

# Potential Contributions of Smectite Clays and Organic Matter to Pesticide Retention in Soils

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Soil organic matter (SOM) is often considered the dominant sorptive phase for organic contaminants and pesticides in soil–water systems. This is evidenced by the widespread use of organic-matter-normalized sorption coefficients ( $K_{OM}$ ) to predict soil–water distribution of pesticides, an approach that ignores the potential contribution of soil minerals to sorption. To gain additional perspective on the potential contributions of clays and SOM to pesticide retention in soils, we measured sorption of seven pesticides by a K-saturated reference smectite clay (SWy-2) and SOM (represented by a muck soil). In addition, we measured the adsorption of atrazine by five different K-saturated smectites and Ca-saturated SWy-2. On a unit mass basis, the K–SWy-2 clay was a more effective sorbent than SOM for 4,6-dinitro-*o*-cresol (DNOC), dichlobenil, and carbaryl of the seven pesticides evaluated, of which, DNOC was sorbed to the greatest extent. Atrazine was sorbed to a similar extent by K–SWy-2 and SOM. Parathion, diuron, and biphenyl were sorbed to a greater extent by SOM than by K–SWy-2. Atrazine was adsorbed by Ca–SWy-2 to a much lesser extent than by K–SWy-2. This appears to be related to the larger hydration sphere of  $Ca^{2+}$  (compared to that of  $K^+$ ) which shrinks the effective size of the adsorption domains between exchangeable cations, and which expands the clay layers beyond the apparently optimal spacing of  $\sim 12.2$  Å for sorption of aromatic pesticide structures. Although a simple relation between atrazine adsorption by different K-smectites and charge properties of clay was not observed, the highest charge clay was the least effective sorbent; a higher charge density would result in a loss of adsorption domains. These results indicate that for certain pesticides, expandable soil clays have the potential to be an equal or dominant sorptive phase when compared to SOM for pesticide retention in soil.

**Keywords:** Sorption; pesticide; clay; organic matter; smectite

## INTRODUCTION

Clay minerals and soil organic matter (SOM) are considered the two most chemically active components of soils. Among clay minerals commonly found in soil environments, expandable 2:1 layer silicate clays are especially important because of their high surface areas and cation exchange capacities (CECs), as well as their surface reactivities (1). Although often present in relatively low amounts in soils, SOM disproportionately influences many important soil processes, including sorption of aqueous-phase organic contaminants and pesticides. Currently, about 4.5 billion pounds of chemicals are used as pesticides each year in the U.S., and agricultural usage accounts for  $\sim 77\%$  of the total (2). Sorption of soil-applied pesticides is an important determinant of their environmental fate and behavior, including bioavailability, persistence, and potential for leaching. Over the past two decades, research on pesticide sorption by soil has focused mainly on the singular role of SOM as the dominant sorptive phase (e.g., 3–6). Reliance on organic-matter-normalized sorp-

tion coefficients ( $K_{OM}$ ) to predict soil–water distribution of pesticides implicitly assumes that SOM is the dominant sorptive phase (4, 7, 8) and ignores the contribution of clays (hereafter used to indicate clay minerals rather than clay-sized particles) to pesticide sorption. The surfaces of clays have often been viewed as being polar in nature (9–12). It has been suggested that the preferential adsorption of water by these purportedly polar surfaces rendered clays ineffective as sorbents for neutral organic compounds (13–15).

The prevailing view of organic solute sorption by SOM generally ignores the role of soil minerals (including clays) in the sorption of organic contaminants and pesticides. Although this may be valid for relatively nonpolar molecules (e.g., benzene and trichloroethylene), it is possible that other neutral organic molecules, including important categories of pesticides, are effectively adsorbed by clays even in the presence of bulk water. In fact, a few recent studies support this contention. Atrazine adsorption by 13 Ca-saturated smectites ranged from very low to nearly complete removal from water, and was inversely dependent on clay properties such as surface charge density and cation-exchange capacity (16). With the measured pH of clay–water suspensions ranging between 4.75 and 6.45, and a  $pK_a$  of 1.7 for atrazine, it seemed apparent that atrazine was adsorbed as the neutral species. Atrazine adsorption by

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a montmorillonite (from Clay Spur, Wyoming) saturated with  $\text{Ca}^{2+}$  or  $\text{Al}^{3+}$  was attributed to the formation of H-bonds between atrazine and polarized waters of hydration (17). Nitro-substituted aromatics, including explosives and some dinitrophenol pesticides, are also significantly adsorbed by clays (18–20). Adsorption of these compounds was shown to be affected by the type of clay and its charge, the type of exchangeable cation, and the type and position of substituents on the aromatic ring. High adsorption of nitroaromatics by clays was attributed to the formation of an electron donor–acceptor complex, in which polarized aromatic rings parallel to the basal surfaces accept electrons from the siloxane oxygens to form the pesticide–clay complex. In addition to the proposed electron donor–acceptor mechanism, smectite clays may also adsorb neutral organic molecules by hydrophobic interactions. Recently, Laird and Fleming (21) presented data on the sorption of butylpyridine from water by Ca-smectite. As much as 95% of added butylpyridine was adsorbed, and  $\text{Ca}^{2+}$  release measurements indicated that ion exchange accounted for <20% of the amount sorbed. These results suggested a hydrophobic interaction between the butyl group of butylpyridine and the siloxane surface of smectite. Earlier work by Jaynes and Boyd (22) indicated that the siloxane surfaces of smectites possessed a hydrophobic character consistent with the results of Laird and Fleming (21).

