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Nature of the Interlayer Environment in an Organoclay Optimized for the Sequestration of Dibenzo-*p*-dioxin

Cliff T. Johnston^{†,*}, Bushra Khan[†], Edwin F. Barth[‡], Sandip Chattopadhyay[§], and Stephen A. Boyd^{||}

[†]Crop, Soil and Environmental Sciences, Purdue University, 915 W. State Street, West Lafayette, Indiana 47907-2054, United States

[‡]Office of Research and Development, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268, United States

[§]Tetra Tech Inc., 250 West Court Street, Suite 200W, Cincinnati, Ohio 45202, United States

^{||}Department of Crop and Soil Sciences, 532 Plant and Soil Sciences Building, Michigan State University East Lansing, Michigan 48824-1325, United States

Abstract

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*Corresponding Author: Phone: 765 496 1716; fax: 765 496 2926; clays@purdue.edu.

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Supporting Information

Additional information as mentioned in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

A Na-smectite clay (Na-SWy-2) was exchanged with various amounts of dimethyldioctadecylammonium bromide (DODA-Br) up to twice the cation exchange capacity (CEC). The organoclay (DODA-SWy-2) with DODA-Br added at $2 \times$ CEC exhibited a maximum 4.2 nm *d*-spacing and a 31.4% carbon content, which demonstrates DODA⁺ intercalation. DODA-SWy-2 was evaluated as an archetype of commercial products used to sequester hydrophobic contaminants, and the nature of the primarily C18 alkylhydrocarbon-chain interlayer environment was emphasized. Shifts in $\nu(\text{CH})$ and CH_2 rocking band positions in DODA-SWy-2-complex FTIR-spectra indicate that DODA C18 chains were more ordered as DODA surface coverage was increased. Differential scanning calorimetry analysis indicated a DODA-SWy-2 gel-to-liquid transition temperature much lower than the melting point of crystalline DODA-Br and similar to that of aqueous DODA-Br vesicles. This suggests that the transition was governed by C18 alkyl tail-tail interactions in the clay interlamellar region. Dibenzo-*p*-dioxin (DD) sorption from water by DODA-SWy-2 was compared to DD sorption by the geosorbents granular activated carbon (GAC), K-exchanged saponite, and a muck soil. The linear K_1 sorption coefficients ($\log K_1$) from a linear fit of the sorption isotherms were 4.37 for DODA-SWy-2, 5.55 for GAC, 3.19 for muck soil, and 2.46 for K-saponite. The DD-organic-matter-normalized sorption coefficient (K_{om}) was ~ 2.4 times the octanol-water partition coefficient (K_{ow}). This indicates that DD has a higher affinity for the nonpolar interlayer DODA organic phase than for octanol. In contrast, the K_{om} for muck soil DD sorption was ~ 10 times less than K_{ow} , which reflects the higher polarity of amorphous soil organic matter relative to octanol. Enhanced DD uptake by the DODA-derived lipophilic phase in the organoclay is attributed to the low polarity, “open” C18 alkyl structure due to the physical dimensions of “v-shaped” DODA⁺ molecular, and low density of the interlamellar phase (~ 0.50 g/cm³) density of intercalated DODA⁺.

INTRODUCTION

The interaction of quaternary ammonium cations (QUATs) with clay minerals is generally well studied and understood.^{1–8} QUATs readily displace naturally occurring inorganic cations on clays and, thereby, form a class of materials known as organoclays.^{6,7} The preference of 2:1 layer silicate surfaces for organic cations over alkali and alkaline-earth cations is attributed to the combined action of the organic cation free energy of hydration, electrostatic interactions with clay surface, and non-Coulombic interactions that involve the organic moieties of organic cations.^{4,9–12} Although the initial organo-clay studies were conducted over sixty years ago,¹³ enhanced interest has occurred more recently due to organoclay use in synthetic clay/polymer nanocomposites as flame retardant materials,¹⁴ bionanocomposites,¹⁵ sensors,¹⁶ and related advanced material applications.¹⁷ Additionally, there continues to be growing interest in the use of organoclays to attenuate organic and inorganic contaminants in a variety of environmental applications.^{18–20} Environmental applications involving organoclays for waste management and contaminated site remediation have evolved since the 1980's ranging from treating water, such as oily waste from discharge waters of oil drilling platforms, leachate or groundwater containing organic contaminants,^{20–22} treating organic vapors,²³ stabilizing organic waste, sludge, or soil to pass EPA hazardous waste leaching criteria,^{24–27} incorporation as sorptive components into vertical or horizontal barrier systems for hazardous waste landfills,^{28,29} and in funnel and gate in situ groundwater treatment systems.³⁰ More recent applications include the use of organoclay soil amendments to lower contaminant bioavailability, and as components in active sediment caps designed to sorb organic contaminants hence reducing advective transport to the water column.³¹

