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# Competitive Sorption between 1,3-Dichlorobenzene or 2,4-Dichlorophenol and Natural Aromatic Acids in Soil Organic Matter

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Previously, we showed that sorption of anthropogenic organic compounds in soils is competitive as a result of the heterogeneous sorption potential of soil organic matter (SOM). We hypothesize that naturally occurring, low molecular weight organic molecules or ions could compete with anthropogenic molecules for sorption sites in SOM. We show here that natural aromatic acids suppress sorption from water of 1,3-dichlorobenzene (1,3-DCB) or 2,4-dichlorophenol (2,4-DCP) by up to ∼40% to two soils, a Pahokee peat (93% SOM) and a Cheshire fine sandy loam (3% SOM). The experiments were performed at the natural pH of the soil suspension (5.0 and 5.6, respectively), at which the aromatic acids were mostly ionized. In a screen test at 100 $\mu$g/mL aromatic acid concentration, 10 out of 11 competed significantly with 2,4-DCP. Five were selected for further study: vanillic, *p*-hydroxybenzoic, *trans*-cinnamic, *p*-coumaric, and ferulic acids. The selected five aromatic acids as well as the two anthropogenic compounds gave nonlinear isotherms (Freundlich exponent, 0.507−0.852), indicating a distribution of site energies in SOM. The pattern in the competitive effect among the aromatic acids was similar for the two soils; since the peat soil is almost mineral-free, this indicates that competition occurred in the SOM phase. In nearly all cases, suppression of sorption decreased exponentially with increasing aromatic acid concentration, as would be expected for direct competition for sites. These results are in accord with the dual-mode model of sorption to SOM we proposed earlier, in which both solid-phase dissolution and hole (site)-filling mechanisms take place and in which competition takes place only in the hole-filling domain. The results show that aromatic acids and possibly other small natural organic molecules can occupy and block adsorption sites in SOM, potentially affecting the fate, transport, and bioavailability of anthropogenic organic compounds in the environment.

## Introduction

Sorption has a critical effect on the transport, reactivity, and bioavailability of anthropogenic organic compounds in soil and sediments. Even though such compounds are often present in mixtures, multisolute systems have historically been ignored in laboratory sorption studies. One reason is that soil organic matter (SOM)—usually the predominant sorbent of neutral organic compounds—has been regarded as a solid-phase dissolution (partition) medium in which competition between sorbates is not expected to occur. We have recently proposed a dual-mode sorption mechanism for SOM, applicable to polar and apolar compounds alike, in which solid-phase dissolution takes place simultaneously with adsorption-like (hole-filling) processes (*1*−*3*). In this mechanism, which is based on polymer theory, the "holes" are postulated to be internal nanovoids in the humic matrix that are associated with the more highly condensed phases of SOM. The existence of these voids is supported by gas adsorption studies and can explain nonideal sorption behaviors that have been observed (see refs 1−3). Among the lines of evidence supporting the dual-mode model is the observation of competitive sorption between pairs of halogenated aliphatic hydrocarbons (*4*), chlorinated benzenes (*3*), or *s*-triazines (*1*). We showed that competition occurs in the adsorption but not the dissolution domain.

Simple single-ring aromatic acids are released from living and decomposing plant residues and, therefore, are ubiquitous in soil. Such acids play an important role in soil formation, dissolution of minerals, humus formation, complexation of heavy metals, allelopathy, and nutrient availability (*5*−*8*). However, to our knowledge, the effect of aromatic acids on sorption of anthropogenic organic compounds in soil has not been investigated. Because aromatic acids are similar in structure and size to many single-ring organic pollutants such as chlorinated phenols and benzenes, aromatic acids may influence the sorption behavior of these organic chemicals in soils and sediments.

Accordingly, this study examined the sorption behavior of individual aromatic acids and their effect on sorption of anthropogenic organic compounds in binary systems. The sorbents were the same as used in our previous studies (*1*−*3*): a high organic peat and a fine sandy loam with a moderate organic matter content.