The studies cited above, along with substantial experimental evidence from earlier studies (e.g., 23, 24), clearly documents the ability of pure clays, particularly expandable 2:1 clays, to effectively bind organic molecules, including pesticides. These studies suggest the potential importance of clays in organic contaminant and pesticide retention by soils. Using sorption data from soils of variable clay and SOM contents, Karickhoff (25) attempted to evaluate conditions under which mineral-phase sorption of organic contaminants in whole soils was important. For the N-heterocyclic simazine and biquinoline, mineral contribution to overall sorption became apparent (i.e., greater than that predicted from  $K_{\text{om}}$  values) at clay/organic matter ratios of >30. Sorption of pyrene, however, was not affected by clay content. It was concluded that the contribution of mineral-phase sorption was a direct function of the polarity of the compound. Grundl and Small (26) evaluated the role of mineral-phase sorption of atrazine and alachlor by a suite of sediments, and concluded that the pesticides were sorbed by both natural organic carbon (OC) and clays. The critical clay/OC ratios at which mineral-phase sorption accounted for 50% of the overall sorption were ca. 62 for atrazine and 84 for alachlor. Hassett et al. (27) evaluated the effect of clay content on sorption of  $\alpha$ -naphthol by soils and sediments with different OC and montmorillonite contents. They concluded that the contribution of mineral-phase sorption to overall uptake was apparent at clay/OC ratios of >10. Although these studies established the importance of clays as sorbents for organic contaminants in soils, they did not isolate or quantify the individual sorptive contributions of clays and SOM.

The adsorption of aqueous phase pesticides by clays differs significantly among the various combinations of pesticides and clays. It is often unclear whether the sorption of pesticides by clays is comparable to that by SOM. In this study, representative pesticides from several major classes were used to compare sorption by

a reference smectite clay to that of a muck soil representing SOM. These data were used to provide some additional perspective on the potential importance of smectite clays and SOM as sorbents for aqueous-phase pesticides.

## EXPERIMENTAL PROCEDURES

**Pesticides.** Seven pesticides were used in the adsorption experiments (Table 1). The pesticides were purchased from ChemService, Inc., West Chestnut, PA, with a purity of >99%, and used as received. Six of them were chosen to represent major classes of pesticides. The seventh, biphenyl, was included as a representative nonpolar unsubstituted pesticide. The pesticides were also selected to encompass a variety of different structural and physicochemical properties. They contained various substituents, including strongly electron-withdrawing groups such as  $-\text{NO}_2$  and  $-\text{CN}$ , and also have a wide range of water solubilities, dipole moments, and octanol/water partition coefficients ( $K_{\text{ow}}$ ). The gas-phase dipole moments were computed using B3LYP density functional calculations (28–30). These are quantum mechanical calculations of reasonably good quality using the Becke three-parameter hybrid method (28) for the exchange functional along with the Lee, Yang, and Parr correlation functional (30). These electronic structure calculations show that molecular thicknesses, as estimated by the 0.02 electron/ $\text{\AA}^3$  isodensity surfaces, were  $3.5 \pm 0.2 \text{ \AA}$  for 4,6-dinitro-*o*-cresol (DNOC) and a wide variety of other planar nitroaromatic molecules. To estimate the effective surface area occupied by DNOC on clay surfaces, we used our force field (31) for organic-clay interactions to perform molecular mechanics calculations. We used Grand Canonical Monte Carlo calculations (32) to model adsorption of DNOC into an uncharged clay with just enough interlayer space (12.8  $\text{\AA}$   $d$  spacing) for the DNOC. For three simulations at two different unit cell sizes (in-layer unit cell vector products  $ab$  were 4534 and 5922  $\text{\AA}^2$ ), we found similar values of 51.9, 54.3, and 52.1  $\text{\AA}^2$  per DNOC. These values should be the upper limit, as the DNOC packing was not perfect. In summary, the surface area of DNOC should be  $\leq 52 \text{ \AA}^2$ , and its thickness should be about 3.5  $\text{\AA}$ . The interlayer space available in a 12.5- $\text{\AA}$  monolayer hydrate clay mineral can be estimated by comparing the 9.19- $\text{\AA}$   $d$  spacing of pyrophyllite (nothing in the interlayer), which yields about 3.3  $\text{\AA}$  for the available interlayer space, agreeing moderately well with the thickness of the organic molecule.

**Sorbents.** A reference smectite, SWy-2, was used in most of the measurements of pesticide adsorption by clays. Five other clays were also studied for atrazine adsorption measurements. The clays were chosen to provide a range of surface charge densities, and differences in the location of charge deficit and the structure of octahedral sheet (dioctahedral vs trioctahedral) (Table 2). All clays were obtained from the Clay Minerals Society Source Clay Repository (Columbia, MO) except beidellite which was from Ward's (Rochester, NY). The <2  $\mu\text{m}$  clay particles were separated by wet sedimentation. The clays were subject to  $\text{K}^+$  saturation, and also  $\text{Ca}^{2+}$  saturation for SWy-2, by dispersing 10-g clay samples in 1 L of KCl (0.1 M) or  $\text{CaCl}_2$  (0.1 M) solution. The clay suspensions were shaken for 24 h, and then fresh chloride solutions were used to displace the original solutions after centrifugation. This process was repeated four times to ensure complete K- or Ca-saturation. Distilled water (1 L) was used to wash the clays to remove excess  $\text{K}^+$  or  $\text{Ca}^{2+}$ . The clays were freeze-dried and stored for later use. The Houghton muck soil was collected from the Michigan State University Muck Farm and air-dried. Its OC content (49.5%) was measured by a carbon analyzer (Rosemount Analytical, Inc., Santa Clara, CA).