The group of expandable 2:1 phyllosilicates known as smectites is the most common type of clay mineral used in the synthesis of organoclays because of their small particle size, high surface area, and high cation exchange capacity (CEC). They are also readily available in geologic deposits, and hence inexpensive. The fundamental particles of smectites are composed of two silica tetrahedral sheets that sandwich an octahedral sheet forming a smectite layer with an overall thickness of ~1 nm. The particles of these 2:1 clays have high aspect ratios (~100 to 500) and morphology similar to a sheet of paper with torn edges.^{16,32} Isomorphic substitution in tetrahedral and/or octahedral sheets creates points of negative charge that are separated by distances ranging from 0.7 to 2 nm depending on the type of smectite whose charge is balanced by a counterion. In nature, the predominant counterions (exchangeable cations) are Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+} which all have large enthalpies of hydration (–300 to –2000 kJ/mol). Hence, these strongly hydrated inorganic cations impart an overall hydrophilic character to natural smectites.³³ These inorganic cations are readily displaced via cation exchange by cationic surfactants of the form $(\text{CH}_3)\text{NR}$ or $(\text{CH}_3)_2\text{NR}_2$ where R is an alkyl or aromatic hydrocarbon.^{7,34,35} The cationic headgroup of the organic cation satisfies the negative charge on the siloxane surface, and the alkyl moieties of the intercalated organic cation create an organophilic environment in the clay interlayer. When R is a long chain alkyl group, the external surface and the interlayer regions of the clay tactoids are characterized by overlapping alkyl chains. When such exchange reactions occur, the clays are transformed into materials with predominantly hydrophobic character.^{3,36} The

agglomerated alkyl chains, anchored on the clay surface by the cationic head groups, create an organophilic phase in the interlamellar region of the clay that functions similar to partitioning medium for hydrophobic organic contaminants. As a result, organoclays are effective sorbents for hydrophobic organic contaminants as vapors or as solutes from aqueous solution.^{1,3,6,36–39}

Organoclays formed using the alkyl cations hexadecyltrimethylammonium (HDTMA), hexadecylpyridinium (HDP), tetramethylammonium (TMA), and trimethylphenylammonium (TPMA) have been extensively characterized.^{3,39–41} Considerably less information is available for the types of organoclays commonly produced commercially for environmental applications which are manufactured using organic cations with multiple large alkyl chains such as those found in dimethyl dihydrogenated tallow;^{42–44} these structures maximize the organic carbon content and sorptive capacity of the resultant organoclay. A structurally similar compound dimethyldioctadecylammonium bromide (DODA-Br; $(\text{CH}_3)_2\text{N}-((\text{CH}_2)_{17}\text{CH}_3)_2\text{Br}$) was utilized in this study as an archetype for such commercial organoclays. The objectives are to advance understanding of how these “commercial type” organoclays function mechanistically as sorbents for nonpolar organic contaminants, and to elucidate factors that optimize sorption.

