Role of Smectite Quasicrystal Dynamics in Adsorption of Dinitrophenol

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Organic matter and clay minerals are the two most important soil constituents in the sorption of pesticides and organic contaminants by soils. Previous studies have concluded that the mineral phase is the dominant sorbent for neutral organic compounds in soils when the clay/organic matter ratio is sufficiently high (e.g., 10–30) (Karickhoff, 1984; Grundl and Small, 1993; Hassett et al., 1981), and that soil clays are especially important for sorption of polar organic compounds (Sheng et al., 2001). Among the various clay minerals, smectites are considered important in this regard due to their widespread occurrence (Allen and Hajek, 1989), high surface area (~800 m² g⁻¹), and reversible interlayer expansibility. Several studies have demonstrated that smectites have the potential to adsorb large amounts of various organic compounds, and that adsorption affinity varies widely depending on the properties of the smectite, the saturating cations, and the sorbate (Jaynes and Boyd, 1990, 1991; Lee et al., 1990; Laird et al., 1992, 1994; Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Boyd and Jaynes, 1994; Laird, 1996; Boyd et al., 2001; Sheng et al., 2002).

The compound 2-methyl-4,6-dinitrophenol (4,6-dinitro-o-cresol, or DNOC) has been widely used in agriculture and industry. Some former uses were as a contact herbicide, larvicide, or dormant spray insecticide especially for fruit trees, or on waste grounds to kill locusts and other insects. Recent uses are as an inhibitor of polymerization in styrene and vinyl and for insecticidal spraying (Hawley, 1981; USEPA, 1988). Insecticidal spraying has been the major source of DNOC that enters the environment (USEPA, 1988). Use of this compound has resulted in contamination of soils and shallow aquifers.
Smeectites are capable of adsorbing large amounts of nitroaromatic compounds (NACs) such as DNOC and there is much current interest in understanding the nature of the interactions between NACs and smectites (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Weismahr et al., 1997; Sheng et al., 2001, 2002; Boyd et al., 2001; Johnston et al., 2001; Li et al., 2003). Interactions between smectites and NACs have been studied using a combination of X-ray diffraction (XRD), molecular dynamic simulations, and Fourier-transform infrared spectroscopy (Sheng et al., 2002). Sorption is greater for smectites saturated with cations having low hydration energies (e.g., K⁺, Cs⁺, and NH₄⁺) compared with smectites saturated with strongly hydrated cations (e.g., Ca²⁺ and Na⁺). Low hydration energies favor direct interactions between the exchangeable cation and −NO₂ groups of the NACs (Li et al., 2004). X-ray diffraction analysis indicated an interlayer spacing of 1.2 to 1.25 nm in the presence of DNOC for both air-dried and rehydrated oriented films of the K-saturated Wyoming montmorillonite K-SWy-2 (Sheng et al., 2002). This d-spacing allows DNOC molecules to interact with the opposing clay layers, thereby minimizing DNOC-water interactions. In the absence of sorbed DNOC, the interlayer spacing of K-smectite increased to about 1.5 nm when rehydrated.

Sheng et al. (2001) used XRD studies to determine the location of DNOC in K-SWy-2 and showed that DNOC sorption was accompanied by an increase in basal spacing of air-dried K-SWy-2. Due to the broad asymmetric nature of the XRD peaks, they concluded that DNOC was randomly interstratified in the interlayers of K-SWy-2. Increased loading of DNOC increased the d-spacing from 1.0 to ~1.22 nm, suggesting that DNOC was intercalated in the interlamellar region of the clay. For the highest loading, DNOC should occupy about 20% of the K-SWy-2 surface area (Sheng et al., 2001).