**Sorption Isotherms.** Pesticides were dissolved in 0.1 M KCl solution with concentrations up to 50% of their water solubilities. A pH 3 KCl solution was used for DNOC. In the case of Ca–SWy-2 and the muck soil, 0.1 M  $\text{CaCl}_2$  was used. Up to 4.4 mL of KCl (or  $\text{CaCl}_2$ ) solution was pipetted into the 7-mL borosilicate glass vials containing clay or muck soil (0.05

**Table 1. Selected Physicochemical Properties of Pesticides Used for Sorption Study**

pesticide	class	structure	water solubility (mg/L)	log $K_{ow}$	dipole moment (D)	$\lambda_{max}$ (nm)	usc
4,6-dinitro- <i>o</i> -cresol	dinitrophenol		198	2.12	4.06	269	insecticide, herbicide
carbaryl	carbamate		104	2.36	2.29	280	insecticide
diuron	substituted urea		38	2.68	-	248	herbicide
atrazine	triazine		28	2.61	4.86	220	herbicide
dichlobenil	benzotrile		18	2.74	5.54	238	herbicide
parathion	organophosphate		13	3.83	7.06	278	insecticide, acaricide
biphenyl			6	3.98	0	248	fungicide

**Table 2. Properties of Clays and the Freundlich Coefficients for Atrazine Adsorption by K-clays**

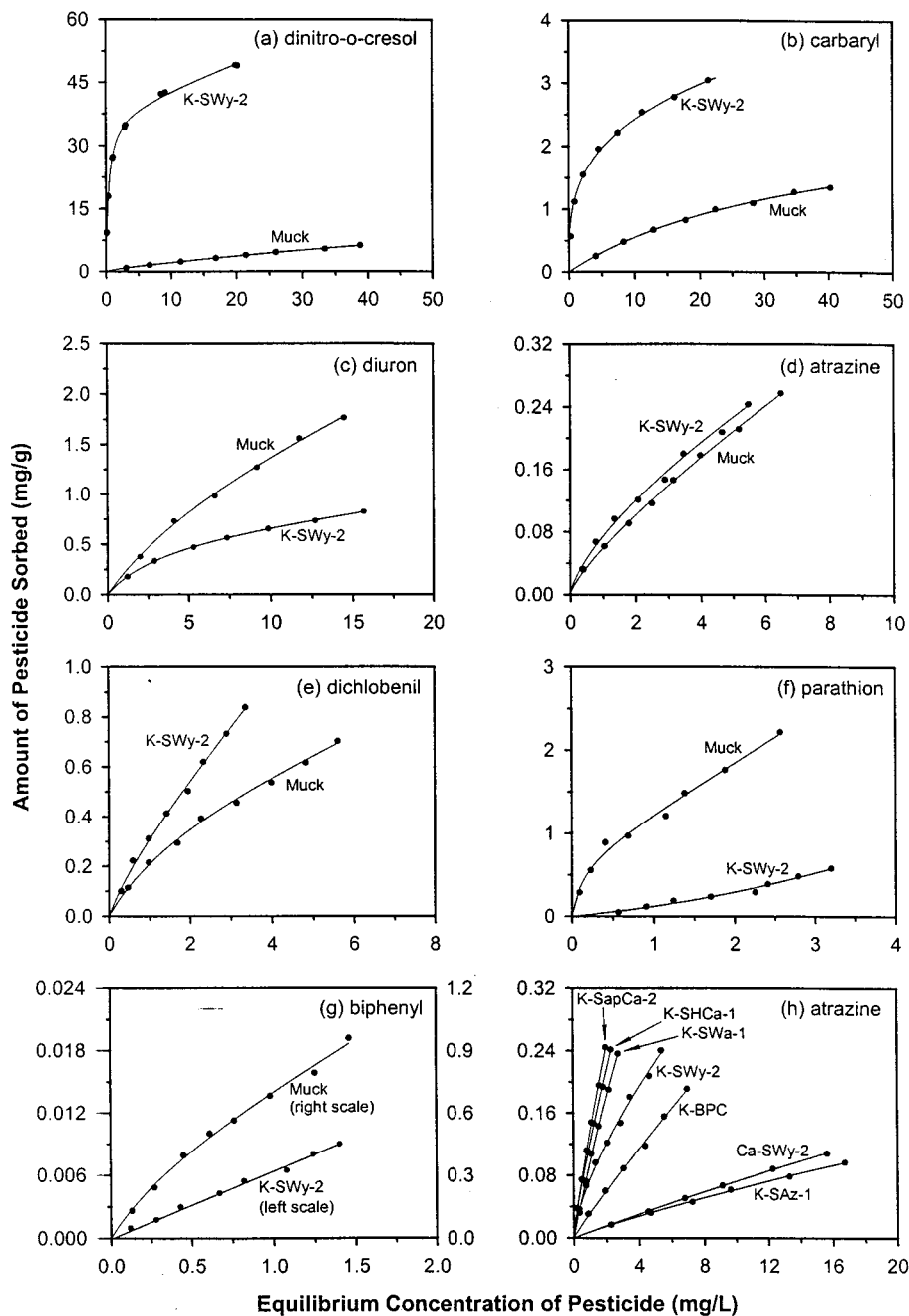
sorbent	mineralogy	cation-exchange capacity (cmol <sub>e</sub> /kg)	% tetrahedral charge	tri-/di-octahedral	$K_f$ (mg/kg)/(mg/L) <sup>n</sup>	<i>n</i>
K-SHCa-1	hectorite	43.9	0	tri-	120	0.821
K-SWy-2	montmorillonite	81.6	0	di-	74.6	0.784
K-BPC	beidellite	84.2	52	di-	31.4	0.925
K-SapCa-2	saponite	94.9	>50	tri-	135	0.841
K-SWa-1	nontronite	107	73	di-	95.3	0.899
K-SAz-1	montmorillonite	130	0	di-	8.47	0.864