The anthropogenic organic compounds were 1,3-dichlorobenzene (1,3-DCB) and 2,4-dichlorophenol (2,4-DCP), which are representative of common soil and water pollutants. 1,3-DCB is generally regarded as *apolar* or *hydrophobic*, as reflected by its solubility (123 mg/L) and solvent−water partition coefficient ($\log K_{ow} = 3.38$) (*9*). The Cl atoms impart hydrophobic character to the molecule due to their large size and lack of H-bonding ability, overshadowing any hydrophilic effect of the polar C−Cl bonds. As a result, 1,3-DCB is capable only of van der Waals−London interactions with the sorbent, which are weak and nondirectional. In contrast, 2,4-DCP is usually regarded as *polar* or *hydrophilic* (solubility = 4000 mg/L; $\log K_{ow} = 2.75$) (*9*) due to the H-bonding ability of the hydroxyl group, although it too has significant hydrophobic surface area. The hydroxyl group permits orientational interactions with the sorbent.

We initially screened 11 aromatic acids for their effect on sorption of 2,4-DCP and then examined five of them more closely. The 11 aromatic acids are benzoic (BEN), caffeic (CAF), *p*-coumaric (COU), ferulic (FER), *p*-hydroxybenzoic (HYB), phenylacetic (PA), phthalic (PHT), salicylic (SAL), syringic (SYR), *trans*-cinnamic (CIN), and vanillic (VAN) acids. Their structures are given in Table 1. All have been identified in soils by Baziramakenga et al. (*10*), who reported that individually their water-extractable soil concentrations depended on depth and sampling times during the year. In

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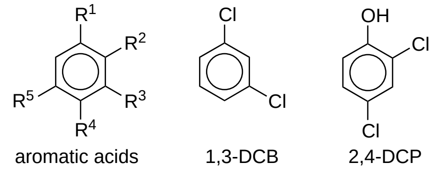
**TABLE 1. Structures of Natural Aromatic Acids, 1,3-DCB, and 2,4-DCP and Fractions of Aromatic Acid in Ionized Form in Solution at pH of Each Soil Suspension**



| | | | | | | | | fraction ionized at pH | |
|---|---|---|---|---|---|---|---|---|---|
| aromatic acid | abbreviation | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $pK_{a1}$ | 5.0 (Pahok.) | 5.6 (Chesh.) |
| benzoic | BEN | COOH | | | | | 4.2 | 0.86 | 0.96 |
| caffeic[a] | CAF | CH=CHCOOH | | OH | OH | | 4.6 | 0.72 | 0.91 |
| *p*-coumaric[a] | COU | CH=CHCOOH | | | OH | | 4.7 | 0.67 | 0.89 |
| ferulic[b] | FER | CH=CHCOOH | | $OCH_3$ | OH | | 4.7 | 0.67 | 0.89 |
| *p*-hydroxybenzoic | HYB | COOH | | | OH | | 4.5 | 0.76 | 0.93 |
| phenyacetic | PA | $CH_2COOH$ | | | | | 4.3 | 0.83 | 0.95 |
| phthalic | PHT | COOH | COOH | | | | 2.9 | 0.99 | 1.00 |
| salicylic | SAL | COOH | OH | | | | 3.0 | 0.99 | 1.00 |
| syringic | SYR | COOH | | $OCH_3$ | OH | $OCH_3$ | 4.3 | 0.83 | 0.95 |
| *trans*-cinnamic | CIN | CH=CHCOOH | | | | | 4.4 | 0.80 | 0.94 |
| vanillic | VAN | COOH | | $OCH_3$ | OH | | 4.5 | 0.76 | 0.93 |

[a] Predominantly trans. [b] All-trans.

surface–horizon soils, the total aromatic acids concentration ranged from 53 to 214 nmol $g^{-1}$, with a mean of 125 nmol $g^{-1}$ dry soil basis. BEN (32–86 nmol $g^{-1}$; mean, 56 nmol $g^{-1}$) and HYB (9.2–56 nmol $g^{-1}$; mean, 31 nmol $g^{-1}$) were more concentrated than the others. Assuming an average molecular weight of 160 g $mol^{-1}$ and a soil moisture content of 20%, then the total aromatic acid concentration on a liquid basis ranged from 42 to 170 $\mu$g/mL with a mean of 100 $\mu$g/mL. Such concentrations are substantial and should not be overlooked in terms of their effects on sorption of anthropogenic organic compounds. We used comparable concentrations in our experiments.