Li et al. (2003) studied the adsorption of DNOC on K- and Ca-saturated reference smectites that were coated with humic substances. Results again emphasized the importance of the size of the hydration sphere of the interlayer cation as well as the charge density of the clay during adsorption of DNOC. X-ray diffraction patterns of air-dried K-SWy-2 films showed a shift in the d-spacing of K-SWy-2 from 1.0 to ~1.22 nm with increasing adsorption of DNOC as direct evidence of DNOC occupying the interlayer space. At high DNOC loadings (>40 mg kg⁻¹), rehydration (or expansion) of the air-dried K-SWy-2–DNOC films on exposure to 100% relative humidity was not observed, whereas K-SWy-2 samples without DNOC showed expansion to 1.5 nm. The results of Li et al. (2003) suggest that DNOC–K-smectite interactions in the interlayers prevent K-smectite swelling from beyond 1.2 to 1.25 nm.

Previous studies have concluded that DNOC–smectite interactions occur mainly within the interlayers of K-smectites at pHs below the acid dissociation constant (pKₐ) of DNOC (Sheng et al., 2002; Li et al., 2003). Recently, however, we observed sorption of DNOC by smectites in aqueous suspensions at pHs above the pKₐ (4.4) where DNOC dominantly exists in the anionic (i.e., phenolate) form (Pereira et al., 2007). Anions should be electrostatically repelled from negatively charged smectite surfaces, thus a priori it was difficult to reconcile adsorption of the phenolate form of DNOC by smectites in aqueous systems. Ultimately, however, we provided evidence for the intercalation of anionic DNOC as an ion pair with K⁺.

In soils, smectites commonly exist as quasicrystals, which are stacks of several to thousands of parallel lamellae separated by zero to four discrete layers of water molecules (Aylmore and Quirk, 1971). In aqueous suspensions, smectite quasicrystals are dynamic (Laird, 2006), as several small quasicrystals may combine to make a single larger quasicrystal and, conversely, a large quasicrystal may break up to form many small quasicrystals. Furthermore, the interlayer hydration state within a quasicrystal changes depending on the nature of the interlayer cations, the activity of water in solution, and both the amount and nature of adsorbed interlayer organic molecules. A transition between discrete hydration phases (0–4 layers of interlayer water molecules) is known as crystalline swelling (Norrish, 1954; Laird et al., 1995). As smectites collapse through these hydration phases, the interlayers become less water-like and more hospitable to weakly polar organic molecules, thereby accommodating organic molecules in the interlayer. Chappell et al. (2005) demonstrated that a change in the extent of crystalline swelling caused an order of magnitude difference in the affinity of a K-smectite for atrazine (2-chloro-4-ethylamine-6-isopropylamino-3-triazine). Thus we anticipate that quasicrystal dynamics will also influence the affinity of smectites for DNOC.

Conventional XRD techniques provide information about the properties of smectite quasicrystals in random powders and oriented films. Because of quasicrystal dynamics, however, the properties of quasicrystals in air-dry and oven-dry powders and films may be different from the properties of quasicrystals in aqueous suspensions where adsorption occurs. Recently developed suspension XRD techniques (Shang et al., 1995; Chappell et al., 2005; Li et al., 2007) provide unique information about the nature of smectite quasicrystals in aqueous suspensions under conditions similar to those that prevail during laboratory adsorption measurements, which commonly use the batch equilibration method. Furthermore, soil and sediment samples are commonly air dried, oven dried, and freeze-dried before their use in laboratory investigations of pesticide sorption. Suspension XRD allows us to examine clay samples that have never been dried and hence may be more representative of suspended clays in rivers and lakes under natural environmental conditions.

In this study, we sought to advance mechanistic understanding of how an anionic molecule, in this instance DNOC, is able to enter the interlayers of smectites. Specifically, we used suspension XRD techniques to elucidate how DNOC adsorption influences the size and swelling of smectite quasicrystals in aqueous suspensions. Furthermore, we compared XRD patterns for samples analyzed using the suspension XRD technique with patterns obtained using conventional XRD techniques to assess changes in smectite quasicrystals that occur during preparation of air-dry and oven-dry oriented films for XRD analysis.