to 1 g). Pesticide solution was then added into each vial to make up a total volume of 5 mL. For DNOC ( $pK_a$  4.35 to 4.46), sorption was measured at pH 3 to ensure the molecular form of the pesticide. The pH of clay suspension before DNOC sorption was adjusted until it remained stable at  $\sim 3$ , and was also measured after sorption to further ensure the stable pH. Clay dissolution under such a pH was not noted. Consistent with previous studies (18, 19) we found that DNOC sorption by clays reached equilibrium within 10 min. In the case of the muck soil the pH of the aqueous  $CaCl_2$  suspension was adjusted to  $3.0 \pm 0.1$  before DNOC solution was introduced. The pH adjustment was repeated as needed until it remained stable after 3 days. The vials were continuously rotated overnight at room temperature and then centrifuged at 1667*g* for 20 min to separate the liquid and solid phases. The concentrations of pesticides in supernatants were analyzed, by direct injection of supernatants (between 10 and 190  $\mu$ L), using a Perkin-Elmer reversed-phase HPLC (Perkin-Elmer, Norwalk, CT) fitted with an UV-visible detector set at the maximum absorption wavelength for each pesticide (Table 1). A platinum extended polar selectivity (EPS) C18 column was used. The mobile phase was a mixture of methanol and water ranging from 55% to 75% methanol with a flow rate of 1.0 mL/min. The amount of pesticide sorption was calculated from the difference between the amount added and that remaining in the final solution.

After sampling for HPLC analysis, the remaining DNOC-K-SWy-2 suspensions were used for X-ray diffraction analysis. The supernatants of 1–2 mL were retained in the vials to resuspend the clay by hand-shaking, and then dropped on glass and air-dried overnight to obtain the oriented films. X-ray diffraction patterns were recorded using  $Cu-K\alpha$  radiation and a Philips APD 3720 automated X-ray diffractometer using an APD 3521 goniometer fit with a  $\theta$ -compensating slit, a 0.2-mm receiving slit, and a diffracted-beam graphite monochromator, from 3 to 14  $^\circ 2\theta$ , in steps of 0.02  $^\circ \theta$ , at 1 s/step.

## RESULTS AND DISCUSSION

Pesticide sorption isotherms based on per unit mass of clay or muck (SOM) versus the equilibrium aqueous concentration of each pesticide are shown in Figure 1-(a–g). The Houghton muck soil was used to evaluate the potential contribution of soil organic matter (SOM) to pesticide sorption. The representation of SOM by the muck soil is supported by the similarities of organic-carbon-normalized sorption coefficients ( $K_{oc}$ ) between a peat soil (49.3% OC) and a mineral soil (1.26% OC) for both nonpolar (ethylene dibromide, EDB) and polar (dichlorophenol, DCP) compounds (33). The reported log  $K_{oc}$  values for the peat and mineral soils were 1.28 and



**Figure 1.** Sorption isotherms representing pesticide uptake from water by a reference homoionic K-smectite (SWy-2) and muck soil representing soil organic matter (a–g), and atrazine uptake by several different K-saturated smectites and Ca-SWy-2 (h).

1.23 for EDB and 2.03 and 1.87 for DCP, respectively. The isotherms representing pesticide sorption on the muck soil display some nonlinearity. Isotherm nonlinearity has been observed previously for polar and nonpolar organic solutes and attributed to a glassy phase in SOM (5, 6, 34, 35), to the presence of a small quantity of high-surface-area carbonaceous material (33, 36), and/or to solute-SOM specific interactions (36, 37). The isotherms for pesticide sorption by K-SWy-2 are either linear, type I, or type III (38), depending on the specific compound. This reflects different types and/or strengths of pesticide-clay interactions. The calculated distribution coefficients (expressed as the ratio of the concentration of sorbed pesticide to the aqueous-phase pesticide concentration) for both K-SWy-2 and muck at a relative concentration (i.e., the ratio of the aqueous-phase concentration to water solubility) of 0.1 are given in Table 3 for each pesticide. The term  $K_{K-SWy-2}/K_{muck}$

**Table 3. Distribution Coefficients (L/kg) of Pesticides Sorbed by K-SWy-2, Muck, or Ca-SWy-2 at the Relative Concentration of 0.1<sup>a</sup>**

pesticide	$K_{K-SWy-2}$	$K_{muck}$	$K_{K-SWy-2}/K_{muck}$
4,6-dinitro- <i>o</i> -cresol	$2.49 \times 10^3$	184	13.6
carbaryl	235	54.2	4.34
diuron	103	173	0.593
atrazine	$54.2 (7.68)^b$	47.1	1.15
dichlobenil	275	179	1.54
parathion	125	$1.08 \times 10^3$	0.116
biphenyl	6.40	791	$8.09 \times 10^{-3}$

<sup>a</sup> Relative concentration equals equilibrium aqueous-phase concentration/water solubility. <sup>b</sup> Distribution coefficient for sorption by Ca-SWy-2.