## Experimental Section

**Materials.** Florida Pahokee peat soil was obtained air-dry from the International Humic Substance Society, Colorado School of Mines, Golden, CO. This reference peat is highly humified (*11*) and has no undecomposed plant matter visible with a microscope. It contains 44.6% C, 6.9% ash, and 1.7% $SiO_2$ on a dry weight basis. The mineral soil was a Cheshire fine sandy loam from our Lockwood Farm (Hamden, CT). It was sieved at field moisture content and stored at 5 °C. The dry soil composition was 56% sand, 36% silt, 8% clay, and 1.4% organic carbon. 1,3-DCB and 2,4-DCP were from Aldrich. [ring-UL-$^{14}$C]-2,4-DCP and the aromatic acids were from Sigma.

**Isotherms.** Sorption experiments were conducted in aqueous suspensions containing 0.01 M $CaCl_2$ and 200 $\mu$g/mL $HgCl_2$ as a bioinhibitor in 8-mL Teflon-lined screw-cap vials, as previously described in detail (*2*, *3*, *12*). Wolf et al. (*13*) concluded that $HgCl_2$ was equivalent to three times autoclaving, yet had little impact on cation-exchange capacity, extractable metal ion concentrations, and pH. The experiments were run at the pH of individual sorbents (5.6 for soil, 5.0 for peat measured in $CaCl_2$ solution). The solids concentration was adjusted to achieved 25–85% uptake of the principal solute. After centrifugation, we measured the solution-phase concentration. Sorbed concentrations were calculated by mass balance because the mass losses were less than 4% in the controls without sorbents.

The Freundlich model, $S = K_F C^N$, where $S$ and $C$ are the sorbed and solution concentrations, respectively, was used to fit sorption data. The Freundlich exponent ($N$) and affinity constant ($K_F$) were determined by linear regression of log-transformed data.

**Competitive sorption** experiments were carried out in 5- or 8-mL vials in triplicate at a constant initial concentration of 1,3-DCB or 2,4-DCP (2 $\mu$g/mL) with varying concentrations of the competing solute. All vials in a series contained the same amount of solid and solution: 0.061 g and 8.5 mL for competition between 1,3-DCB and aromatic acids in Pahokee soil; 0.061 g and 7.1 mL for 2,4-DCP and aromatic acids in Pahokee soil; 2.1 g and 6.0 mL for 2,4-DCP and aromatic acids in Cheshire soil; and 1.3 g and 4.2 mL for 1,3-DCB and aromatic acids in Cheshire soil. The headspace was kept to a minimum. In the absence of aromatic acid, the sorbed concentrations of 1,3-DCB were 174 $\mu$g/g for Pahokee and 3.9 $\mu$g/g for Cheshire soils; and the sorbed concentrations of 2,4-DCP were 172 $\mu$g/g for Pahokee and 4.6 $\mu$g/g for Cheshire soils. The pH of each aromatic acid stock solution was adjusted to the pH of the sorbent suspension (i.e., pH 5.6 for Cheshire and pH 5.0 for Pahokee soil) before mixing. In selected cases, the pH of suspensions was measured after the 2-day equilibration and found to be essentially unchanged ($<$0.05 unit). Other experimental conditions are as described above.

**Analysis.** 1,3-DCB was hexane-extracted from supernatant samples and analyzed by GC on 0.53 mm × 30 m DB 624 capillary column (J&W Scientific, Folsom, CA) using electron capture detection. 2,4-DCP was determined by scintillation counting of the supernatant in Opti-Fluor cocktail (Packard Instrument CO., Meriden, CT). The aromatic acids were determined by HPLC on a C-18 column (S 5 ODS2, Phase Sep, Clwyd, U.K.) using a 40:60 ratio of $CH_3CN$:deionized water with monitoring at 254 nm after first adjusting the solution to pH 7 to convert the acid completely to its anionic form.