**MATERIALS AND METHODS**

**Reference Smeectites**

Reference smectites used in this study were obtained from the Source Clays Repository of the Clay Minerals Society maintained at Purdue University, West Lafayette, IN. Wyoming montmorillonite (SWy-2) is a low-charge-density smectite from Crook County, WY;
the Arizona montmorillonite (SAz-1) is a high-charge-density smectite from Apache County, AZ. The cation exchange capacities and layer charge densities of SWy-2 and SAz-1 are 82 and 125 cmol_\( \text{kg}^{-1} \), and 1.09 and 1.67 \( \text{mmol} \cdot \text{m}^{-2} \), respectively (Li et al., 2003).

Carbonate removal from SWy-2 was achieved by adding 0.5 mol L\(^{-1} \) NaOAc buffer at pH 5 to SWy-2 (Gee and Bauder, 1986). After exposure to NaOAc for 2 d, the sample was repeatedly washed with 0.5 mol L\(^{-1} \) NaCl to prepare a homoionic Na-smectite and remove any excess acetate buffer.

Equal portions of the <2-μm clay-size fraction were collected by gravity sedimentation. Homionic K\(^+ \) and Ca\(^{2+} \) clays were prepared by washing the clays five times in 0.5 mol L\(^{-1} \) KCl and CaCl\(_2\) solutions, and then dewatered by vacuum filtration using an autoclave flask. The K-SWy-2 clay suspension was dialyzed sequentially for 9 d using Spectra/Por 3 membrane dialysis tubing (Spectrum Laboratories, Rancho Domincuz, CA) against 0.1, 0.01, and 0.001 mol L\(^{-1} \) KCl solutions. Similarly, the Ca-SWy-2 clay suspension was dialyzed sequentially against 0.05, 0.005, and 0.0005 mol L\(^{-1} \) CaCl\(_2\) solutions. Electrolytes were refreshed three times per day until electrical conductivity stabilized.

The SAz-1 smectite was found to be free of carbonates and was therefore not treated with NaOAc; otherwise, size fractionation and cation saturation treatments were performed in the same manner as for SWy-2 to obtain K-SAz-1 and Ca-SAz-1 suspensions. Half of each clay suspension was lyophilized and is hereafter referred to as the “freeze-dried” clays. The remaining halves of each sample were stored at 4°C as suspensions and are hereafter referred to as the “never-dried” clay suspensions.

**Dinitrophenol Herbicide**

The compound DNOC was purchased from Aldrich Chemical Co, (Milwaukee, WI) with purity >97% and was used as received. A DNOC solution (150 mg L\(^{-1} \)) in Milli-Q water was prepared and had an unadjusted pH of 3.2. To adjust the pH of DNOC to the desired values, 0.01 mol L\(^{-1} \) HCl, 0.01 mol L\(^{-1} \) KOH, or 0.005 mol L\(^{-1} \) Ca(OH)\(_2\) were added accordingly. The structural formula and ionization of DNOC are illustrated in Fig. 1.

**Preparation of Samples**

Suspensions of the freeze-dried clays (100 mg clay mL\(^{-1} \)) were prepared by resuspending K\(^+ \)– and Ca\(^{2+} \)–saturated freeze-dried SWy-2 and SAz-1 in 0.001 mol L\(^{-1} \) KCl or 0.0005 mol L\(^{-1} \) CaCl\(_2\) solutions. The suspensions were shaken for 48 h at 25°C.

Neved-dried clay suspensions were prepared by diluting the K\(^- \)– and Ca\(^{2+} \)–saturated SWy-2 and SAz-1 suspensions with 0.001 mol L\(^{-1} \) KCl or 0.0005 mol L\(^{-1} \) CaCl\(_2\) to the desired solid/solution ratio of 100 mg clay mL\(^{-1} \) of electrolyte. Weighed amounts of each suspension (100 mg of K-SAz-1, Ca-SAz-1, CaSWy-2 and 2 g of K-SWy-2) were shaken in Corex tubes for 24 h at 25°C.