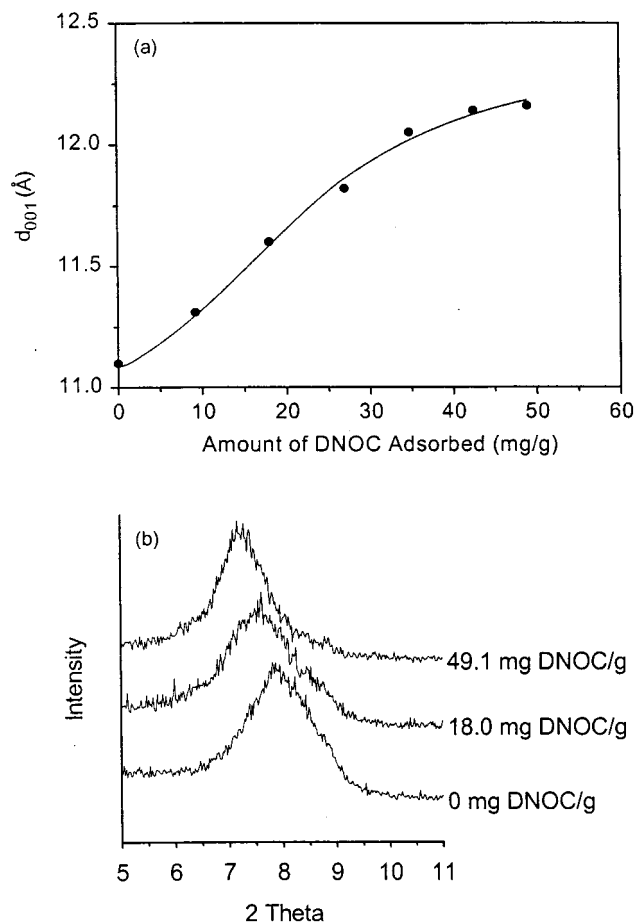
is the ratio of the two distribution coefficients for each pesticide and allows comparison of the relative effectiveness of K-SWy-2 clay and SOM as sorbents for pesticides. It shows that some pesticides, i.e., DNOC, car-

baryl, and dichlobenil, were more effectively sorbed by K-SWy-2 clay than by SOM. Others, i.e., diuron, parathion, and biphenyl, were sorbed more effectively by SOM than by clay. Atrazine is sorbed by K-SWy-2 clay and SOM to a similar extent. Direct correlations between pesticide adsorption ( $K_f$  values) by K-SWy-2 and water solubility,  $K_{OW}$ , or dipole moment were not found, reflecting the complexity of pesticide-clay interactions.

Biphenyl was highly sorbed by the muck soil. In contrast, K-SWy-2 clay was a relatively ineffective sorbent for biphenyl (Figure 1g). The smectite was approximately 120 times less effective than SOM for biphenyl sorption (Table 3). Biphenyl is a nonpolar, poorly water-soluble aromatic molecule. These characteristics manifest its high uptake by SOM, consistent with previous findings (39). These molecular properties, however, were apparently not sufficient for significant sorption by K-SWy-2, despite indications that the siloxane surfaces of smectites are hydrophobic in nature (21, 22). This suggests that, in addition to hydrophobic interactions, other mechanisms may be necessary for substantial retention by smectites.

Sorption of DNOC by K-SWy-2 was highest among all pesticides studied (Figure 1a), although it is pH-dependent due to ionization of the phenolic hydroxyl. For example, raising the pH from 3 to 5 caused ~50% reduction in the sorption of DNOC by K-SWy-2 (data not shown), but the sorption was still substantially higher than that by SOM. We have observed similar or slightly higher sorption of the nonionizable compounds 1,3- and 1,4-dinitrobenzene by K-SWy-2 (40). Based on distribution coefficients at a relative aqueous concentration of 0.1 (Table 3), sorption of DNOC was ~9 times greater than the next most highly sorbed pesticide (dichlobenil); the difference is even greater at lower concentrations. Also, K-SWy-2 was ~14 times more effective than SOM as a sorbent for DNOC (Table 3).

The basal spacing of K-SWy-2 increased gradually from ~11.1 to ~12.2 Å with increasing DNOC adsorption (Figure 2a). Selected X-ray diffraction (XRD) patterns (Figure 2b) show that the diffraction peaks were broad and generally symmetrical, indicating the random interstratification of DNOC molecules in the interlayers of K-SWy-2. The X-ray diffraction peaks corresponded to distributions of clay mineral  $d$  spacings from roughly 10 to 13 Å. Thus, the clay films typically contained a continuum of domains ranging from dehydrated K-smectite (10 Å) to an interlayer containing a monolayer of  $K^+$ , water, and/or DNOC (12 to 13 Å). As the DNOC loading increased, the  $d$  spacing corresponding to the centroid of this diffraction peak increased to 12.2 Å for the DNOC loading corresponding to a solution-phase DNOC concentration of 20 mg/L. The increase in basal spacing suggests that DNOC is intercalated in the interlamellar region of the clay, with an increasing fraction of the clay domains at larger  $d$  spacings (12 to 13 Å). The surface area of K-SWy-2 is 750 m<sup>2</sup>/g and the estimated cross-sectional area of the DNOC molecule is 52 Å<sup>2</sup>. The surface area occupied by DNOC molecules ( $f$ ) was ca. 10%. This was calculated as follows:



**Figure 2.** (a) 4,6-dinitro-*o*-cresol adsorption-dependent variation in the basal spacing of K-SWy-2, and (b) selected X-ray diffraction patterns.