## Results

In the first set of experiments, the 11 aromatic acids listed in Table 1 were screened for their effect on sorption of 2,4-DCP (initial concentration 2 $\mu$g/mL) in the Cheshire and Pahokee soils after a 48-h contact period. The initial aromatic acid concentration was 100 $\mu$g/mL except for FER, SYR, and

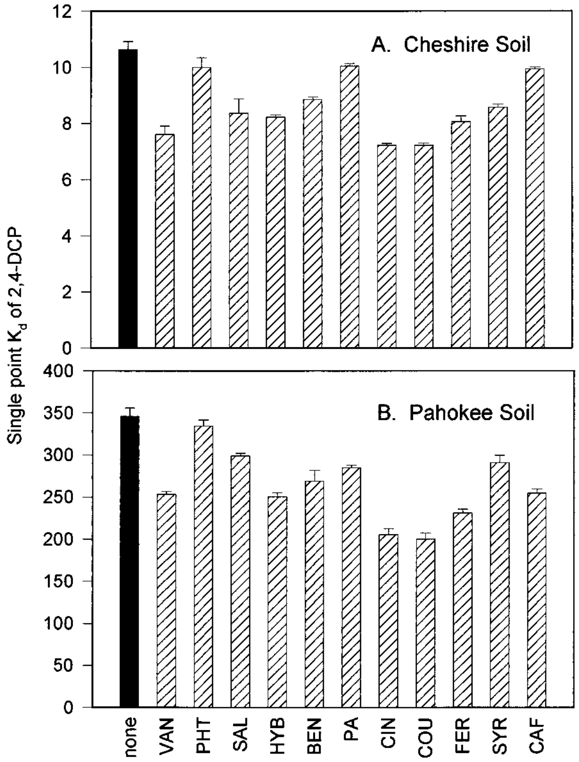


**FIGURE 1. Screen of 11 natural aromatic acids at fixed initial concentration for their effect on the $K_d$ of 2,4-DCP at fixed initial concentration. Error bars indicate standard deviation of triplicates. Key to abbreviations is in Table 1.**

CAF, which were tested at 50, 50, and 30 $\mu$g/mL, respectively, due to solubility limitations. In solution 2,4-DCP (p$K_a$ = 7.7) is >99% undissociated in both soil systems. The p$K_{a1}$ and species distribution of each aromatic acid in solution at each pH are listed in Table 1. It can be seen that in the Cheshire soil suspension at pH 5.6 the aromatic acids are almost completely ionized, while in the Pahokee soil at pH 5.0, the degree of ionization ranges from 67 to 99%. The species distribution of aromatic acids in the sorbed state is unknown. Since the background electrolyte is $CaCl_2$, the sorbed state may include, in addition to neutral molecules (HA) and free ions ($A^-$), the ion pairs $CaA^+$ and $CaA_2$. The species $CaA^+$ seems to have a strong tendency to sorb; Jafvert et al. (*14*) found that the octanol–water partition coefficient of $CaA^+$, where $A^-$ is pentachlorophenate, is only slightly smaller than that of undissociated pentachlorophenol (log $K_{ow}$, 4.72 and 5.09, respectively). Also, addition of $CaCl_2$ promoted sorption of 2-methyl-4,6-dinitrophenol to a sediment at a pH (8.3) where the anion was the predominant form in solution (*14*).

The results of the screen are shown Figure 1. All aromatic acids reduced the sorption distribution ratio ($K_d$) of 2,4-DCP, which is defined as the ratio of sorbed to aqueous concentration, *S*/*C*. However, the reduction was not statistically significant for PHT, PA, and CAF in Cheshire soil, nor for PHT in Pahokee soil. VAN, HYB, CIN, COU, and FER were more effective than the other aromatic acids, causing a 24–42% reduction in $K_d$. Although the effect on 2,4-DCP sorption is somewhat greater for the Pahokee soil in most cases, the *pattern* of reduction among the aromatic acids is quite similar for the two soils. This suggests that the mechanism of inhibition is the same.

Subsequent studies focused on the five aromatic acids that competed most strongly with 2,4-DCP in the screen: VAN, HYB, CIN, COU, and FER. Figure 2 shows that these five acids at the same concentration used in the screen for 2,4-DCP also suppress the $K_d$ of 1,3-DCB.

