

Sorption and Desorption of Pesticides by Clay Minerals and Humic Acid-Clay Complexes

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ABSTRACT

In soils, organic matter and minerals are often associated such that it is unclear how the presence of the former component influences the sorptive properties of the latter one. In this study, sorption and desorption of the herbicides 4,6-dinitro-*o*-cresol ($C_7H_6N_2O_5$) and dichlobenil ($C_7H_3Cl_2N$) by Ca^{2+} -, K^+ -smectites, and humic acid-smectite complexes, was investigated using batch-equilibrations and x-ray diffraction (XRD). Greater sorption of 4,6-dinitro-*o*-cresol compared with dichlobenil was observed for both smectites and humic acid-smectite complexes. For both pesticides, K^+ smectites were more effective sorbents than Ca^{2+} smectites, with the lower charge-density clay (SWy-2) displaying a greater sorption capacity than the higher charge-density clay (SAz-1). The presence of humic acid did not impact pesticide sorption by K^+ clays, but could enhance or suppress pesticide sorption by Ca^{2+} -clays. A composite model for estimating pesticide sorption, which assumes mineral and organic matter function individually as sorbent phases, predicted sorption within a factor of 0.8 to 1.5 times the measured values. Humic acid did not contribute to pesticide desorption hysteresis in K^+ -humic acid-clay complexes, but was a source of hysteresis in the corresponding Ca^{2+} complexes. The basal spacings of K-SWy-2 and humic acid-modified K-SWy-2 increased gradually from approximately 10.4 to 12.2 Å with increasing 4,6-dinitro-*o*-cresol loadings. Also, XRD patterns of humic acid-modified and unmodified K-SWy-2 smectite clays were found identical. These results demonstrate the intercalation of 4,6-dinitro-*o*-cresol and suggest that humic acids are restricted to the external surfaces of clay tactoids. Together, these results indicate that clay mineral fractions in soils, including those with organic coatings, may play an important role in the retention of certain pesticides.

ORGANIC MATTER and clay minerals are generally considered as the two most important soil components in the retention of soil-applied pesticides. It is well established that the uptake of nonpolar organic compounds from aqueous solution is strongly correlated with soil organic matter (or organic C) content (Chiou et al., 1979, 1983; Karickhoff et al., 1979; Kile et al., 1995; Kleinedam et al., 1999; Weber and Huang, 1996; Xia and Ball, 1999; Xing and Pignatello, 1997). Reliance on soil-organic-matter (or organic-C) normalized sorption coefficients (K_{OM} , K_{OC}) to predict the transport of neutral organic compounds in soil and subsurface environments implies that soil organic matter is the singular sorptive domain, and ignores the potential contributions of soil mineral fractions. Previous research by Chiou and coworkers (Chiou and Shoup, 1985; Chiou et al., 1985) noted that in hexane-soil systems, the addition of

small amounts of water to soil reduced the sorption of organic compounds relative to the sorption by the dehydrated soil in hexane, and that organic vapor adsorption by soil was significantly depressed by increasing relative humidity. Based on these observations, they concluded that soil behaves as a dual sorbent in which soil organic matter functions as a partitioning medium and mineral fractions as conventional adsorbents. Furthermore, the adsorption of organic compounds by the mineral fractions was thought to be restrained by ambient moisture because water molecules preferentially occupied the adsorptive sites on mineral surfaces. This hypothesis may be valid for nonpolar organic compounds (e.g., aromatic hydrocarbons) and those containing slightly polar functional groups (e.g., -Cl), however, for moderately and strongly polar functional group-containing compounds including many pesticides, multiple sorption mechanisms may be operative. These include solute partitioning into soil organic matter as well as specific interactions with mineral components such as clays (Karickhoff, 1984). In some cases, mineral fractions may contribute more than soil organic matter to the retention of certain neutral organic contaminants and pesticides (Sheng et al., 2001).

Polar functional group-containing compounds interact with clays through a variety of mechanisms (Mortland, 1970). These include interactions with exchangeable cations on clay surfaces via ion-dipole interactions, and with siloxane surfaces via surface adsorption. The ion-dipole mechanism may involve direct interactions of organic compounds with exchangeable cations or indirect interactions through the intermediation of water molecules surrounding the cations. Ion-dipole interactions may be enhanced with increasing charge valence of exchangeable cations. For example, pesticide (e.g., clomazone, atrazine) adsorption on montmorillonite saturated with a variety of cations decreased in the order: $Al^{3+} > Mg^{2+} \geq Ca^{2+} > Li^+ > Na^+$ (Bowman, 1973; Loux et al., 1989; Sawhney and Singh, 1997). For the Al^{3+} -saturated clays, strong polarization of water molecules associated with Al^{3+} manifests strong H-bonding with pesticides leading to greater adsorption (Sawhney and Singh, 1997). Alternatively, water molecules surrounding strongly hydrated cations such as Ca^{2+} and Mg^{2+} may weaken ion-dipole interactions by inhibiting the direct interaction between polar functional groups and exchangeable cations (Johnston et al., 2001, Sheng et al., 2002). Nonpolar surface interactions between organic compounds and the siloxane surfaces of clays may also occur (Jaynes and Boyd, 1991; Laird and Fleming, 1999). In clays exchanged with less strongly hydrated

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Abbreviations: EDA, electron donor acceptor; XRD, x-ray diffraction.

cations (e.g., NH_4^+ , K^+ , and organic cations), the smaller size of the cation hydration sphere results in increased size of adsorptive domains among exchangeable cations hence enhancing organic compound sorption to siloxane surfaces. Jaynes and Boyd (1991) measured the adsorption of aromatic hydrocarbons on trimethylphenylammonium-saturated smectites and found that adsorption increased as clay layer charge and exchanged organic cation content decreased, implying that the exposed clay siloxane surfaces are the effective adsorptive domains. Others have noted that the adsorption of organic compounds on clay siloxane surfaces increase with decreasing clay surface charge density (Lee et al., 1990; Laird et al., 1992) and decreasing hydration energies of exchangeable cations (Haderlein and Schwarzenbach, 1993; Johnston et al., 2001; Sheng et al., 2002).

