_w$  of the cosolute is appreciably higher than the upper  $C_e/S_w$  limit (0.010–0.015) of the sorption nonlinearity for nonpolar solutes.

## Discussion

A number of the isotherm features at low  $C_e/S_w$  of the solutes observed in this study are quite similar to the findings of Xing et al. (10) and Xing and Pignatello (17). The similarities include (i) the smaller nonlinearity effects for nonpolar than for polar solutes; (ii) the relatively small suppression of the sorption of a polar solute (e.g., atrazine) by a nonpolar cosolute (e.g., TCE) over a range of cosolute concentrations; and (iii) the significant suppression of the sorption of a polar solute (atrazine) by other polar cosolutes (e.g., prometon and other triazines). Moreover, the linear plots used in this study are much better adapted than the log-log plots in the preceding studies for displaying the different extents of nonlinear sorption in the different systems.

The unique isotherm shape, i.e., nonlinear at low  $C_e/S_w$  but virtually linear at other  $C_e/S_w$ , suggests that more than a single mechanism is operative over the entire concentration range. Since the (apparent) nonlinear capacity and the associated point of saturation are not the same for polar and nonpolar solutes, it is reasonable to suppose that the primary causes of their nonlinear sorption at low concentrations are different. We consider first the probable source of the sorption nonlinearity for nonpolar solutes on soil, where the nonlinear capacity is relatively small and approaches apparent saturation at very low  $C_e/S_w$  (0.010–0.015). On peat soil, the nonlinear capacities of about 0.18 mg/g for EDB and 0.15 mg/g for TCE are well within the allowed monolayer adsorption capacity of the soil based on its BET ( $N_2$ ) surface area of 1.4 m<sup>2</sup>/g. The same is true for EDB and LND on Woodburn soil, where the nonlinear capacities of EDB and LND are <0.008 mg/g and the surface area of the soil is 11.2 m<sup>2</sup>/g. Since there is little tendency for nonpolar solutes to engage in specific interaction with SOM and since the peat soil has a very low mineral content, these features may reasonably be explained in terms of strong solute adsorption at low  $C_e/S_w$  on a small amount of HSACM (e.g., charcoal-like materials) in soil (15), on which water has a weak competitive adsorption. At moderate to high  $C_e/S_w$ , this adsorption is largely saturated and the partition in SOM predominates to give an essentially linear isotherm. This hypothesis remains to be further tested against others that may also reconcile the nonlinear sorption capacity with the soil surface area.

The HSACM hypothesis is in line with the characteristics of solute adsorption on activated carbon. For adsorbates with a density of about 1 g/mL on a typical activated carbon, 1 m<sup>2</sup>/g of the carbon surface area corresponds to about 0.25 mg/g of the adsorbate monolayer capacity; the saturation capacity is about twice as high. Adsorption on activated carbon rises rapidly at low  $C_e/S_w$ . At  $C_e/S_w = 0.01$ – $0.02$ , the adsorbed capacity is about 40–50% of the saturation capacity (21, 29, 30). From this point up to  $C_e/S_w = 1$ , adsorption approaches full saturation more gradually. With a small quantity of assumed HSACM and a significant amount of SOM in soil, the isotherms for nonpolar solutes at  $C_e/S_w > 0.01$ – $0.02$  would therefore become relatively linear as the (linear) partition into SOM outweighs the adsorption on HSACM. On peat soil, the nonlinear EDB and TCE capacities (0.15–0.18 mg/g) are consistent with the HSACM hypothesis, if most of the soil surface area (1.4 m<sup>2</sup>/g) comes from a small amount of HSACM. For Woodburn soil, the surface area is much higher and the nonlinear capacity for nonpolar EDB is much smaller. The large surface area results presumably from mineral surfaces, on which the strong interaction with water minimizes the solute adsorption (6, 7). The lower nonlinear capacity of EDB on Woodburn soil may be attributed to a trace amount of HSACM in the soil. Since adsorption on activated carbon occurs primarily by London forces (29) and the same is expected for adsorption on the assumed HSACM, solute polarity is not the relevant property for competitive power; this is illustrated by the nonspecific suppression of EDB sorption on peat by both polar and nonpolar cosolutes.