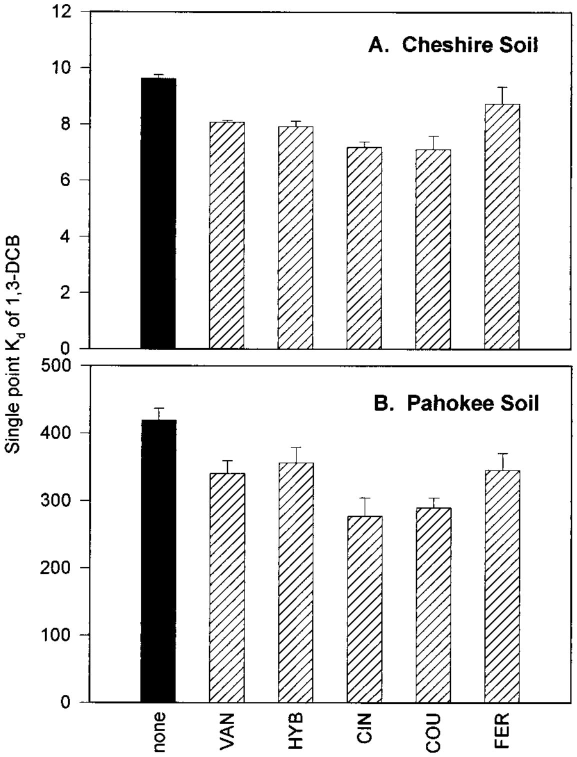


**FIGURE 2. Competitive sorption between 1,3-DCB at fixed initial concentration and VAN, HYB, CIN, COU, or FER at fixed initial concentration. Key to abbreviations is in Table 1.**

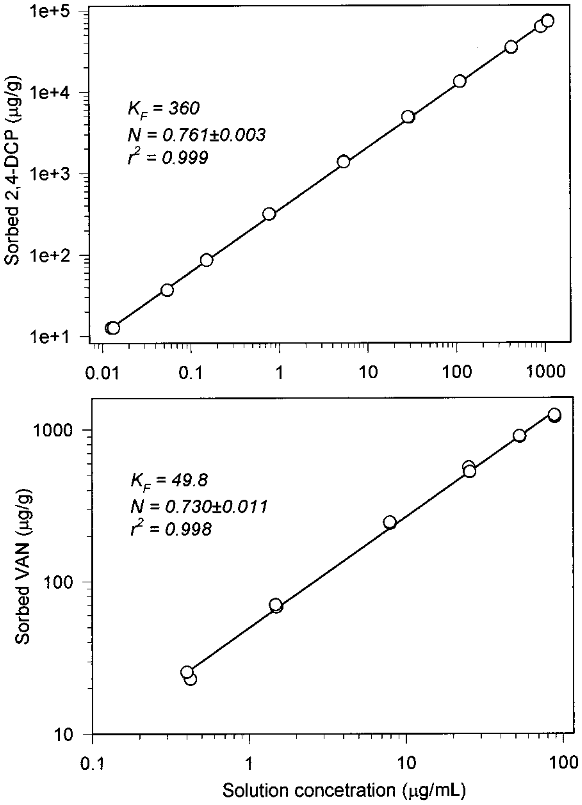


**FIGURE 3. Sorption isotherms of 2,4-DCP and VAN in Pahokee peat soil. Key to abbreviations is in Table 1.**

The 48-h Freundlich parameters, *N* and $K_F$, of 2,4-DCP, 1,3-DCB, and the five strongest competing aromatic acids are given in Table 2, and examples of the isotherms (2,4-DCP and VAN in peat) are shown in Figure 3. All isotherms in

**TABLE 2. Freundlich Parameters, $N$ and $K_F$, of Isotherms of Test Compounds[a]**

| chemical | $N$ | $K_F$ [$\mu$g/g)-($\mu$g/mL)$^{-N}$] | $r^2$ |
|---|---|---|---|
| | **Pahokee Soil** | | |
| 2,4-DCP | 0.761 ± 0.003[b] | 360 | 0.999 |
| 1,3-DCB | 0.852 ± 0.008 | 340 | 0.999 |
| VAN | 0.734 ± 0.014 | 50.6 | 0.997 |
| HYB | 0.729 ± 0.013 | 44.5 | 0.996 |
| CIN | 0.673 ± 0.005 | 130 | 0.999 |
| COU | 0.752 ± 0.005 | 231 | 0.999 |
| FER | 0.686 ± 0.011 | 280 | 0.997 |
| | **Cheshire Soil** | | |
| 2,4-DCP | 0.771 ± 0.003 | 9.39 | 0.999 |
| 1,3-DCB (24 h)[c] | 0.858 ± 0.007 | 8.02 | 0.999 |
| 1,3-DCB (30 day)[c] | 0.801 ± 0.006 | 11.1 | 0.999 |
| VAN | 0.576 ± 0.010 | 14.3 | 0.994 |
| HYB | 0.796 ± 0.006 | 1.04 | 0.999 |
| CIN | 0.756 ± 0.007 | 1.82 | 0.998 |
| COU | 0.734 ± 0.005 | 2.67 | 0.999 |
| FER | 0.507 ± 0.015 | 71.1 | 0.990 |