$f =$

$$\frac{49 \text{ mg/g}}{198 \text{ g/mol}} \times 10^{-3} \text{ mol/mmol} \times 6.023 \times 10^{23} / \text{mol} \times 52 \text{ Å}^2 \times 10^{-20} \text{ m}^2 / \text{Å}^2}{750 \text{ m}^2} \times 100\% = 10.3\%$$

If the aromatic ring of DNOC is oriented parallel to the siloxane surface, and it simultaneously interacts with the opposing clay layers, as much as 21% of the smectite clay surface may be occupied at this loading.

The reasons that K-SWy-2 is a highly effective adsorbent for DNOC are not fully understood. The molecule is planar and aromatic, and it has two nitro groups that are strongly electron-withdrawing. According to Haderlein and Schwarzenbach (18), these molecular characteristics favor the formation of an electron donor-acceptor complex, in which the aromatic molecule acts as an acceptor of electrons donated from sites of negative charge in the clay. FTIR studies showed that the aromatic ring of adsorbed DNOC molecule is nearly parallel with respect to the siloxane surfaces of K-SWy-2 (41). The partial negative charge associated with the nitro groups may result in electrostatic interactions between the nitro groups and interlayer  $K^+$ . This is indicated by the fact that the FTIR stretching vibration bands of nitro groups shift depending on the interlayer cation (42). Thus, the high effectiveness of K-SWy-2 for DNOC appears to result from a combination of more than one mechanism.

Two other pesticides, carbaryl and dichlobenil, are also more favorably sorbed by K-SWy-2 than by SOM

(Figure 1b and e). The dichlobenil molecule may form an electron donor–acceptor complex with the siloxane surfaces because of the strong electron-withdrawing character of the cyano group on the aromatic ring, in analogy with nitroaromatics. The two-ring  $\pi$ -electron system of carbaryl may participate in the formation of an electron donor–acceptor complex depending on the inductive and resonance properties of the *N*-methylcarbamate (–OCONHCH<sub>3</sub>) moiety. The functional groups of carbaryl and dichlobenil may also interact with the exchangeable cations in analogy with DNOC, but we have no direct evidence for this currently.

Atrazine adsorption by K–SWy-2 was comparable to that by SOM (Figure 1d) but considerably less than that for DNOC. In comparison to DNOC, atrazine is larger and more structurally complex. In addition to the presence of –Cl, atrazine possesses two large substituted amino groups. These three substituents are positioned *meta* to each other on the triazine ring and may manifest a degree of steric hindrance in the adsorption of atrazine by K–SWy-2. Steric effects were also found in the adsorption of nitroaromatics with ortho substitution or large alkyl substituents (18, 19). Laird et al. (16) reported that smectite clays with lower charge densities and CECs were more effective adsorbents of atrazine; these characteristics may increase the size of the adsorptive domains between exchangeable cations. The adsorption of diuron and parathion is comparably low and less extensive by K–SWy-2 than by SOM (Figure 1c and f). These two pesticides contain large substituents on the aromatic ring (two –Cl and *N,N*-dimethylurea for diuron, nitro and diethylphosphorothionate for parathion) (Table 1) which may sterically hinder adsorption. The presence of bulky alkyl substituents has been observed to substantially diminish the adsorption of nitroaromatics by clay minerals (19). The type III isotherm for parathion adsorption by K–SWy-2 indicates weak parathion–clay interactions. However, both of these pesticides are sorbed by K–SWy-2 to a greater extent than is biphenyl.

Adsorption of atrazine was affected by the type of exchangeable cation on the smectite clay. Homoionic Ca–SWy-2 was a much less effective sorbent for atrazine than homoionic K–SWy-2 (Figure 1h). Atrazine adsorption indicates that K–SWy-2 ( $K_f = 54.2$ ) is seven times more effective than Ca–SWy-2 ( $K_f = 7.68$ ) (Table 3). Similar effects were observed by Haderlein and Schwarzenbach (18) and Haderlein et al. (19) for the adsorption of nitroaromatics by clays saturated with different cations. The lower effectiveness of Ca–SWy-2 may be due in part to the higher hydration energy and hence larger hydrated radius of Ca<sup>2+</sup> than that of K<sup>+</sup>. Presumably, the waters of hydration associated with Ca<sup>2+</sup> obscure a greater portion of the clay surface than those associated with K<sup>+</sup>, and this may effectively shrink the size of the adsorptive domains between exchangeable cations. Similar effects were observed by Kukkadapu and Boyd (43) for the adsorption of aromatic and chlorinated hydrocarbons by tetramethylphosphonium- and tetramethylammonium-smectites.