Nitroaromatics comprise an important class of environmental contaminants (explosive chemicals) and pesticides that are strongly adsorbed by certain clay minerals (Boyd et al., 2001; Haderlein et al., 1996; Johnston et al., 2001; Sheng et al., 2002; Weissmahr et al., 1998). Haderlein and coworkers proposed an electron donor-acceptor (EDA) mechanism to account for the strong adsorption of nitroaromatic compounds by aluminosilicate clays (Haderlein et al., 1996; Weissmahr et al., 1997). According to this mechanism, the electron-deficient π -system of nitroaromatics, which results from the electron-withdrawing properties of $-\text{NO}_2$ groups, accepts electrons from siloxane oxygens with negative charge character (because of isomorphous substitution) to create the proposed EDA complexes. However, quantum calculations for the adsorption of trinitrobenzene on the siloxane sites of clays suggest that the EDA interactions should not play a significant role in sorption (Pelmenchikov and Leszczynski, 1999). Boyd et al. (2001) studied the adsorption of nitroaromatics by smectites using Fourier Transform Infrared (FTIR) spectroscopy, XRD, quantum calculations, and molecular dynamics simulations. They concluded that the adsorption of substituted nitroaromatics on K^+ -saturated smectite clays results from the complexation of $-\text{NO}_2$ groups with the interlayer K^+ ions, and the energy gained by partitioning of nitroaromatics into the subaqueous environment of the clay interlayers where the sparingly soluble organic compound is less hydrated than in bulk water.

Clay minerals can strongly adsorb certain aqueous phase organic compounds containing polar functional groups, suggesting the potential contributions of clay minerals to the retention of organic contaminants and pesticides in soils and subsoils. Among the clay minerals commonly found in the soil environment, expandable 2:1 layer silicate clays are especially important because of their wide distribution, high surface areas, and cation-exchange capacities as well as their chemical surface reactivities (Laird et al., 1992). Several previous studies have attempted to identify the critical ratio of clay minerals/soil organic matter at which sorption by the mineral phase plays an important role (Grundl and Small, 1993; Hassett et al., 1981; Karickhoff, 1984; Means et al., 1982). The critical ratios of swelling clays to organic C were estimated between 10 and 30 for compounds

such as naphthol, amino-substituted polynuclear aromatic hydrocarbons, simazine and biquionoline (Hassett et al., 1981; Karickhoff, 1984; Means et al., 1982). Grundl and Small (1993) estimated critical ratios of 62 for atrazine and 84 for alachlor at which mineral phase sorption accounted for 50% of the total sorption. No important role of soil clays was found for the sorption of aqueous phase nonpolar organic compounds such as pyrene (Karickhoff, 1984), although significant adsorption of phenanthrene from aqueous phase by smectite clays has been reported recently (Hundal et al., 2001). Sheng et al. (2001) measured the sorption of several pesticides by a reference K^+ -saturated montmorillonite (K-SWy-2) and a muck soil, and quantified the individual contribution of smectite clay and organic matter to sorption. On a unit mass basis of sorbent, K-SWy-2 was more effective for sorption of certain compounds containing polar functional groups (e.g., 4,6-dinitro-*o*-cresol and dichlobenil), but less capable for slightly polar or nonpolar compounds (e.g., biphenyl) relative to sorption by muck soil that represented soil organic matter.

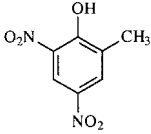
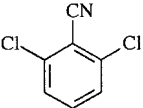
Clay minerals and organic matter both contribute to the sorption of certain soil-applied pesticides. The potential contributions of these components have been measured individually (Sheng et al., 2001). However, in whole soils, organic matter and clays are often associated. The influence of soil organic matter on the sorptive properties (e.g., availability) of the clay minerals is still not fully understood despite previous studies of organic compound and pesticide sorption/desorption by synthetic humic acid-clay model sorbents (Celis et al., 1998; Cox et al., 1998; Murphy et al., 1990; and Onken and Traina, 1997). In this study, two reference smectites (SWy-2 and SAz-1) and the corresponding humic acid-smectite complexes were prepared and used as sorbents. The sorption/desorption isotherms of 4,6-dinitro-*o*-cresol and dichlobenil from water by Ca^{2+} - and K^+ -saturated smectites, and the corresponding humic acid-smectite complexes were measured using a batch-equilibration method. The influence of humic acid and exchangeable cations on pesticide sorption and desorption was evaluated, and the relative contributions of the mineral fraction and humic acid phase to sorption and to desorption hysteresis of pesticides were estimated.

MATERIALS AND METHODS

Chemicals

4,6-Dinitro-*o*-cresol was purchased from ChemService Inc. (West Chestnut, PA) with a reported purity >99%, and dichlobenil (2,6-dichlorobenzonitrile) was purchased from Aldrich Chemical Company Inc. (Milwaukee, WI) with a reported purity >97%. These pesticides were used as received. Selected physical and chemical properties of these compounds are given in Table 1. Humic acid was obtained from Aldrich Chemical Company Inc. Calcium chloride dihydrate (>99%), KCl (>99%), HCl (GR), glacial acetic acid (AR select), methanol (HPLC grade), and acetonitrile (HPLC grade) were purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ).

Table 1. Selected properties of pesticides investigated.

Chemical	Molecular weight g mol ⁻¹	S _w [†] mg L ⁻¹	log K _{ow} [†]	pK _a [†]
4,6-Dinitro-o-cresol 	198.14	198	2.12–2.85	4.35–4.46
Dichlobenil 	172.02	25	2.74	–

[†] Data from Montgomery (1997).

Humic Acid–Clay Complex Preparation

The reference smectite clays, SWy-2 and SAz-1, were purchased from the Source Clays Repository of Clay Minerals Society (Columbia, MO). The <2- μm clay fractions were obtained by wet sedimentation and subsequently exchanged with K⁺ by washing the clay fractions with 0.5 M KCl solution four times. The excess KCl was removed by repeatedly washing with Milli-Q water until negative Cl⁻ was determined by reacting with AgNO₃ solution. The clay suspensions were then quick frozen, freeze-dried, and stored in closed containers prior to use. Homoionic Ca²⁺-saturated clays were prepared by exchanging the clays with 0.5 M CaCl₂, removing the excess CaCl₂ by washing (as above), and then freeze-dried.

The humic acid–clay complexes were prepared by dissolving humic acid (1.0 g for SAz-1, 1.0 and 2.0 g for SWy-2) in 1 L of 0.5 M KCl or CaCl₂ solution, followed by mixing with 10 g of the corresponding K⁺- or Ca²⁺- clays for 1 wk. The humic acid–clay complexes obtained by centrifugation were mixed with either 0.5 M KCl (for K⁺-clays) or CaCl₂ (for Ca²⁺-clays) solution (three times) to saturate the cation-exchange sites in humic acid, dialyzed against distilled water, and then washed repeatedly (>20 times) with Mill-Q water until neither light brown-colored humic substances in supernatants nor humic acid particulates accumulating on the top of clay fractions after centrifugation were visualized. Controls were also prepared without humic acid. The humic acid–clay complexes were quick frozen, freeze-dried, and analyzed for organic C contents. Selected properties of the clay and humic acid–clay complexes are given in Table 2. The humic acid–clay complexes are hereafter referred to as K-HA-SWy-2a/2b, K-HA-SAz-1, Ca-HA-SWy-2a/2b, and Ca-HA-SAz-1.