The specific aims of this paper are 3-fold. The first is to characterize the interaction of DODA⁺ with Na–SWy-2 with emphasis on providing new insight into the physicochemical properties of the intercalated organophilic phase, and how these affect contaminant sorption, using a combination of structural, spectroscopic, and thermal analysis tools. Although DODA-modified smectites have been the subject of prior work,^{40,45–51} details about their properties as functional geosorbents is lacking, especially regarding the nature of the interlayer environment where most sorption occurs. The second is to examine the sorption of dibenzo-*p*-dioxin (DD) by DODA–SWy-2 in aqueous suspension. Dibenzo-*p*-dioxin is structurally representative of an important class of polychlorinated dibenzodioxins and dibenzofurans (PCDDs/PCDFs) that are common targets for sequestration using environmental geosorbents. Comparatively, little is known about the characteristics of commercial type organoclays (e.g., dimethyl dihydrogenated tallow) as sorbents for poorly water-soluble organic contaminants (aqueous solubilities $< 1 \text{ mg/dm}^3$) in general, and for dioxins specifically. The third aim is to compare the sorption of DD by DODA–SWy-2 smectite to that by three common geosorbents.

MATERIALS AND METHODS

Clay Preparation

The clay mineral used in this study was a Na-exchanged SWy-2 smectite obtained from the Source Clays Repository of the Clay Minerals Society at Purdue University, West Lafayette, IN. Physicochemical details about this clay have been reported previously.^{52–54} The clay was exchanged with Na⁺ by placing 40 g of the clay in 1 dm³ of 0.5 M NaCl for 24 h. The resulting Na–smectite suspension was “washed” with 0.5 M NaCl twice. Excess salts were removed by repeated centrifugation with Millipore water until a negative Cl[−] test using AgNO₃ was obtained. When salt-free, the $< 2 \mu\text{m}$ size fraction was collected by centrifugation. The resulting clay suspension was subsequently quick-frozen, freeze-dried.

Dimethyldioctadecylammonium bromide (DODA-Br) was obtained from Sigma-Aldrich Inc., St. Louis, MO and used without further purification.

Two sets of DODA⁺ modified clay samples were prepared in this study. The first consisted of small batches (25 mg samples) which were prepared to examine the change in thermal, spectroscopic, and structural properties as a function of fractional surface coverage of DODA⁺ ranging from 0 to 2 times the cation exchange capacity (CEC). A series of ten solutions containing 20 mL of 0–2 mM DODA dissolved in water (Millipore deionized water) and 25 mg of Na–SWy-2 smectite in 30-mL Corex centrifuge tubes were sonicated for 10 min and shaken overnight. After being shaken, the tubes were centrifuged at 6000 rpm for 30 min and the supernatants were removed. The resulting organoclay was washed with distilled–deionized water and centrifuged twice. The clay plug was dispersed in water and half of the volume (containing 12.5 mg clay) was deposited on a glass slide and allowed to dry for X-ray diffraction (XRD) analysis as an oriented mount. The other half was allowed to air-dry for spectroscopic and thermal analysis. In addition, larger scale batches of the DODA–SWy-2 complex treated with 1.5 times CEC of DODA (>40 g) were prepared to conduct sorption studies (described in the Supporting Information (SI)). Experimental details regarding analyses using XRD, FTIR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and HPLC analysis of DD are given in the SI.

Geosorbents

In addition to the DODA–SWy-2 smectite organoclay, additional geosorbents including granular activated carbon (GAC), K-exchanged saponite (SapCa2), and muck soil were used. In related work we have shown that K-exchanged saponite (and Cs-saponite) has a high affinity for dibenzo-*p*-dioxin,^{54,55} hence it was included in this study. The Houghton organic muck soil (low mineral content, 46.5% OC, and a CEC of 214 cmol_c kg^{−1}) was provided by Prof. Hui Li at Michigan State University and used to represent natural soil organic matter. The activated carbon (Calgon Carbon Corp.) was provided by TetraTech Inc. This GAC has an effective porosity of 0.53 (volume of void space/total volume), particle density of 1.4 g/cm³, N₂ BET surface area of 1050 m²/g, permeability of 1 × 10^{−3} cm/s min, and mass-to-area ratio of 0.4 lb/ft².