Differences in swelling behavior between K– and Ca–SWy-2 may also contribute to their differential pesticide adsorption. Many K-smectites equilibrate with ~12.5-Å layer spacings (monolayer structures) at 100% humidity and even in aqueous suspension (44–47), although some low-charge K-smectites can swell more. For example, K–hectorite (48) and K–SWy-2 (47) are likely to swell

to 15 Å and beyond at 100% humidity in the absence of organic sorbates. All Ca-smectites, on the other hand, swell to more than 15 Å. Because there is apparently a fine line between ~12.5-Å or larger swelling for K-smectites, it is quite possible that the presence of pesticides could cause the monolayer structure to be more favored, even in cases where the smectite might swell further in the absence of pesticide. In this scenario, each pesticide molecule contacts both clay surfaces simultaneously and thereby avoids contact with most water molecules. As the free energy of hydration for many small organic solutes is in the range of +10 to +30 kJ/mol (45, i.e., *n*-hexane, +27.5; cyclohexane, +23.7; toluene, +18.4 kJ/mol), removal of these solutes from aqueous solution may well provide enough energy to prevent K-smectite from swelling beyond 12.5 Å. For a Ca-smectite, in contrast, the energy penalty for compressing the interlayer and thereby dehydrating the pesticide (and the cation) is presumably too large.

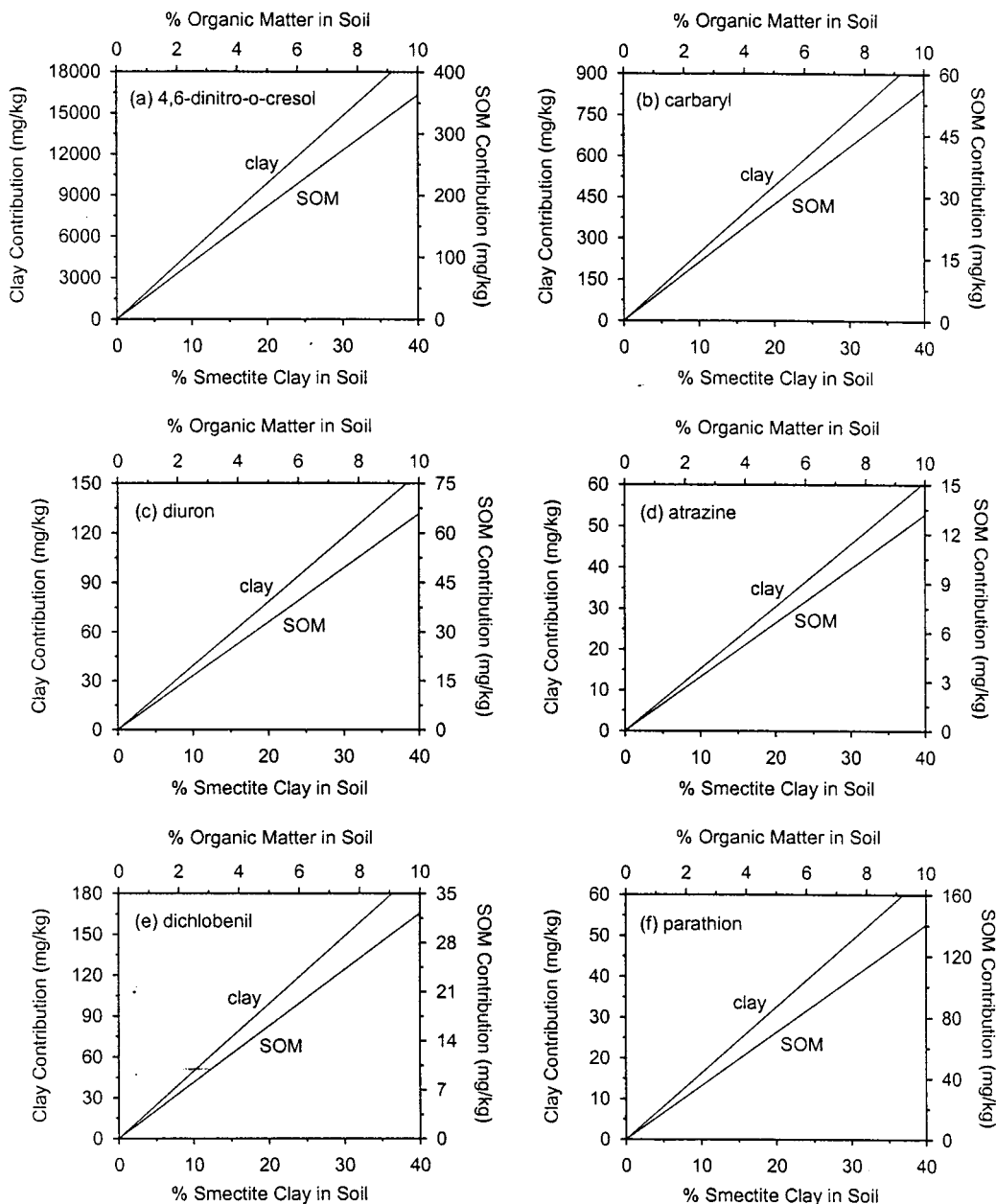
The specific type of smectite clay also affects pesticide adsorption. This is illustrated by atrazine adsorption by six different species of K-smectites (Figure 1h). In a study of atrazine adsorption by 13 Ca-saturated smectites, Laird et al. (16) found that the logarithm of the Freundlich adsorption constant ( $K_f$ ) was inversely correlated to clay CEC. We obtained  $K_f$  values (ranging from 8.5 to 135 L/kg, Table 2) for atrazine adsorption to six K-smectites, but we did not observe an obvious relationship between  $K_f$  and CEC. However, it was apparent that the clay with the highest CEC (and charge density), i.e., K–SAz-1, was the least effective adsorbent for atrazine. For this clay, it seems likely that atrazine adsorption decreased because of loss of adsorption domains of sufficient size to accommodate atrazine. Decreasing adsorption with increasing clay layer charge has been observed previously for the adsorption of nonpolar aromatics from water by tetramethylammonium- and trimethylphenylammonium-smectites (22, 49).