Sorption and Desorption Studies

The sorption and desorption of 4,6-dinitro-o-cresol and dichlobenil from aqueous 0.01 M KCl matrix for K⁺-saturated clays and humic acid–clay complexes, and from aqueous 0.005 M CaCl₂ matrix for Ca²⁺-saturated clays and the corresponding complexes was measured using a batch equilibration method. A series of initial solute concentrations were prepared ranging from 0.05 to 0.8 relative concentration (aqueous concentration/aqueous solubility) of each solute. For 4,6-dinitro-o-cresol sorption measurements, HCl was added to the initial solutions to obtain equilibration solution pH values of approximately 3. At this pH, more than 96% of 4,6-dinitro-o-cresol exists as the neutral form that is the predominantly sorbed species (Sheng et al., 2002). Clays were weighed into glass centrifuge

Table 2. Properties of reference smectite clays (SWy-2, SAz-1) and the corresponding humic acid (HA)–clay complexes.

Clay	CEC [†] cmol _c kg ⁻¹	Charge density [‡] $\mu\text{mol}_c \text{m}^{-2}$	OC [§] %
SWy-2	82	1.09	–
K-HA-SWy-2a			1.24
K-HA-SWy-2b			1.66
Ca-HA-SWy-2a			2.12
Ca-HA-SWy-2b			4.75
SAz-1	125	1.67	–
K-HA-SAz-1			0.55
Ca-HA-SAz-1			2.83

[†] Cation-exchange capacity.

[‡] Calculated by assuming the clay surface area is 750 m² g⁻¹.

[§] Organic C content.

tubes, initial solutions were added, and the tubes were closed with Teflon-lined screw caps. The ratios of clay mass/aqueous solution (M/V) are reported in Table 3. The tubes were then mixed end-over-end (40 rpm) for 24 h at room temperature (23 \pm 2°C), followed by centrifugation at 4880 \times g for 30 min. Previous studies have shown that equilibrium was reached within this period of time (Sheng et al., 2001, 2002). An aliquot of supernatant was transferred to a clean vial for analysis. Desorption was evaluated using a decant and refill technique. After centrifugation and supernatant sampling, the remaining solution was immediately removed using a disposable glass pipette. The residual supernatant that could not be removed prior to desorption was determined gravimetrically, and the solute concentration in the residual solution was assumed to be the same as that measured in the bulk supernatant. A corresponding amount of solute-free background solution was weighed into the centrifuge tubes in combination with the residual solution. The tubes were rotated for another 24 h, centrifuged at 4880 \times g for 30 min., and the supernatants were collected for analysis. All samples were prepared in duplicate.

Supernatants were assayed for solute concentration using a Perkin-Elmer high performance liquid chromatography (HPLC) system (Binary LC pump 250 with a Series 200 autosampler, Perkin-Elmer, Norwalk, CT) equipped with a Waters UV-Visible detector (Lambda-Max Model 480, Waters Chromatography Div., Millipore Corp., Milford, MA), and an Alltech platinum extended polar selectivity reversed-phase column (15 cm by 4.6 mm i.d.) (Alltech Assoc. Inc., Applied Science Labs, Deerfield, IL). The absorption wavelength was 254 nm for 4,6-dinitro-o-cresol and 238 nm for dichlobenil. The mobile phase was 45/55 (volume ratio) acetonitrile/1% (v/v) aqueous acetic acid solution for 4,6-dinitro-o-cresol and 60/40 (volume ratio) methanol/water for dichlobenil, respectively, with a flow rate of 1.0 mL min⁻¹. Controls consisted of the combination of clay and electrolyte solution, the stock solution of each initial concentration in the supporting electrolyte, and blanks of electrolyte solution. No changes in solute concentrations were detected in the tubes containing only stock solutions, therefore, solute mass not detected in the supernatant in the presence of clay was assumed to be sorbed by clays. Concentrations of pesticide sorbed on clay versus those in aqueous solution were used to construct isotherms with the sorbed mass calculated by the difference between the initial and equilibrium solute concentration in aqueous solution.

X-Ray Diffraction Analysis

After the desorption sample was collected, the remaining supernatant was removed leaving approximately 1 to 2 mL residue in the tubes. The clay slurry was resuspended using a vortex mixer then dropped on a glass slide using a disposable

Table 3. Summary of sorption and desorption isotherm parameters for muck soil, reference clays (SWy-2, SAz-1), and humic acid (HA)-clay complexes.

Sorbsent	M/V [†] g mL ⁻¹	Sorption			Desorption			Relative Ratio (R)	Sorption/Desorption
		log K_f	N	r^2	log K_{fd}	N_d	r^2		
Dinitro-o-cresol									
Muck soil [‡]		2.550	0.780	1.000	ND [§]	ND	ND	—	—
K-SWy-2	0.02/20	4.288	0.271	0.992	4.361	0.356	0.982	—	0.66–0.74
K-HA-SWy-2a	0.02/20	4.314	0.251	0.987	4.398	0.304	0.994	1.01–1.06	0.70–0.76
K-HA-SWy-2b	0.02/20	4.291	0.269	0.988	4.375	0.328	0.976	1.01–1.04	0.69–0.75
Ca-SWy-2	0.04/5.0	0.447	2.360	0.996	1.192	1.940	0.996	—	0.35–0.63
Ca-HA-SWy-2a	0.04/5.0	0.579	2.206	0.994	1.206	1.939	0.992	0.87–0.96	0.36–0.53
Ca-HA-SWy-2b	0.04/5.0	0.849	1.979	0.991	1.436	1.726	0.992	0.85–0.91	0.39–0.55
K-SAz-1	0.03/15	4.021	0.248	0.995	4.064	0.256	0.994	—	0.88–0.89
K-HA-SAz-1	0.03/15	4.022	0.243	0.995	4.046	0.268	0.988	0.99–1.02	0.88–0.91
Ca-SAz-1	0.1/5.0	0.633	0.863	0.991	0.952	0.766	0.991	—	0.56–0.64
Ca-HA-SAz-1	0.1/5.0	1.159	0.869	0.994	1.333	0.906	0.991	0.69–0.77	0.60–0.63
Dichlobenil									
Muck soil		2.312	0.712	0.996	ND	ND	ND	—	—
K-SWy-2	0.08/4.0	2.407	0.654	0.996	2.439	0.715	0.990	—	0.85–0.93
K-HA-SWy-2a	0.08/4.0	2.393	0.675	0.990	2.407	0.790	0.986	0.96–1.04	0.83–0.97
K-HA-SWy-2b	0.08/4.0	2.404	0.679	0.991	2.398	0.784	0.987	1.02–1.09	0.88–1.01
Ca-SWy-2	0.2/4.0	1.039	0.848	0.986	1.100	0.860	0.991	—	0.85–0.87
Ca-HA-SWy-2a	0.2/4.0	1.303	0.911	0.996	ND	ND	ND	—	—
Ca-HA-SWy-2b	0.2/4.0	1.535	0.792	0.993	1.564	0.810	0.994	0.96–0.98	0.91–0.94
K-SAz-1	0.08/4.0	1.810	0.812	0.994	1.814	0.874	0.988	—	0.91–0.98
K-HA-SAz-1	0.08/4.0	1.797	0.803	0.992	1.812	0.824	0.979	0.98–1.03	0.94–0.97
Ca-SAz-1	0.2/3.0	0.042	0.648	0.985	0.048	0.608	0.984	—	0.99–1.04
Ca-HA-SAz-1	0.2/3.0	1.125	0.803	0.992	1.169	0.877	0.984	0.81–0.90	0.82–0.90

[†] M/V is mass of clay/volume of solution

[‡] From Sheng et al. (2001).