**X-ray Diffraction Analysis of Clay Suspensions**

X-ray diffraction studies were performed on the freeze-dried and never-dried smectite suspensions at pHs ranging from 3 to 7. The pH of the smectite suspensions was adjusted by adding 0.01 mol L\(^{-1} \) HCl, 0.01 mol L\(^{-1} \) KOH, or 0.005 mol L\(^{-1} \) Ca(OH)\(_2\). The DNOC solutions with a matching pH were added to make a total volume of 10 mL with a final DNOC concentration of 120 mg L\(^{-1} \). Blank suspensions without DNOC at pH 7 were prepared for both freeze-dried and never-dried clay suspensions. The tubes were shaken on a reciprocating shaker for 24 h at 25°C.

The pH-adjusted smectite–DNOC suspensions were centrifuged at 11,951 \( \times \) g for 25 min to separate the solid and liquid phases. The supernatant pHs were recorded and then analyzed on a spectrophotometer to determine DNOC concentrations as described previously (Pereira et al., 2007). A small amount (~10 mg) of the smectite–DNOC sediment was smeared on glass microscope slides. Blank smectite suspensions (without DNOC) at pH 3, 4, and 6 were similarly prepared. The glass slides containing the smectites were air dried in a desiccator at 25°C. The relative humidity (RH) in the desiccator was controlled at 54% with a saturated solution of Mg(NO\(_3\))\(_2\) (Greenspan, 1977). These air-dried samples were maintained at 54% RH until analysis by XRD.

The K-saturated clay films were oven dried at 105°C for 15 h, and the Ca\(^{2+} \)–saturated clay films were oven dried for 30 h. The oven-dried samples were then placed in a desiccator over desiccant to maintain RH close to 0% until XRD analysis was performed.

The XRD patterns of the films were collected using the same instrument as for the suspension XRD. A step size of 0.05° and a scanning rate of 0.5° 20 min\(^{-1} \) were used for analysis of both air-dried and oven-dried clay films. The slides were mounted in reflection mode, and the analysis took about 15 min per sample. The air-dried smectite films were run under a stream of air maintained at 54% RH by a saturated Mg(NO\(_3\))\(_2\) solution, and the oven-dried films were run under a stream of desiccated air (0% RH).

**Analysis of Air-Dried and Oven-Dried Clay Films by X-ray Diffraction**

The pH-adjusted smectite–DNOC suspensions were centrifuged at 11,951 \( \times \) g for 25 min to separate the solid and liquid phases. The supernatant pHs were recorded and then analyzed on a spectrophotometer to determine DNOC concentrations as described previously (Pereira et al., 2007). A small amount (~10 mg) of the smectite–DNOC sediment was smeared on glass microscope slides. Blank smectite suspensions (without DNOC) at pH 3, 4, and 6 were similarly prepared. The glass slides containing the smectites were air dried in a desiccator at 25°C. The relative humidity (RH) in the desiccator was controlled at 54% with a saturated solution of Mg(NO\(_3\))\(_2\) (Greenspan, 1977). These air-dried samples were maintained at 54% RH until analysis by XRD.

The K-saturated clay films were oven dried at 105°C for 15 h, and the Ca\(^{2+} \)–saturated clay films were oven dried for 30 h. The oven-dried samples were then placed in a desiccator over desiccant to maintain RH close to 0% until XRD analysis was performed.

The XRD patterns of the films were collected using the same instrument as for the suspension XRD. A step size of 0.05° and a scanning rate of 0.5° 20 min\(^{-1} \) were used for analysis of both air-dried and oven-dried clay films. The slides were mounted in reflection mode, and the analysis took about 15 min per sample. The air-dried smectite films were run under a stream of air maintained at 54% RH by a saturated Mg(NO\(_3\))\(_2\) solution, and the oven-dried films were run under a stream of desiccated air (0% RH).