The potential contributions of smectite clay (K–SWy-2) and SOM to pesticide retention in soils (at relative pesticide concentration of 0.1, Table 3) can be calculated by the following equations, assuming these sorbent phases function independently:

$$C_{\text{clay}} = K_{\text{K-SWy-2}} \times C_e \times \text{clay \%}$$

$$C_{\text{SOM}} = K_{\text{muck}} \times C_e \times \text{SOM \%}$$

where  $C_{\text{clay}}$  and  $C_{\text{SOM}}$  are the respective clay-sorbed and SOM-sorbed pesticide concentrations normalized to the whole soil at the aqueous phase concentration of  $C_e$ . Calculations using the distribution coefficients listed in Table 3 for model (hypothetical) soils over a range of SOM (0–10%) and smectite clay (0–40%) contents that might reasonably be found in mineral soils are graphically shown in Figure 3. These plots can be used to compare the potential contributions of smectite clays and SOM to the pesticide retention in a soil with known smectite clay and SOM contents. For example, from Figure 3, we estimate that clay (K–SWy-2) contributes (~390 mg/kg) ~35 times more to carbaryl retention than SOM (~11 mg/kg) in a soil with 16% clay and 2% SOM. For parathion in the same soil, contributions by smectite clay and SOM are about equivalent. For some pesticides, even low amounts of smectite clay could potentially exert a strong influence on sorption. For example, assuming a soil containing 2% K–SWy-2 and 2% SOM,



**Figure 3.** Potential contributions of smectite clay (represented by K-smectite, SWy-2) and soil organic matter (SOM, represented by a muck soil) to pesticide immobilization in model (hypothetical) soils.

the amounts of DNOC sorbed at the relative concentration of 0.1 are ca. ~980 mg/kg by clay and ~70 mg/kg by SOM. Although this illustrates the potential dominant role of certain clay minerals in the retention of specific pesticides in soils, caution must be taken in extrapolating these results. Humic substances in soils may form coatings on clay particles thereby rendering these surfaces unavailable for pesticide adsorption. However, this effect is probably limited to the external surfaces of expandable clays, as there is no evidence for the intercalation of humics by naturally occurring clays. This effect is further minimized in subsoils and aquifer materials with inherently low organic matter contents.

In considering the applicability of these results to real soil clays,  $K^+$  is one of the most abundant exchangeable cations in soils and subsoils, but it is not normally the dominant exchangeable cation. The phenomenon of cation demixing in clays (50–52) results in entire interlayer regions being occupied by a single exchangeable cation (e.g.,  $K^+$ ) even in the presence of other

cations (e.g.,  $Ca^{2+}$ ) because of differences in cation hydration. Thus, K-rich domains with high affinity for pesticides such as nitroaromatics are likely to exist in many soils. Indeed, the widely occurring phenomenon of K-fixation by soil clays (53–55) proves that K-rich domains are common. Even for a variety of Ca-saturated smectites, Laird et al. (16) reported very high removal of atrazine from water, so the efficacy of smectites as adsorbents of pesticides is not limited to K-saturated clays. Improved understanding of pesticide adsorption by clays makes it possible to enhance the retentive properties of subsoils and aquifer materials for certain pesticides by controlling the base saturation of the matrix via in-situ electrolyte injection (e.g., KCl) as suggested by the recent findings of Weissmahr et al. (56).

In summary, pesticides can be sorbed effectively by either clays or SOM. Sorption depends on the specific type of clay, saturating cation, and pesticide structure. Whereas pesticide sorption by SOM is generally deter-

mined by pesticide water solubility, adsorption by clays is dependent on both pesticide and clay properties. Our study builds upon previous work to probe the dependence of pesticide sorption on the structure of the pesticide, on the exchangeable cation saturating the smectite clay, and on the smectite clay layer charge. Understanding these dependencies will help constrain the interpretation of more mechanistic spectroscopic studies underway in our laboratories. The existence of multiple sorption mechanisms appears to favor pesticide sorption by smectite clays. Planar aromatic structures and electron withdrawing substituents (e.g.  $-\text{NO}_2$ ,  $-\text{CN}$ ) seem to favor pesticide adsorption, possibly via the formation of an electron donor-acceptor complex between pesticide molecules and siloxane surfaces. Polar substituents may interact via a  $\text{H}_2\text{O}$ -bridge with hydrated exchangeable cations; substituents with negative charge character (e.g.  $-\text{NO}_2$ ) may interact directly with exchangeable cations. Hydrophobic interactions between the pesticide and the siloxane surfaces may also contribute to adsorption. Large substituents associated with pesticide structure may cause steric constraints that diminish adsorption. A steric effect may also arise from the hydration of cations saturating clays, i.e., a large hydration sphere may diminish the size of the adsorption domains between exchangeable cations. Exchangeable cations may also influence sorption due to effects on basal spacing. A spacing of  $\sim 12.2 \text{ \AA}$ , such as that associated with K-smectites, appears optimal for adsorption of nitro-aromatic pesticides. Finally, low surface charge density may increase the size of the adsorptive domain, hence increasing adsorption. In this limited study of seven pesticides and reference smectite clays, the K-SWy-2 clay was shown to be a more dominant sorptive phase than SOM in over half the cases.

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