[§] Not determined.

glass pipette. The clay suspensions were air-dried to obtain oriented films that were subject to XRD analysis. X-ray diffraction spectra of clay films were obtained using a Philips APD 3720 automated x-ray diffractionmeter equipped with Cu-K α radiation, an APD 3521 goniometer (Philips Electronic Instrument Co., Mahwah, NJ) and a diffracted-beam monochromator (Philips Electronic Instrument Co., Mahwah, NJ). The scanning angle (2θ) ranged from 3 to 15° at steps of 0.02°, and the scanning time was 2 s per step.

RESULTS AND DISCUSSION

Pesticide Sorption by Homoionic K⁺- and Ca²⁺-Clays

Isotherms representing sorption of 4,6-dinitro-o-cresol and dichlobenil by Ca-, K-SWy-2, and SAz-1 are shown in Figure 1. Nonlinear sorption isotherms were observed with all pesticide-clay combinations. The isotherms are concave to the abscissa except for 4,6-dinitro-o-cresol sorption on Ca-SWy-2 that is convex to the abscissa (upward curvature). All sorption isotherms were fit to the Freundlich equation (shown as the solid lines in Fig. 1),

$$S = K_f C^N \quad [1]$$

where S (mg kg⁻¹) is the amount of pesticide sorbed by clay or humic acid-clay complex, C (mg L⁻¹) is the equilibrium aqueous concentration of pesticide, K_f (mg^{1-N} L^N kg⁻¹) is the Freundlich sorption coefficient and N (unitless) is a descriptor of isotherm curvature. The results from Freundlich equation fittings are listed in Table 3. The magnitude of sorption on clays is much greater for 4,6-dinitro-o-cresol compared with dichlobenil. The sorption of 4,6-dinitro-o-cresol and dichlobenil follows the order: K-SWy-2 > K-SAz-1 > Ca-SWy-2 >

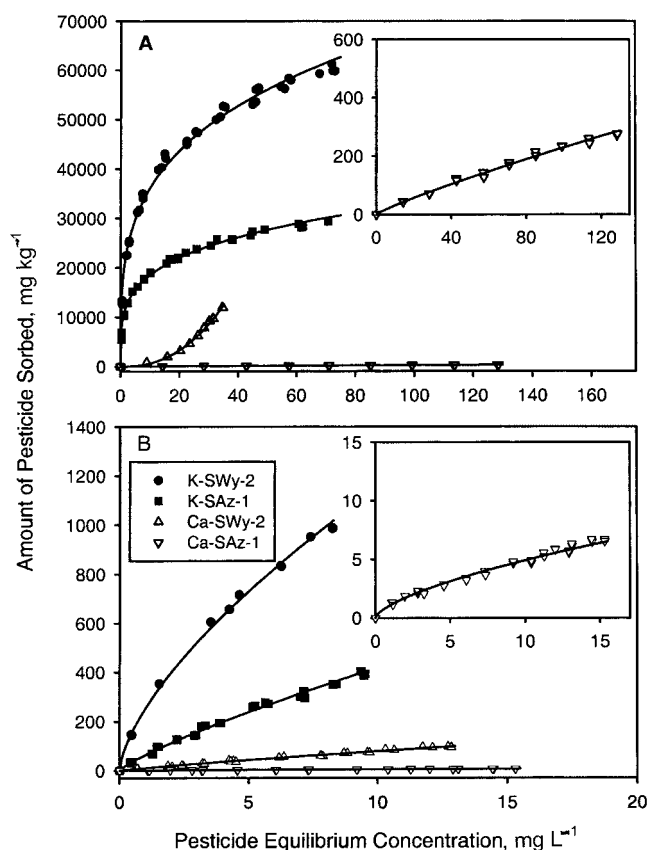


Fig. 1. Isotherms representing sorption of (A) 4,6-dinitro-o-cresol and (B) dichlobenil by Ca²⁺- and K⁺-saturated SWy-2 and SAz-1 smectite clays.

Ca-SAz-1. The high affinity of K^+ -clays for 4,6-dinitro-o-cresol is apparently because of multiple (two) nitro-substituents that complex directly with K^+ , as well as through the intermediation of water (Boyd et al., 2001). The comparatively lower adsorption by Ca^{2+} -saturated clays is attributed to the larger enthalpy of hydration of Ca^{2+} (as compared with K^+), which inhibits direct interactions between pesticide functional groups (e.g., $-NO_2$, $-CN$) and the exchangeable cation (Johnston et al., 2001); also larger hydration sphere around Ca^{2+} obscured a greater portion of the neutral siloxane surface thereby reducing hydrophobic interactions between these surfaces and the pesticide. The lower-charge-density clay (SWy-2) manifested greater adsorption compared with the corresponding higher-charge-density SAz-1 clay. The lower charge clay apparently has the larger exposed areas between exchangeable cations on the neutral siloxane surfaces, which contribute more favorable pesticide adsorptive domains. Crowding interlayer cations upon pesticide adsorption may increase the electrostatic repulsion among these cations, thereby contributing to the reduction of pesticide adsorption by the higher charge clay. Additionally, interlayer water is more strongly bound in the higher charge clay hence more difficult to displace (Boyd et al., 2001; Sheng et al., 2002).