Sorption of Dibenzo-*p*-dioxin

Dibenzo-*p*-dioxin (DD) was obtained from Chem Service, West Chester, PA, with a purity of 99%. A stock solution of DD (800 mg/dm³) in anhydrous methanol was used to make aqueous solutions of DD; the methanol content in these solutions was 0.1% to minimize any cosolvent effect. The diluted aqueous solutions of DD were sonicated for 60 min at room temperature in a water bath sonicator. The mass-to-volume ratio for sorption experiments was optimized to achieve ~50% sorption at the highest initial aqueous concentration of DD. The solid/solution values (mg sorbent/mL solution) for DODA–SWy-2, GAC, K-saponite, and muck soil were 5:15, 2.5:30, 15:7, and 10:25, respectively.

Batch Sorption Experiments

Batch sorption experiments were conducted in duplicate using five initial aqueous DD concentrations. The initial applied DD concentrations ranged from 0.18 to 0.8 mg/dm³. Aqueous DD solutions were added to the various geosorbents contained in 30-mL glass centrifuge tubes (Kimble HS-5600-30) which were immediately sealed using polytetrafluoroethylene (PTFE)-lined screw caps. Samples were shaken on a rotary shaker for 24 h to achieve apparent equilibrium as determined in preliminary studies. After 24 h the samples were centrifuged at 3000g for 1–2 h, then 1 mL of the aqueous supernatant was removed and added to 0.5 mL of methanol in HPLC vials with caps; each vial was then stirred for 30 s prior to analysis by HPLC. The amount of DD sorbed was calculated by difference in the initial and final DD aqueous phase concentrations. Duplicate control samples containing 0.8 mg/dm³ DD, without sorbent, were prepared to quantify losses of DD, which were insignificant (<1%) and hence sorption data were not adjusted. Supernatant (1 mL in glass vials) was analyzed by HPLC to quantify DD concentrations. Standard solutions of DD were prepared in the same (3:1) H₂O/MeOH solution to avoid matrix effects. Details about the HPLC procedure used to analyze DD are given in the SI.

RESULTS AND DISCUSSION

Layer Expansion of DODA-Treated SWy-2 Smectite

X-ray diffraction (XRD) patterns of the Na-SWy-2 smectite treated with different concentrations of DODA⁺ were obtained (region from 2 to 12° 2 θ shown in Figure 1). Prior to the addition of DODA⁺, the *d*-spacing of the air-dried clay at a relative humidity of 25% was 1.22 nm corresponding to a single layer hydrate of the clay.⁵² Addition of DODA⁺ to the SWy-2 smectite resulted in a stepwise expansion of the *d*-spacing to a maximum value of 4.21–4.26 nm based on the positions of the 002 and 003 reflections. The stepwise increase in *d*-spacing with increasing amount of added DODA⁺ (Figure 2A) is in good agreement with previous results.^{45–49} The values reported here also agree with an observed spacing of 3.7 nm obtained from a nematic liquid crystal using small-angle X-ray scattering (SAXS).⁵⁰

The increase in *d*-spacing to a value of 4.2 nm is consistent with prior results obtained by XRD, TEM, and SAXS.^{46,47,49,50} The specific configuration of the “v-shaped” DODA⁺ molecule, with the two octadecyl chains extending away from the onium headgroup (hence forming the “V” shape) in the clay interlayer is unknown. However, the “end-to-end” length of DODA⁺ is approximately 2.7 nm, the angle between the chains is approximately 45 degrees, and the corresponding “physical length” of the molecule is about 2.5 nm. Together with the thickness of a single SWy-2 layer of 0.96 nm, the maximum combined thickness would be ca. 3.56 nm. Reconciling the observed *d*-spacing of 4.2 nm requires overlapping tilted chains extending toward one another from the opposing surfaces of two clay layers (see depiction in Figure 2A^{46,51}). The observation of well-defined higher order 002 and 003 reflections indicates a high degree of ordering among the modified clay layers stacked on top of each other.⁵⁶ Maximum interlayer expansion was obtained when the clay was treated with 1.5 $\times$ CEC corresponding to the minimum amount of DODA⁺ to achieve

“full” interlayer expansion. This “optimized” concentration of $1.5 \times \text{CEC}$ was subsequently used for the sorption studies.