**Fig. 1. Structural formula and ionization of 4,6-dinitro-o-cresol (DNOC) below and above the acid dissociation constant (pK\(_a\)).**
RESULTS AND DISCUSSION

Suspension XRD patterns illustrating the effects of pH and DNOC on freeze-dried and never-dried K-SWy-2 are shown in Fig. 2A and 2B, respectively. No XRD peaks are evident in the suspension XRD patterns for the blank K-SWy-2 at pH 7 or for the K-SWy-2–DNOC suspension at pH 6. The lack of a distinct peak indicates that the K-SWy-2 was substantially delaminated in the 0.001 mol L\(^{-1}\) KCl systems. A very broad 001 peak centered at 1.3 nm is apparent in the suspension XRD pattern of K-SWy-2 with DNOC at pH 4 and a less apparent peak is observed at pH 3. The results indicate that a few small quasicrystals with one (1.25 nm) or two (1.50 nm) layers of interlayer water were present in the K-SWy-2 suspensions at pH 3 and 4. Small peaks at approximately 2.5° 20 are also evident in the XRD patterns for the never-dried K-SWy-2 suspensions (Fig. 2B) but not in the XRD patterns of the freeze-dried K-SWy-2 suspensions (Fig. 2A). The spacing of these low-angle peaks (3.5 nm) is within the double-layer swelling range (Laird, 2006) and therefore attributed to interparticle x-ray scattering.

The XRD patterns of air-dried K-SWy-2 films (Fig. 3A) have distinct peaks centered at 1.16 nm for blanks and 1.18 nm for samples treated with DNOC regardless of pH. The position of these peaks is between the anticipated peak positions for a smectite with no interlayer water (1.0 nm) and one layer of interlayer water (1.25 nm), and therefore indicates random interstratification of these phases. The small peak at 8.8° 20 (1.0 nm) indicates a separate fully collapsed phase. The slight peak shift from 1.16 to 1.18 nm on DNOC adsorption is evidence that at least some DNOC was intercalated by quasicrystals of the air-dried smectite films.

Oven drying K-SWy-2 DNOC-treated and blank films (Fig. 3B) dehydrated the interlayer cations and caused collapse of the layers, manifesting a 1.0-nm peak; however, the 1.0-nm peaks on the XRD patterns of the oven-dried K-SWy-2 samples that were treated with DNOC are asymmetrical. The asymmetric peak shape is most evident for the XRD pattern of the K-SWy-2 DNOC-treated sample at pH 3. The low-angle tail on these asymmetrical peaks suggests that interlayer DNOC domains may tend to cluster but do not form a discrete separate phase.

Suspension XRD patterns of the freeze-dried K-SAz-1 are nearly flat but do have a small broad peak centered near 1.27 nm (Fig. 4A). By contrast, suspension XRD patterns for the never-dried K-SAz-1 exhibit distinct 1.50-nm peaks at pH 7 that shift to 1.47 nm with decreasing pH. The difference between the XRD patterns for the freeze-dried and never-dried K-SAz-1 suspensions demonstrates hysteresis in both quasicrystal formation and crystalline swelling (Laird et al., 1995). The never-dried K-SAz-1 was prepared by dialyzing a Na-SAz-1 suspension against various KCl solutions. Because this sample was never dried during or after the K-saturation process, the suspension contained relatively large quasicrystals with two layers of water molecules between each smectite lamella. When the K-SAz-1 suspension was freeze-dried, however, the large quasicrystals were broken up into smaller quasicrystals that were dehydrated and hence collapsed to 1.0 nm. When the freeze-dried K-SAz-1 was resuspended in 0.001 mol L\(^{-1}\) KCl, the small quasicrystals formed during freeze-drying became dispersed. Some of the collapsed layers within the small quasicrystals imbibed one layer of water, expanding to 1.27 nm, but were not able to expand completely to 1.5 nm.

The XRD patterns for the air-dried and oven-dried K-SAz-1 films (Fig. 5A and 5B) demonstrate collapse of K-SAz-1 to 1.2 nm at 54% RH and 1.0 nm at 0% RH. The only evidence of DNOC in the interlayers of K-SAz-1 is the difference
between the XRD patterns for the oven-dried blank and the oven-dried DNOC-treated K-SAz-1 at pH 3. The peak for the oven-dried blank at pH 3 is shifted slightly to the right relative to the peaks for blanks prepared at pH 4 and 6 (Fig. 5B). This shift is probably due to the partial replacement of interlayer K⁺ by H⁺. In contrast, the peak for the oven-dried DNOC-treated K-SAz-1 at pH 3 is both shifted slightly to the left and broader than peaks for the other oven-dried K-SAz-1 samples.