[a] 48 h, except where noted. Key to abbreviations is in Table 1. [b] Standard error of slope. [c] From Xing and Pignatello (*2*).

both soils were nonlinear. Although we used a contact time of only 48 h and equilibrium typically requires longer time (*2*), comprehensive studies reported elsewhere demonstrate that the nonlinearity of 1,3-DCB and 2,4-DCP isotherms (*2*, *3*), as well as those of other compounds (*2, 15*) increases with approach to equilibrium. This is illustrated by data from a previous study (*2*) reproduced in Table 2 for 1,3-DCB sorption in Cheshire soil after 1 and 30 day contact times.

The $N$ values of aromatic acids in Table 2 range from 0.686 to 0.752 in Pahokee peat soil and from 0.507 to 0.796 in Cheshire soil. For some compounds (especially VAN and FER), the $N$ values are markedly different in the two soils. As indicated by the values of $K_F$, sorption of the acids and the two chlorinated organic compounds to the peat is much greater than to the mineral soil.

We determined the effect of competitor concentration on $K_d$ for selected cases, and the results are shown in Figures 4 and 5. In all but one case, the $K_d$ relative to the value with no competing solute declines exponentially with increasing aromatic acid concentration, indicating direct competition of the aromatic acid for sorption sites. A similar exponential decline with cosolute concentration was also observed during competition between *s*-triazines and their analogues (*1*), halogenated hydrocarbons (*4*), and chlorinated benzenes (*3*). An exponential decay, moreover, is inconsistent with an effect of the competing aromatic acid on the bulk properties of the sorbent or on the activity of the principal solute in water—properties that could influence sorption. Had either of these effects occurred, competition would have been weak at low cosolute concentration and displayed an exponential *increase* with the cosolute concentration.

The one exception to the above exponential decay in the relative $K_d$ curve is displayed by FER in competition with 2,4-DCP in Cheshire soil. At relatively low concentrations (≤20 $\mu$g/mL), FER slightly *promotes* sorption of 2,4-DCP, but then as the concentration exceeds 20 $\mu$g/mL FER begins to suppress the sorption of 2,4-DCP, ultimately by about the same magnitude as the other acids at ~60 $\mu$g/mL. This curve was reproducible (data not shown). As can be seen in Figure 4b, the effect of FER was normal in the peat soil, so it plausible that the effect in the Cheshire soil has to do with the mineral component that is present in much greater amounts. One possible explanation is that FER adsorption on mineral surfaces creates adsorption sites for 2,4-DCP, which at very low FER concentration counteracts the decline in $K_d$ of 2,4-DCP from competition within SOM.

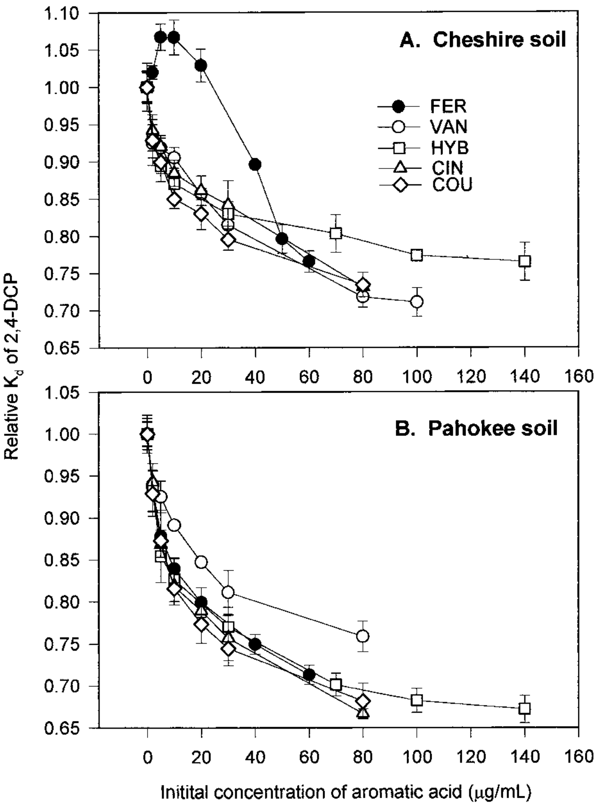


**FIGURE 4. Competitive sorption between 2,4-DCP at fixed initial concentration and VAN, HYB, CIN, COU, or FER at variable initial concentration. Key to abbreviations is in Table 1.**