The nonlinear sorption characteristics of nonpolar solutes on peat are internally consistent with the N<sub>2</sub> adsorption data on the sample. The N<sub>2</sub> adsorption exhibits a similar sharp rise and a downward concavity at low relative pressures ( $P/P_0$ ) ( $\leq 0.02$ ) with a monolayer capacity of 0.36 mg/g (27); this behavior is suggestive of the existence of a small amount of high-affinity adsorption sites as pictured by the HSACM postulate. The HSACM concept is consistent with the widespread occurrence of charcoal-like materials in natural environments that are likely produced by biomass burning. The ubiquity of low levels of charcoal-like materials in sediments has been well documented (31–33). Many soils may thus be “contaminated” by small amounts of charcoal-like materials. At this point, the HSACM postulate does not rule out the possibility that the small amount of high-affinity adsorption sites comes from a specific fraction of the SOM. However, a previous finding (10) that the TCE sorption on a Cheshire soil, which contains a significant SOM content ( $f_{om} > 0.02$ ), exhibits little nonlinearity at low  $C_e/S_w$  (and thus presumably little HSACM in the soil) suggests that the SOM itself is not the source of nonlinearity. (In this respect, the HSACM is not considered as a component of SOM, despite that it may be counted as part of the soil organic carbon in SOM analysis by a high-temperature combustion method.) More work is needed to clearly establish whether a direct relation exists between nonlinear capacity and SOM content. We now consider the sorption data of polar solutes on peat soil and Woodburn soil, after which we will consider other postulates for sorption nonlinearity.

For polar solutes on soil, the greater nonlinear capacity requires an additional nonlinear model. For DCP on peat, for instance, the observed nonlinear capacity (25 mg/g) exceeds greatly the amount accountable by the small surface area of the soil. The nonlinear capacities for MON and DUN on peat are smaller but are still higher than can be reconciled with the soil surface area. These findings imply that the relatively large nonlinear sorption at low  $C_e/S_w$  of polar solutes is strongly related to solute polarity and occurs within the interior network of SOM. The data are intrinsically consistent with the specific-interaction model of Spurlock and Biggar

(9) for the nonlinear sorption of polar pesticides at low (relative) concentrations. The model postulates that the specific interaction of polar solutes with highly active sites of SOM approaches saturation at a much lower concentration than does the concurrent partition to SOM, and hence the isotherm is nonlinear at low (relative) concentrations.

Since the assumed specific-interaction model involves presumably the polar groups of solute and SOM, it makes sense that the magnitude of sorption nonlinearity and the solute competitive power depend on the solute polarity, as manifested by the present data. Accordingly, a nonpolar cosolute is unable to suppress the large nonlinear uptake of a polar solute. The small reduction of the atrazine uptake at low concentrations on soil by cosolute TCE in a previous work (10) and that of the DUN uptake on peat by cosolute EDB (with  $C_e/S_w = 0.30$ ) in this study may be attributed to the adsorptive competition on a small amount of HSACM in the soil. The finding that the nonlinear sorption capacities of a polar solute (e.g., DCP) on peat and Woodburn soil (Table 2) correlate largely with respective SOM contents is consistent with assumed specific interactions of polar solutes with the interior active sites of SOM. That the lowering of solution pH to 2.0 in the DCP/peat system does not affect the nonlinear behavior suggests further that the active SOM sites are not confined to ionizable groups. Overall, the combination of the specific-interaction model of Spurlock and Biggar (9) and the present HSACM hypothesis reconcile the outstanding features of the nonlinear and the competitive sorption data of both polar and nonpolar solutes.

We now consider other suggested mechanisms for sorption nonlinearity. One current view of the nonlinear sorption on soil is that the solute interacts with two structurally distinct (rubbery and glassy) components of the SOM by different kinetic rates (8, 14). However, the time-dependent study of the solute isotherms between 1 and 30 days manifests only small changes in Freundlich constants and exponents (17). In addition, although the SOM may display such a dual state at some temperatures because of the heterogeneity of SOM composition, this two-component SOM model lacks the specificity to explain the difference in behavior of the polar and nonpolar solutes in single-solute and binary-solute systems, as described in the earlier section.