In a related study on the adsorption of DNOC as a function of pH by the same K-SWy-2 and K-SAz-1 samples, and using similar sample preparation and equilibration conditions as used in the present study, Pereira et al. (2007) demonstrated that essentially 100% of added DNOC was adsorbed (12,000 mg kg⁻¹) by K-SWy-2 at pH 3 and 4, but adsorption decreased to 62% as pH increased to 7. For the K-SAz-1, adsorption of DNOC decreased from 94% at pH 3 to ~31% at pH 7. That study (Pereira et al., 2007) also provided evidence for co-adsorption of K⁺ and DNOC, consistent with previous molecular modeling and spectroscopic evidence (Johnston et al., 2002) for the formation of K-DNOC complexes in the interlayers of K-smectites. The formation of K-DNOC complexes in the interlayers of smectites explains the apparent stability of DNOC in the interlayers of smectites at pHs above the pKₐ of DNOC, which should be predominantly in the phenolate form and hence electrostatically repelled from the negatively charged smectite surfaces. Our results (Fig. 2) show that K-SWy-2 is largely delaminated in 0.001 mol L⁻¹ KCl suspensions, which means that most smectite surfaces in the 0.001 mol L⁻¹ KCl suspensions are “external” rather than “internal” surfaces. We hypothesize that phenolate anions are co-adsorbed with K⁺, possibly as an ion pair, onto exposed external surfaces of smectites. When the smectite suspension is subsequently dehydrated to form an oriented film for XRD analysis, K-DNOC complexes that had been adsorbed on external surfaces would become intercalated between layers as the small quasicrystals coalesced during formation of the oriented film.

Suspension XRD patterns for freeze-dried and never-dried Ca-SWy-2 are presented in Fig. 6A and 6B, respectively. All of the XRD patterns exhibit distinct peaks centered near 1.96 nm, which is close to the anticipated peak positions of a four-layer hydrate (2.0 nm). The symmetry and size of the 1.9-nm peaks indicate the existence of relatively large quasicrystals in the Ca-SWy-2 suspensions. The freeze-dried Ca-SWy-2 suspensions (Fig. 6A) show slightly broader and less intense peaks than the never-dried Ca-SWy-2 suspensions (Fig. 6B), suggesting that the legacy of the freeze-drying treatment for a Ca-saturated smectite is smaller quasicrystals.

X-ray diffraction patterns for air-dried Ca-SWy-2 are presented in Fig. 7A. The air-dried Ca-SWy-2 peaks are centered at ~1.5 nm, indicating two layers of interlayer water molecules. The peak for the air-dried DNOC-treated Ca-SWy-2 at pH 3 is shifted to the left of peaks for the other samples, indicating the presence of interlayer DNOC. There is no evidence in the XRD patterns for the air-dried samples, however, that DNOC was present in the interlayers at pH 4 and 6. The results are consistent with adsorption data (Pereira et al., 2007) showing substantial amounts of DNOC adsorbed by Ca-SWy-2 at pH 3 (82%) and much less adsorption at pH 4 and 6 (18%). The DNOC is dominantly a neutral molecule at pH 3, and hence could enter the interlayers of Ca-SWy-2 quasicrystals without electrostatic repulsion. At higher pHs, the phenolate anion would be electrostatically excluded from the interlayers but could potentially adsorb on external surfaces of the quasicrystals. There was no evidence for co-adsorption of Ca and DNOC, which would be required if Ca-DNOC complexes were forming (Pereira et al., 2007).

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**Fig. 4.** Suspension x-ray diffraction pattern of (A) freeze-dried and (B) never-dried K-saturated Arizona montmorillonite (K-SAz-1) with added 4,6-dinitro-o-cresol (DNOC).