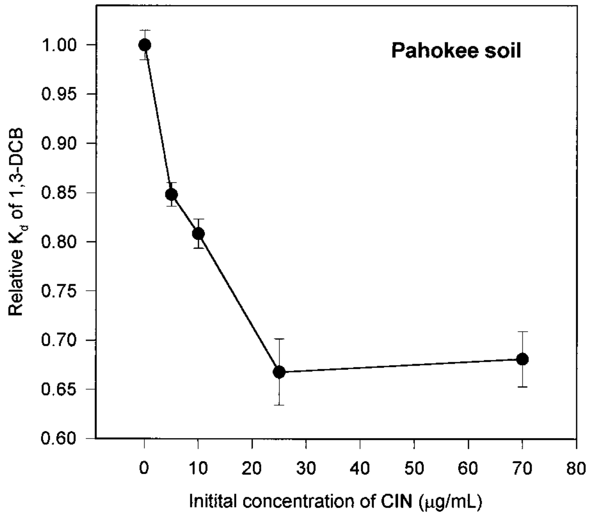


**FIGURE 5. Competitive sorption between 1,3-DCB at fixed initial concentration and CIN at variable concentration in Pahokee soil. Key to abbreviations is in Table 1.**

## Discussion

Taken together, the results indicate that competition exists between the anthropogenic organic compounds and the natural aromatic acids and that it occurs within the SOM domain. First, we may conclude the following regarding 1,3-DCB and 2,4-DCP: that they sorb predominantly to the SOM fraction, that sorption within SOM gives rise to the nonlinearity of their isotherms, and that the quality of SOM with respect to their sorption in the two soils appears to be similar.

It is commonly observed that SOM is the major retentive fraction in soils of uncharged organic compounds, whether they are polar or apolar. Apolar compounds, in particular, have an extremely low affinity for hydroxylated mineral surfaces in the absence of organic matter; for example, the $K_d$ of 1,4-dichlorobenzene is $4.5(\pm0.9) \times 10^{-3}$ mL/g on $\alpha$-$Al_2O_3$ (surface area, 11 $m^2$/g) and $1.05(\pm0.3) \times 10^{-3}$ mL/g on $\alpha$-$Fe_2O_3$ (2.7 $m^2$/g) (*16*). Thus, significant mineral adsorption of 1,3-DCB can be discounted. Although we cannot completely rule out mineral adsorption of 2,4-DCP because of its H-bonding ability, it is highly unlikely to contribute significantly in either of these soils because (a) 2,4-DCP sorbs strongly to Pahokee peat despite the extremely low mineral content and (b) the carbon-normalized $K_F$ of 2,4-DCP is comparable in the two soils—807 in Pahokee peat and 670 ($\mu$g/g) ($\mu$g/mL)$^{-N}$ in Cheshire soil. In the dual-mode mechanism, isotherm nonlinearity is due to association of the sorbate at specific sites within SOM, each unique site characterized by a Langmuir-type distribution relation that lends curvature to the isotherm as a whole. Elsewhere, we showed that removal of the small mineral component (~7%) of Pahokee peat by HF/HCl treatment had an insignificant effect on the Freundlich $N$ of 1,3-DCB (*3*). For both 1,3-DCB and 2,4-DCP, the degree of nonlinearity is comparable in the organic and mineral soils. This suggests that the SOM in these two soils is of a similar quality. This similarity is supported also by earlier results (*1*) showing that the contribution of hole-filling component of atrazine (2-chloro-4-(ethylamino)-6-isopropyl-*s*-triazine) sorption to its overall sorption was approximately identical in the two soils.