Pesticide Sorption by Humic Acid-Clay Complexes

Pesticide sorption isotherms for the humic acid-clay complexes are shown in Figures 2 and 3 along with isotherms for the corresponding homoionic K^+ - and Ca^{2+} -clays. All sorption isotherms were nonlinear. For K^+ -saturated smectites, pesticide sorption was not impacted measurably by the presence of humic acid associated with the clays (Fig. 2) indicating that sorption could

be attributed to mineral domains. The strong sorptive capability of mineral fractions as compared with organic matter (Sheng et al., 2001) and the much larger fractional mass of smectite vs. humic acid apparently result in a minimal sorptive contribution from the humic acid phase. For Ca^{2+} -saturated smectites, pesticide sorption was affected by humic acid associated with the clays (Fig. 3). 4,6-Dinitro-o-cresol sorption was enhanced in Ca-HA-SAz-1 relative to Ca-SAz-1 consistent with the larger K_f for sorption by organic matter vs. Ca-SAz-1 (Table 3) (Fig. 3B). Similarly, humic acid modifications enhanced dichlobenil sorption by both Ca^{2+} -saturated smectites relative to sorption by the unmodified clays (Fig. 3C, D). Similar enhanced sorption was observed by Celis et al. (1998) for atrazine and simazine on Ca-SWy-humic acid complexes. In contrast, 4,6-dinitro-o-cresol sorption was suppressed by the humic acid associated with Ca-SWy-2, with the greater reduction occurring at the higher humic acid contents (Fig. 3A). Also note that the sorption isotherms of Ca-SWy-2 and Ca-HA-SWy-2 clays in combination with 4,6-dinitro-o-cresol are convex to the abscissa ($N > 1$).

Estimates of the contributions of mineral fractions and humic acid phase to the sorption of pesticides were attempted using a simple composite model with the assumptions that mineral and humic acid phases contribute independently to pesticide sorption, and are completely available for interacting with pesticides. With these assumptions, the following relationship was derived (Karickhoff, 1984),

$$S = S_{\text{clay}} + S_{\text{om}} = f_{\text{clay}}K_{f,\text{clay}}C^N_{\text{clay}} + f_{\text{om}}K_{f,\text{om}}C^N_{\text{om}} \quad [2]$$

where S (mg kg^{-1}), C (mg L^{-1}), K_f ($\text{mg}^{1-N} \text{L}^N \text{kg}^{-1}$), and N (unitless) are the same parameters defined in Eq. [1], f (g g^{-1}) is the mineral or organic fraction in the humic acid-clay complexes, and $f_{\text{clay}} + f_{\text{om}} = 1$. The subscripts

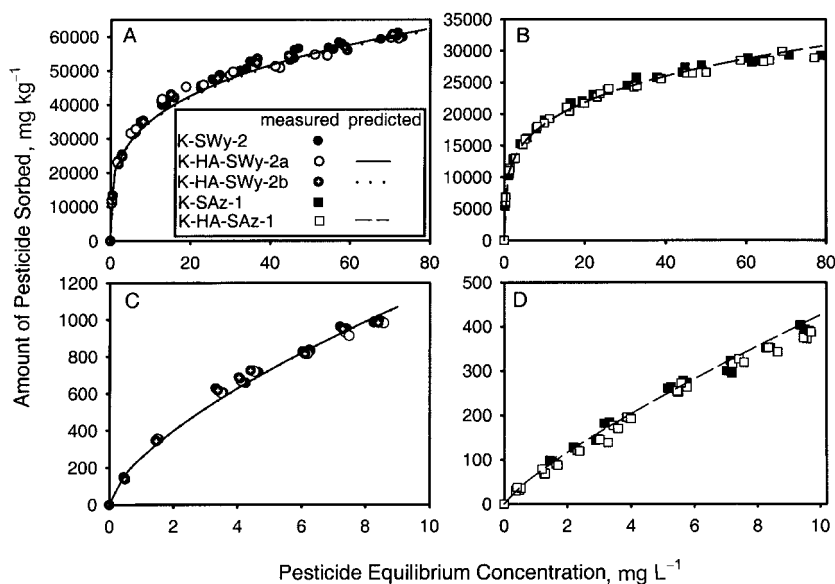


Fig. 2. Isotherms representing pesticide sorption by reference smectite clays (SWy-2 and SAz-1) and the corresponding humic acid (HA)-clay complexes. Sorption of 4,6-dinitro-o-cresol by (A) K-HA-SWy-2/K-SWy-2, (B) K-HA-SAz-1/K-SAz-1, sorption of dichlobenil by (C) K-HA-SWy-2/K-SWy-2, and (D) K-HA-SAz-1/K-SAz-1. The lines represent the predicted curves obtained by summing up individual and independent contribution of humic acid and smectite clays to pesticide sorption.

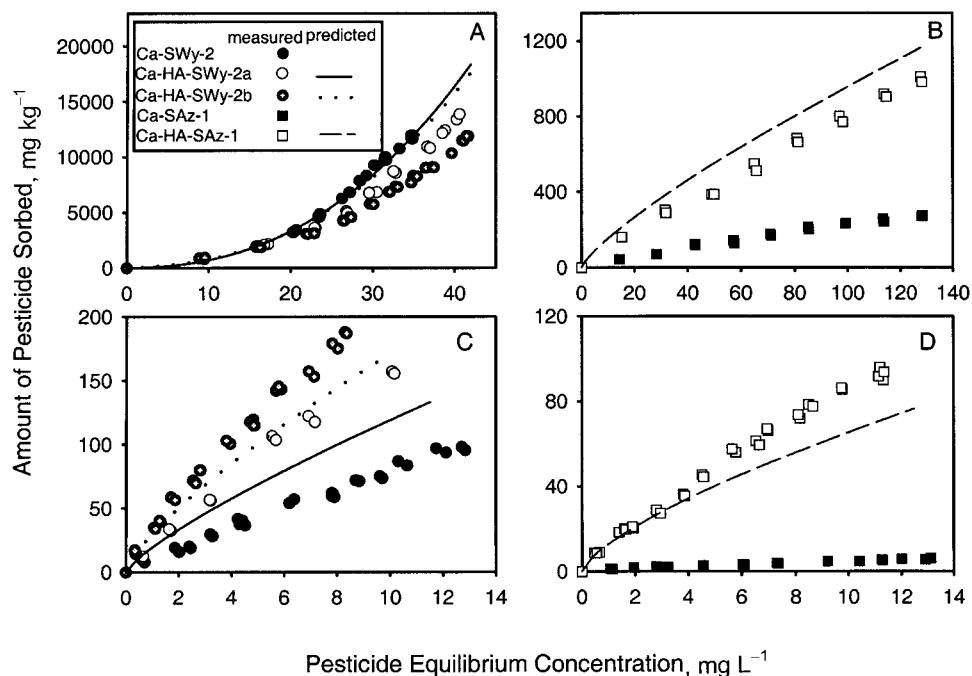


Fig. 3. Isotherms representing pesticide sorption by reference smectite clays (SWy-2 and SAz-1) and the corresponding humic acid (HA)-clay complexes. (A) Sorption of 4,6-dinitro-o-cresol by Ca-HA-SWy-2/Ca-SWy-2, (B) Ca-HA-SAz-1/Ca-SAz-1, (C) sorption of dichlobenil by Ca-HA-SWy-2/Ca-SWy-2, and (D) Ca-HA-SAz-1/Ca-SAz-1. The lines represent the predicted curves obtained by summing up individual and independent contribution of humic acid and smectite clays to pesticide sorption.