**Fig. 5.** X-ray diffraction pattern of (A) air-dried K-saturated Arizona montmorillonite (K-SAz-1) at 54% relative humidity (RH) and (B) oven-dried (105°C) K-SAz-1 at 0% RH with or without added 4,6-dinitro-o-cresol (DNOC).
Oven-dried Ca-smectites spontaneously rehydrate when they are exposed to ambient humidity and typically exhibit a 1.5-nm d-spacing. The XRD peaks for the oven-dried Ca-SWy-2 samples at pH 4 and 6 are symmetrical and centered near 1.0 nm (Fig. 7B), indicating that the samples were fully collapsed and that DNOC was not present in the diffracting domains. The peak for the oven-dried Ca-SWy-2 sample at pH 3 is slightly asymmetrical, suggesting that some interlayers contained DNOC. In general, the XRD peaks for the DNOC-treated Ca-SWy-2 samples are slightly broader and less intense than the peaks for the corresponding controls, suggesting that the quasicrystals were smaller in the DNOC-treated samples. These results suggest that adsorbed DNOC was predominantly on the external surfaces of the Ca-saturated quasicrystals rather than in the interlayers, except at pH 3 where the neutral form of DNOC dominated.

The XRD patterns for both freeze-dried (Fig. 8A) and never-dried (Fig. 8B) Ca-SAz-1 suspensions show distinct 001 peaks centered at about 1.9 nm, which is close to the anticipated peak position for a four-layer hydrate (2.0 nm). The freeze-dried Ca-SAz-1 suspensions show broader peaks than the never-dried Ca-SAz-1 suspensions, again suggesting that freeze-drying treatments leave a legacy of smaller quasicrystals in suspensions. The peaks for the blanks in both freeze-dried and never-dried Ca-SAz-1 suspensions are substantially more intense than the peaks for the DNOC-treated samples. This indicates that the DNOC-treated samples had smaller quasicrystals in the suspensions. Perhaps DNOC adsorbed on external surfaces of quasicrystals inhibited small quasicrystals from coalescing into larger quasicrystals. There is no indication in the suspension XRD pattern that DNOC was present in the interlayers of the Ca-SAz-1 samples.

The XRD patterns of the air-dried and oven-dried Ca-SAz-1 are presented in Fig. 9A and Fig. 9B, respectively. The peaks for the air-dried Ca-SAz-1 are broad and symmetrical for both blanks and samples with DNOC. Peaks are centered at about 1.52 nm, which is close to the anticipated peak for a two-layer hydrate. There is no apparent difference in the XRD patterns for the DNOC-treated and untreated air-dried Ca-SAz-1 samples. The peaks for the oven-dried blank Ca-SAz-1 films are all centered at about 1.0 nm. The peaks of the oven-dried Ca-SAz-1–DNOC films appear to be slightly broader and more asymmetrical than those of the blank Ca-SAz-1 films at pH 3 and 4. This is evidence that DNOC was on the external surfaces of the quasicrystals in the suspension and disrupted regularity of the stacking sequence when the oriented film was formed on drying. At pH 6, no difference is apparent between the XRD patterns of the DNOC-treated and untreated oven-dried Ca-SAz-1 samples.

Only small amounts of added DNOC (12%) were adsorbed by both the freeze-dried and never-dried Ca-SAz-1 suspensions across the entire pH range (Pereira et al., 2007). By contrast, Ca-SWy-2 adsorbed 82% of added DNOC at pH 3 and 18% of the DNOC at pH 4 and 6. The SWy-2 smectite is a low-charge smectite with comparatively large hydrophobic nanosites (siloxane surface between exchangeable cations) capable of adsorbing neutral organic molecules including NACs (Boyd et al., 2001; Sheng et al., 2002). By contrast, SAz-1 is a high-charge smectite with smaller hydrophobic nanosites and therefore with less capacity for adsorption of neutral organic molecules. Our data suggest that at pH 3 the neutral form of
DNOC was adsorbed on the larger hydrophobic nanosites in the interlayers of SWy-2, but not on the smaller hydrophobic nanosites of SAz-1. At higher pHs, the phenolate form of DNOC was apparently unable to adsorb in the interlayers of either clay but was retained on the external surfaces.