To account for nonlinear and disparate competitive sorption data of polar and nonpolar solutes on soil, Xing et al. (10) proposed the selective adsorption of different solutes to compound-specific internal holes (pores) within the SOM in addition to solute partition. This hypothesis is difficult to prove (or disprove) because these internal holes and their “internal surface areas” cannot be verified by conventional porosity and surface-area measurement methods using inert gases (such as N<sub>2</sub>). Whereas one could postulate that such cellular “holes” are not accessible to N<sub>2</sub> because of the low solubility of N<sub>2</sub> in SOM, it is more difficult to explain the low competition of nonpolar solutes that dissolve in SOM and could therefore have equal access to these “holes”. In the work of Xing and co-workers (10, 17), the data on nonlinear sorption of the solutes were reported in a form that does not allow for a check in consistency with soil surface area. Since the nonlinear capacities of nonpolar solutes on peat soil are well accounted for by the measured BET (N<sub>2</sub>) surface area of the sample, the assumption of “internal holes” in SOM is superfluous. In addition, the concept of internal holes within SOM cannot effectively explain the nonspecific suppression of the nonlinear sorption of nonpolar solutes by both polar and nonpolar cosolutes nor the unequal nonlinear capacities and apparent saturation points for polar and nonpolar solutes.

In soil–water systems where the isotherm of a solute is nonlinear at low  $C_e/S_w$  and virtually linear at moderate to high  $C_e/S_w$ , as shown in this work, the log–log plot of the

data tends to give a skewed picture of the solute behavior, as it puts more weight on sorption data at low  $C_e/S_w$ . The slope in such a plot for depicting the degree of isotherm linearity is heavily biased by the low  $C_e/S_w$  data, and hence the linear isotherm shape at higher  $C_e/S_w$  is obscured. By contrast, the isotherm on linear scales by use of  $C_e/S_w$  as the abscissa offers advantages of depicting the transition of isotherm shape and the nonlinear capacity, which serves as a useful basis to evaluate the possible sources of sorption nonlinearity and to define unequivocally the (linear) partition coefficients of solutes on SOM. As shown in Table 2, the  $K_{oc}$  values derived from the linear sections of the isotherms are relatively comparable for given solutes between the soils; the small variations reflect presumably the differences in SOM composition. We shall now consider the consequences of such sorption nonlinearity for organic contaminants at low  $C_e/S_w$  in both laboratory and natural systems.

Since the nonlinear sorption occurs at low  $C_e/S_w$  and is competitive in nature, the sorption coefficient of either a nonpolar solute or a polar solute on soil in single-solute systems may be highly variable at low  $C_e/S_w$ , if the soil contains a significant amount of HSACM (or similar materials). In single-solute systems, which are most applicable to laboratory studies, the principal factor for nonpolar solutes would be the amount of assumed HSACM, while for polar solutes the SOM itself may become the dominant factor. If the amount of HSACM relative to SOM is small, one would expect to find the sorption coefficients for most nonpolar solutes at moderate to high  $C_e/S_w$  to be relatively constant, as the linear partition outweighs the nonlinear sorption. At low  $C_e/S_w$  in natural water, where many organic solutes (contaminants) may be present, it is important to keep in mind the effect of mutual solute competition on the sorption coefficients of individual contaminants. As such, the magnitude of the nonlinear effect on the sorption coefficients of individual solutes may be differently reduced by the mutual competition. The extent of reduction depends on (i) the amount of assumed HSACM in soil or sediment, (ii) the relative concentrations of all solutes, and (iii) the polarities of solutes involved.

If the amount of HSACM in soil or sediment is at trace levels and if the system contains multiple solute species, the nonlinear sorption would be most significant when there are relatively few solute species present and/or if they all are at extremely low  $C_e/S_w$ . On the other hand, if the system contains a dominant component (of high  $C_e/S_w$ ), the sorption of all nonpolar solutes, irrespective of the number of solute species, at low  $C_e/S_w$  would become relatively linear because of the suppression of adsorption on HSACM by adsorptive competition. In this case, the sorption coefficients of all contaminants, including the dominant species, should conform closely to their respective linear partition coefficients with SOM. The same is expected for nonpolar solutes if the system contains a large number of solute species, each at about the same  $C_e/S_w$ . For polar solutes in multiple-solute systems, the sorption coefficients could be more subject to variation with concentration, since the suppression of nonlinear sorption takes place at higher  $C_e/S_w$  and since the suppressive power is more related to solute polarity. However, if a powerful polar contaminant (e.g., PHL) dominates, the nonlinear sorption effects of the less-polar contaminants would all again be significantly reduced. The present finding that the suppression of the nonlinear polar-solute sorption by polar cosolutes occurs between chemical classes reduces the complexity of the multiple-solute system. Despite that

some of these expectations have been demonstrated in this study, it is of interest to further verify these important consequences.