of clay and om refer to the reference clay and the associated humic-acid phase. If sorption by humic-acid phase ($K_{f,om}C^{N_{om}}$) is greater than that by clays ($K_{f,clay}C^{N_{clay}}$), then the overall sorption by humic acid-clay complexes should be enhanced compared with that by the reference clays. Alternatively, if the humic acid phase sorbs less solute than clays, then the overall sorption will be reduced on a unit mass basis of sorbent. Reductions in the availability of mineral surfaces by humic acid coatings would further decrease sorption. The Freundlich equation parameters for clays were obtained by fitting the sorption data of the unmodified clays (Table 3). The sorption parameters for humic acid were estimated using sorption data reported in our previous study (Sheng et al., 2001). The humic-acid phase (f_{om}) was estimated by dividing the measured organic C content by the fractional C content of humic acid (0.454 reported by Laor et al., 1998); the remaining mass was assumed to be the clay mineral fraction (f_{clay}). The summation of predicted sorption by humic and clay fractions are shown as the lines in Fig. 2 and 3. The predicted values are within a factor of 0.8 to 1.5 of the measured values for both pesticides, indicating that in general sorption by humic acid-clay complexes can be reasonably estimated by summing up their individual contributions to pesticide sorption. The composite model predicted that 4,6-dinitro-o-cresol sorption in K-HA-SWy-2 clays should decrease with increasing humic acid content, however, because $K_{f,clay} \gg K_{f,om}$, this diminutive difference fell within the range of experimental error (Fig. 2A). There is evidence that 4,6-dinitro-o-cresol is intercalated by K^+ -smectites, and it is unlikely that humic materials occupy these interlayer regions (see XRD results below). Thus

pesticide sorption occurred primarily in clay interlayers and was not diminished substantially by humic acids associated with the external surfaces of clay tactoids. For 4,6-dinitro-o-cresol sorption by Ca-HA-SAz-1 and dichlobenil sorption by both humic acid-modified Ca^{2+} -smectites (Fig. 3B,C, and D), the composite model provided reasonable estimations for the observed enhancement of sorption. For 4,6-dinitro-o-cresol sorption by Ca-SWy-2 and Ca-HA-SWy-2 clays, the composite model slightly underestimated the observed reduction in sorption. In this case, humic acid may obscure some mineral surfaces or access to clay interlayers hence inhibiting sorption (Fig. 3A). The Ca-SWy-2 and Ca-HA-SWy-2 clays in combination with 4,6-dinitro-o-cresol are somewhat anomalous in that sorption isotherms were convex to the aqueous concentration axis. This isotherm shape has been attributed to weak adsorbent-adsorbate forces at low relative concentrations, followed by cooperative adsorbate-adsorbate interactions that promote adsorption (Gregg and Sing, 1982). The initial intercalation of small amounts of 4,6-dinitro-o-cresol may promote further pesticide adsorption in the interlayers.

Pesticide Desorption

All 4,6-dinitro-o-cresol and dichlobenil desorption isotherms were fitted with the logarithmic form of the Freundlich equation, and the resulting parameter values are summarized in Table 3. Representative 4,6-dinitro-o-cresol and dichlobenil sorption/desorption isotherms and Freundlich-fitting lines for selected sorbents are shown in Figure 4 (other data not shown). All desorption isotherms were nonlinear. Both pesticides exhibited

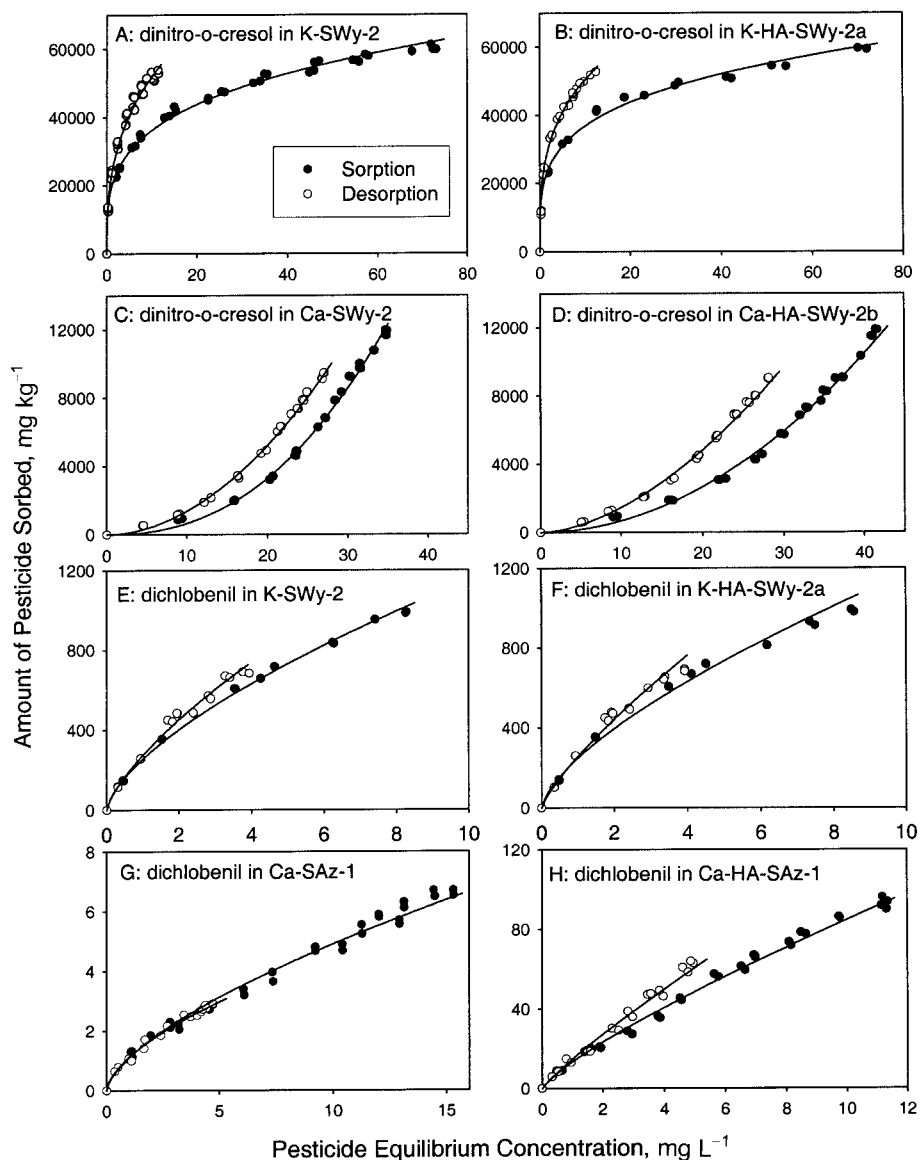


Fig. 4. Sorption/desorption isotherms of pesticides in reference smectite clays (SWy-2, SAZ-1) and the corresponding humic acid (HA)-clay complexes: 4,6-dinitro-o-cresol in (A) K-SWy-2, (B) K-HA-SWy-2a, (C) Ca-SWy-2, (D) Ca-HA-SWy-2b; and dichlobenil in (E) K-SWy-2, (F) K-HA-SWy-2a, (G) Ca-SAZ-1, (H) Ca-HA-SAZ-1.