Li et al. (2007) have recently demonstrated that 1,3-dinitrobenzene (1,3-DNB) readily enters the interlayers of a K-smectite in aqueous suspension. The results showed that a 1,3-DNB loading of 20 g kg\(^{-1}\) clay resulted in a shift in d-spacing from 1.5 to \(~1.23\) nm in a 0.3 mol L\(^{-1}\) KCl suspension. In dilute 0.01 mol L\(^{-1}\) KCl suspension, no 001 peak was observed for the blank but a distinct 1.23-nm peak was observed when 1,3-DNB was added, suggesting that 1,3-DNB promoted formation of quasicrystals in the otherwise delaminated suspension. In our study, we saw no evidence of interlayer occupancy of DNOC while in aqueous suspension at pH > pK\(_a\), which we attribute to the anionic character of DNOC.

X-ray diffraction is a valuable tool for investigating interactions between organic molecules and smectites. Caution must be exercised, however, when extrapolating XRD patterns of air-dried and oven-dried smectite films to adsorption processes that occur in aqueous suspensions (i.e., before the films were made). The process of drying a smectite suspension causes the suspended quasicrystals and individual lamellae to coalesce, forming a clay film that is arguably a single large quasicrystal (Fig. 10A). Anionic organic molecules that are adsorbed only on external surfaces of quasicrystals in aqueous suspensions may become entrapped between substacks of quasicrystals as the clay dries, disrupting the stacking sequence in a clay film (Fig. 10B). At pHs < pK\(_a\), the neutral form of a weak acid such as DNOC may be adsorbed directly into smectite interlayers or become incorporated into new interlayers as the clay dries (Fig. 10C). The ability of K-smectites to delaminate in aqueous suspensions, and the ability of the phenolate form of DNOC to form a neutral complex with K ions allows large amounts of K-DNOC to be incorporated into newly formed smectite interlayers as the clay dries (Fig. 10D).

Our results demonstrate the importance of quasicrystal dynamics in controlling the sorption of DNOC by smectites in aqueous suspensions. Quasicrystal dynamics in soils and sediments is not well understood, but smectite quasicrystals are undoubtedly several orders of magnitude more stable in soils than in aqueous suspensions. In a soil, only a relatively small and stable fraction of the total smectite surface area is exposed on external surfaces of quasicrystals at any one time. In an aqueous suspension, quasicrystals are continuously breaking apart and reforming or may be completely delaminated; thus a large fraction of the total surface area of a smectite is directly exposed to the bulk solution. This difference could result in substantially lower sorption potentials in undisturbed soils than would be predicted by batch equilibration studies. This will be particularly important for molecules that readily adsorb on external surfaces of quasicrystals but have difficulty diffusing into the interlayers of stable quasicrystals. Clearly more research is needed to understand the impact of quasicrystal dynamics on the fate of pesticides and other organic chemicals in soil environments.

**Fig. 8.** Suspension x-ray diffraction pattern of (A) freeze-dried and (B) never-dried Ca-saturated Arizona montmorillonite (Ca-SAz-1) with added 4,6-dinitro-o-cresol (DNOC).

**Fig. 9.** X-ray diffraction pattern of (A) air-dried Ca-saturated Arizona montmorillonite (Ca-SAz-1) at 54% relative humidity (RH) and (B) oven-dried (105°C) Ca-SAz-1 at 0% RH with or without added 4,6-dinitro-o-cresol (DNOC).
Fig. 10. Schematic diagram showing the interaction between 4,6-di-nitro-o-cresol (DNOC) and smectite quasicrystals. In suspension, DNOC is adsorbed on surfaces of individual layers and external surfaces of quasicrystals. On drying, the phenolate form of DNOC disrupts formation of large Ca-smectite quasicrystals but the neutral form of DNOC and neutral K-saturated DNOC complexes fit in the interlayers of smectite quasicrystals. The lines represent smectite lamellae, open dots represent phenolate DNOC molecules, black dots represent neutral form of DNOC, and K indicates K ions that form complexes with the phenolate form of DNOC. Not shown are exchangeable cations or water molecules. $pK_a$ is the acid dissociation constant.

REFERENCES