Nonlinearity is also characteristic of the aromatic acid isotherms. Because they contain hydroxyl and carboxyl(ate) functional groups, which can interact in a directional manner, the aromatic acids have the potential of adsorbing appreciably to mineral surfaces in addition to sorbing to SOM. Mineral adsorption can contribute to nonlinearity if the surface sites are nonuniform in energy—a condition expected to exist in soil minerals. Compounds with phenolic or carboxylate groups can H-bond, undergo ion exchange, and coordinate with structural or adsorbed metal ions on mineral surfaces (*17*−*20*). Ali and Dzombak (*21*) found that PHT and another organic acid each sorbed competitively with sulfate ions on goethite. Dalton et al. (*5*, *6*) observed sorption of FER by both SOM and oxides in soils. On the other hand, the importance of SOM was demonstrated by Dalton et al. (*6*), who observed that sorption of VAN, COU, HYB, and FER was consistently higher in surface horizons where the SOM content was high and that the recovery of added aromatic acid in soils decreased with increasing SOM content.

On examining Table 2, we find that the $N$ values of the aromatic acid isotherms do not follow the same order in the two soils—i.e., FER < VAN < COU < CIN < HYB in Cheshire soil, while CIN < FER < HYB < VAN < COU in Pahokee peat soil. Likewise, the order in affinity for the sorbent as $K_F$ is HYB < CIN < COU < VAN < FER in Cheshire soil, whereas it is HYB < VAN < CIN < COU < FER in Pahokee peat soil. That these two soils, which have widely dissimilar mineral contents, give different orders in Freundlich parameters among the aromatic acids may be construed as lending support to a role of mineral adsorption. Moreover, the anomalous behavior of FER in competitive sorption against 2,4-DCP in Cheshire soil (Figure 4) might also be interpreted as the result of a special interaction of FER with the surface.

We conclude, nevertheless, that most of the aromatic acid sorption must be to the SOM and that this component is primarily responsible for the nonlinearity of the aromatic acid isotherms and the competitive effects observed with the two anthropogenic organic compounds. Supporting this conclusion are the following: (a) The aromatic acid isotherms are nonlinear in the peat, which is 93% SOM, as well as in the mineral soil, which is only 3% SOM. The degree of nonlinearity is comparable overall—for example, the mean $N$ is 0.715 in Pahokee peat soil and 0.673 in Cheshire soil—although it varies between the soils for individual aromatic acids. (b) The observed pattern of the competitive response of 2,4-DCP (Figure 1) and 1,3-DCB (Figure 3) are quite similar in the two soils. Since the sorption of 2,4-DCP and 1,3-DCB is overwhelmingly to the SOM fraction, the competitive effect must take place in SOM.

Therefore, aromatic acids compete for specific sites in the SOM matrix that bind the chlorinated organic compounds. We believe, based on previous studies (*1*−*3***)**, that competition occurs in the hole-filling and not the dissolution domain. The magnitude of the competitive effect likely depends on the extent of overlap between the hole-filling domain of the aromatic acid and the hole-filling domain of 1,3-DCB or 2,4-DCP. Insufficient data exist to draw any meaningful structural correlations with degree of competition.

This is the first report of competitive sorption between organic pollutants and aromatic acids in soils. This information is important for understanding the behavior of pollutants in soil and subsurface environments. Due to the competitive effect, aromatic acids may be capable of increasing the mobility and bioavailability of anthropogenic organic compounds. In addition, researchers should be aware that competitive sorption by aromatic acids and other natural organic compounds may, under certain circumstances, contribute to experimental sorption anomalies such as hysteresis and particle concentration effects. Hysteresis refers to the apparent increase in affinity for sorbate when the isotherm is measured in the reverse (release) direction as compared to the forward (uptake) direction (*22*, *23*). Particle concentration effect refers to the apparent decrease in sorption coefficient with increasing solids concentration (*24*, *25*). These effects are often observed in experiments that involve serial dilution of a soil−water suspension with water, which concomitantly would result in dilution of natural competing molecules. In a modeling exercise, Curl and Keolelan (*26*) showed that desorption of an “implicit adsorbate” present initially in the soil can increase the $K_d$ of a newly adsorbing species, generating hysteresis between adsorption and desorption isotherms, and creating an inverse dependence of $K_d$ on particle concentration, simply as a result of the competitive process. This competitive process was observed for aromatic acids in the two soils tested in this study.

## Acknowledgments

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