desorption hysteresis with greater hysteresis observed for 4,6-dinitro-o-cresol. Dichlobenil exhibited some degree of hysteresis at higher aqueous concentrations (i.e., $>2 \text{ mg L}^{-1}$), but comparatively little at lower concentrations. No hysteresis was observed for the dichlobenil and Ca-SAZ-1 combination (Fig. 4G). To assess the contribution of mineral fractions in humic acid-clay complexes to pesticide desorption hysteresis, the difference ($S_{d,\text{clay}} - S_{\text{clay}}$) between sorption and desorption on the reference clays were quantified, multiplied by f_{clay} , and superadded to the sorption isotherms (S) for the corresponding humic acid-clay complexes. This provides an estimate of the sorbed concentration ($S_{d,\text{est}}$) after desorption assuming pesticide desorption only occurs from mineral domains. A relative factor (R) was defined as the ratio of estimated sorbed concentration ($S_{d,\text{est}}$) to the measured concentration ($S_{d,\text{obs}}$) after desorption from

the humic acid-clay complex at a given aqueous pesticide concentration,

$$R = \frac{S_{d,\text{est}}}{S_{d,\text{obs}}} = \frac{S + f_{\text{clay}} (S_{d,\text{clay}} - S_{\text{clay}})}{S_{d,\text{obs}}} \quad [3]$$

where all S (mg kg^{-1}) values in the right-side term were estimated using the fitted Freundlich sorption and desorption parameters listed in Table 3. The subscript of d refers to the desorption equilibrium. The range of R values were quantified within the measured pesticide aqueous concentrations after desorption, and reported in Table 3. The ratios of sorption/desorption ($S/S_{d,\text{obs}}$) reflecting desorption hysteresis are also provided in Table 3. Value of $S/S_{d,\text{obs}} \approx 1$ implies that no desorption hysteresis occurs; $R \approx 1$ and $S/S_{d,\text{obs}} < 1$ imply that mineral fractions in the complexes fully account for pesticide desorption hysteresis with humic acid fraction playing

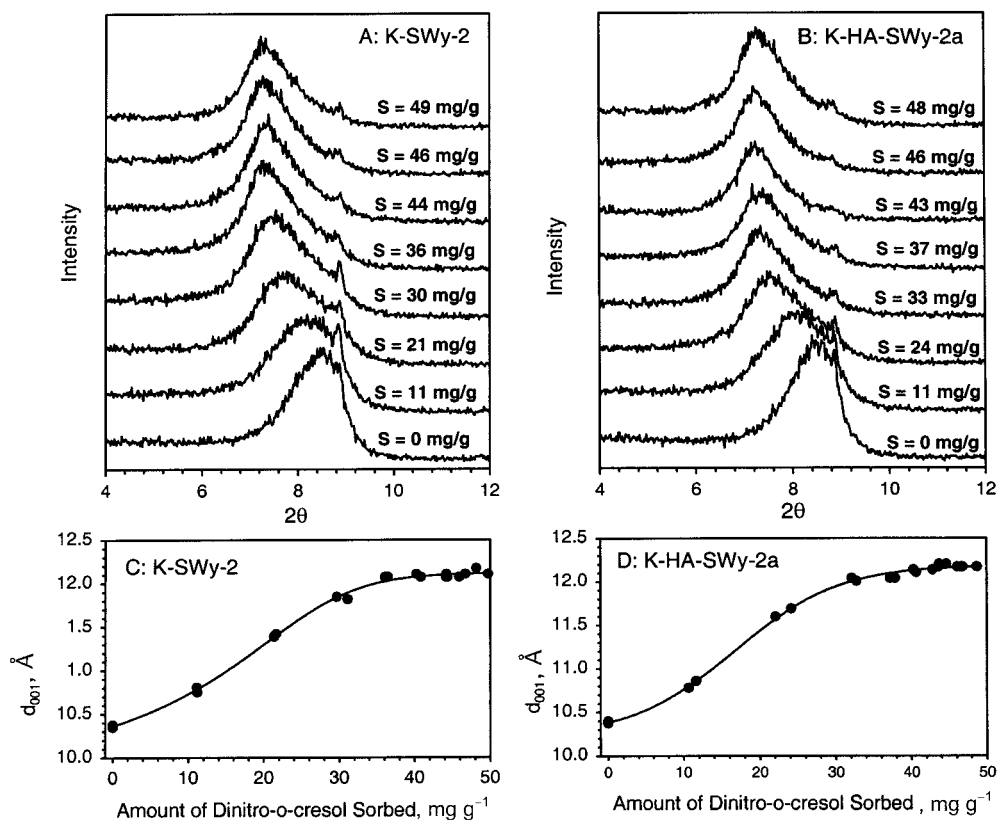


Fig. 5. X-Ray diffraction patterns of oriented films of (A) K-SWy-2, and the corresponding humic acid (HA)-clay complexes (B) K-HA-SWy-2a, and (C,D) the associated d -spacings as a function of 4,6-dinitro-*o*-cresol loadings.

a negligible role. Values of $S/S_{d,obs}$ and R falling within the same range and both <1 imply that minerals have insignificant effects on desorption hysteresis, that is, the source of hysteresis is from the pesticide molecules sorbed by the humic acid fraction. Examination of R results for pesticide sorption by K^+ -saturated humic acid-clay complexes (approximately 1.0 and greater than $S/S_{d,obs}$) reveals that the desorption hysteresis originates from pesticide sorbed by clays rather than by the humic-acid phase. Mineral fractions dominate pesticide retention to such an extent that the humic-acid phase plays only a minor role, consistent with the results predicted by the composite model (i.e., Eq. [2]). No hysteresis was observed for dichlobenil on Ca-SAZ-1 ($S/S_{d,obs}$ approximately 1.0). However, hysteresis was observed for dichlobenil sorbed by Ca-HA-SAZ-1 (Fig. 4H), and the R and $S/S_{d,obs}$ values of Ca-HA-SAZ-1 fell within the same range (approximately 0.82–0.90). This indicates that desorption hysteresis originates from dichlobenil retained in the humic acid phase. Recall that coated humic acid is the primary domain for dichlobenil retention in Ca-HA-SAZ-1 (Fig. 3D). For 4,6-dinitro-*o*-cresol desorption in humic acid-Ca-smectite complexes and dichlobenil desorption in Ca-HA-SWy-2, pesticides desorbed not only from mineral sites but also from humic acid phase as evidenced by R values greater than the $S/S_{d,obs}$ ratios but <1.0 .