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## Literature Cited

- (1) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831.
- (2) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241.
- (3) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227.
- (4) Rutherford, D. W.; Chiou, C. T.; Kile, D. E. *Environ. Sci. Technol.* **1992**, *26*, 336.
- (5) Kile, D. E.; Chiou, C. T.; Zhou, H.; Li, H.; Xu, O. *Environ. Sci. Technol.* **1995**, *29*, 1401.
- (6) Chiou, C. T.; Shoup, T. D. *Environ. Sci. Technol.* **1985**, *19*, 1196.
- (7) Chiou, C. T.; Shoup, T. D.; Porter, P. E. *Org. Geochem.* **1985**, *8*, 9.
- (8) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1995**, *29*, 92.
- (9) Spurlock, F. C.; Biggar, J. W. *Environ. Sci. Technol.* **1994**, *28*, 996.
- (10) Xing, B.; Pignatello, J. J.; Gigliotti, B. *Environ. Sci. Technol.* **1996**, *30*, 2432.
- (11) Laird, D. A.; Barriuso, E.; Dowdy, R. H.; Koskinen, W. C. *Soil Sci. Soc. Am. J.* **1992**, *56*, 62.
- (12) Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1993**, *27*, 316.
- (13) Weissmahr, K. W.; Haderlein, S. B.; Schwarzenbach, R. P.; Handy, R.; Nuesch, R. *Environ. Sci. Technol.* **1997**, *31*, 240.
- (14) Weber, W. J., Jr.; Huang, W. *Environ. Sci. Technol.* **1996**, *30*, 881.
- (15) Chiou, C. T. *Environ. Sci. Technol.* **1995**, *29*, 1421.
- (16) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1.
- (17) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1997**, *31*, 792.
- (18) Seidell, A. *Solubilities of Organic Compounds*; D. Van Nostrand Co., Inc.: New York, 1941.
- (19) Fujita, T.; Iwasa, J.; Hansch, C. *J. Am. Chem. Soc.* **1964**, *86*, 5175.
- (20) *Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: Boca Raton, FL, 1991.
- (21) Chiou, C. T.; Manes, M. J. *Phys. Chem.* **1974**, *78*, 622.
- (22) Schellenberg, K.; Leuenberger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1984**, *18*, 652.
- (23) Briggs, G. G. *J. Agric. Food Chem.* **1981**, *29*, 1050.
- (24) Chiou, C. T.; Freed, V. H. *Chemodynamic Studies on Bench Mark Industrial Chemicals*, PB-274263; National Technical Information Service: Springfield, VA, 1977.
- (25) U.S. EPA. 40 Code of Federal Regulations, Part 264, Appendix IX, PB-92-233287; National Technical Information Service: Springfield, VA, 1992.
- (26) Chiou, C. T.; Schmedding, D. W.; Manes, M. *Environ. Sci. Technol.* **1982**, *16*, 4.
- (27) Chiou, C. T.; Rutherford, D. W.; Manes, M. *Environ. Sci. Technol.* **1993**, *27*, 1587.
- (28) Hance, R. J. *Weed Res.* **1965**, *5*, 98.
- (29) Manes, M.; Hofer, L. J. E. *J. Phys. Chem.* **1969**, *73*, 584.
- (30) Wohleber, D. A.; Manes, M. J. *Phys. Chem.* **1971**, *75*, 61.
- (31) Smith, D. W.; Griffin, J. J.; Goldberg, E. D. *Nature* **1973**, *241*, 268.
- (32) Griffin, J. J.; Goldberg, E. D. *Environ. Sci. Technol.* **1983**, *17*, 244.
- (33) Lim, B.; Cachier, H. *Chem. Geol.* **1996**, *131*, 143.

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