X-Ray Diffraction Analysis

The XRD patterns obtained from oriented films of K-SWy-2 and K-HA-SWy-2a with increasing amounts

of sorbed 4,6-dinitro-*o*-cresol are shown in Figure 5A and 5B. The diffraction peaks were broad and generally converted from skewed to symmetrical with increasing 4,6-dinitro-*o*-cresol sorption. There was a shoulder at 9.98 Å possibly because K^+ ions were fixed into hexagonal cavities in clay sheets resulting in the collapse of some interlayer regions. This was further indicated by the absence of such a peak in the corresponding Ca^{2+} -homoionic clays. The basal spacings of K-SWy-2 and K-HA-SWy-2a increased gradually from 10.4 to 12.2 Å with increasing 4,6-dinitro-*o*-cresol loadings, clearly demonstrating intercalation of the pesticide (Fig. 5C and 5D). At the high 4,6-dinitro-*o*-cresol loadings (>40 mg kg^{-1}), rewetting (exposure to 100% relative humidity) the air-dried clay films did not result in further swelling of clay interlayers, whereas in the absence of sorbed 4,6-dinitro-*o*-cresol expansion of the clay interlayer to approximately 15 Å was observed. Previous research has shown that 4,6-dinitro-*o*-cresol molecules penetrate clay interlayers, replace water molecules and form a K^+-NO_2 -complex with the pesticide. Energy is gained from such ion-dipole interactions and from the partitioning of 4,6-dinitro-*o*-cresol from bulk water into the subaqueous environment of the clay interlayers (Sheng et al., 2002; Boyd et al., 2001). The basal spacing of approximately 12.2 Å appears to be an optimal distance for 4,6-dinitro-*o*-cresol adsorption wherein the pesticide molecules can interact directly with the opposing siloxane surfaces hence minimizing pesticide interactions with water (Sheng et al., 2002). Basal spacings of K-SWy-2 were identical to those of K-HA-SWy-2a with a similar

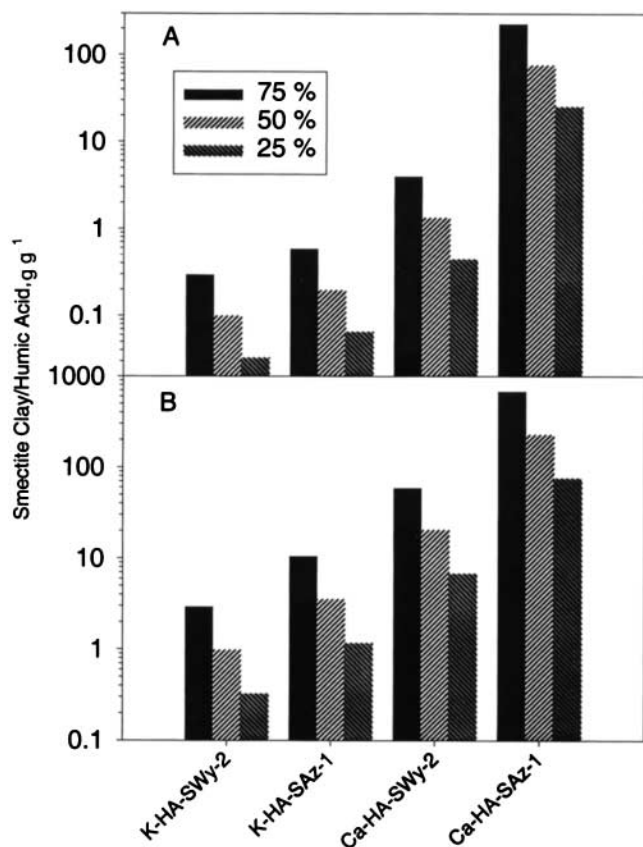


Fig. 6. The ratios of smectite to humic acid required to achieve 25, 50, and 75% of the total (A) 4,6-dinitro-o-cresol and (B) dichlobenil sorption by humic acid (HA) complexes of reference smectite clays (SWy-2, SAz-1).

amount of sorbed 4,6-dinitro-o-cresol (also without sorbed 4,6-dinitro-o-cresol) indicating humic acids were associated with the external surfaces of the clay tactoids leaving the internal surfaces available for pesticide sorption (Fig. 5). This is consistent with the observation of little impact of humic acid on 4,6-dinitro-o-cresol sorption by K-HA-SWy-2. Thus, the internal clay surfaces of K-SWy-2 and K-SWy-2-humic acid complexes are the primary sorption domains for 4,6-dinitro-o-cresol.

Relative Contribution of Humic Coatings and Clay Minerals

The smectite clay/humic-acid mass ratios required to achieve 25, 50, and 75% of the total pesticide sorption by the clay fraction at the relative concentration of 0.1 were calculated based on Eq. [2] which assumes the sorptive contributions of the mineral and humic acid phases are independent (Figure 6A,B). The relative contributions of humic acid and clay fractions to pesticide sorption are related to the type of mineral, ratios of mineral/humic substances, exchangeable cations present and pesticide sorption coefficients. Smectite clays with weakly hydrated exchangeable cations (e.g., K⁺) and clays with low surface-charge density (e.g., SWy-2) commonly display strong affinities for nitroaromatics. Calculations reveal that for 4,6-dinitro-o-cresol sorption by K⁺-saturated clays, the prepared humic acid-clay com-

plexes with the smectite clay/humic acid ratios ≥ 1 would result in more than 80% of 4,6-dinitro-o-cresol sorbed by the mineral fraction. A smectite clay/humic-acid ratio of 25 for 4,6-dinitro-o-cresol, and 75 for dichlobenil, is required for mineral sorption to account for 25% of the total sorption by a less reactive mineral sorbent such as Ca-SAz-1. For the K⁺-saturated clays, the clay/humic acid ratios are significantly lower than the empirical values reported previously for whole soils (Grundl and Small, 1993; Karickhoff, 1984). This is likely because of the fact that the 2:1 expandable smectites used as mineral matrixes in this study are potentially the most adsorptive mineral components among soil mineral fractions, and they were fully saturated with K⁺. In a bulk soil, 2:1 expandable smectites comprise only a portion of soil clay mineral fractions, and K⁺ is not normally the dominant exchangeable cation. Furthermore, the associations of soil cementing agents (e.g., carbonates and Fe oxides) with soil clay fractions might obscure some of the clay sorptive domains, and reduce access to clay interlayers by inhibiting swelling, thereby diminishing the availability of clay surfaces for pesticide adsorption. These results suggest the potential important role of clays in pesticide retention in soils. However, caution should be exercised in extrapolation these results to natural systems since this study utilized laboratory-prepared clay-humic acid complexes.

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