Thermal Analysis and Carbon Content

The organic carbon (OC) contents of the DODA–SWy-2 complexes prepared with varying amounts of DODA⁺ were calculated from TGA data (Figure 2B). The TGA-derived OC content of the Na–SWy-2 smectite was low (<1% w/w). Upon addition of DODA⁺, the %OC content increased linearly to a maximum value of 42% (wt/wt) at a DODA⁺ loading of two times the CEC ($2 \times \text{CEC}$). The corresponding TGA–DTG thermograms in the range of 25 to 1000 °C (Figure 3) revealed the loss of carbon from the organoclay in the 150–550 °C region as indicated by four discrete “peaks” with mass-loss-maxima at 221, 305, 367, and 421 °C. The relative proportion of these four carbon-mass-loss peaks varied depending on the surface coverage of DODA⁺ (see Figure S-1 in SI). At the lower surface coverage of DODA⁺ (e.g., $0.6 \times \text{CEC}$), the high-temperature TGA features at 421 and 367 °C account for 85% of the total carbon loss. These temperatures are well above the thermal decomposition of DODA-Br, observed at 305 and 355 °C, indicating that intercalation of the DODA⁺ cation into the clay structure thermally stabilizes the organic cation. The clay structure is also affected as the dehydroxylation peak of the clay shifted from 699 °C (no organic cation) to progressively lower temperatures with increasing surface coverage of DODA⁺; a value of 610 °C was observed at the highest surface coverage ($2 \times \text{CEC}$).

Since the amount of organic cation intercalated and the volume of the clay interlayer are known, it is possible to estimate the density of the organophilic phase in the clay interlayer. For SWy-2 clay treated with $1.5 \times \text{CEC}$, the d_{001} value (d -spacing) increased to 4.2 nm and the organic carbon content was 31.4%. Based on the surface area of the clay (754 m²/g), the thickness of one layer of clay (0.96 nm), and the dry density of the SWy-2 clay (2.761 g/cm³), the density of DODA in the clay interlayer is ca. 0.50 g/cm³. Details of the density estimation are given in the SI. This low value is presumably due to a loose packing of the v-shaped C₁₈ chains. Despite the “inefficient” packing of the C₁₈ chains, it is unlikely that water contributes significantly to the mass of the organoclay since both the FTIR spectra (SI) and TGA curves (Figure 3A) indicate a lack of water present attesting to the hydrophobic nature of the clay interlayer regions. In addition, the value of 0.50 g/cm³ certainly includes some DODA⁺ bound to the external surface of the clay particles, lowering the interlayer density value further (see SI).

The differential scanning calorimeter (DSC) thermograms for the DODA⁺ modified clay were compared to that of pure DODA-Br in the lower temperature region of –30 to 200 °C (Figure 3B). Upon heating the clay in this region, the main transition endotherm for the organoclay occurs at a temperature of 53 °C with another smaller endothermic peak at 84.1 °C. With cooling, the main exothermic transition occurs at an onset temperature of 52.4 °C. For pure DODA-Br, two endothermic transitions are observed at higher temperatures of 87.3 and 164 °C. Interestingly, DODA-X (X = Cl[–], Br[–]) is one of the most studied vesicle-forming cationic amphiphiles, and DSC among other methods (ESR, NMR, surface tension) have been used to study the thermotropic phase behavior. DSC measurements on aqueous DODA-Br solutions taken above the critical micelle concentration reveal gel-to-liquid

transitions in the temperature range of 35–53 °C depending on the concentration of DODA⁺.^{57–59} This provides further support for a DODA-derived organic phase in the clay interlayers consisting of overlapping C-18 alkyl chains structurally similar to the interior of a DODA surfactant micelle. The position of both the $\nu_{as}(\text{CH})$ and $\nu_s(\text{CH})$ bands in the FTIR spectrum of DODA–SWy-2 increased with increasing temperature, and this shift was coincident with the endothermic feature observed in the upscan DSC thermogram at 53 °C (see SI).

FTIR Spectra of DODA–SWy-2 Complexes

Upon addition of DODA⁺ to the Na–SWy-2 smectite the most prominent changes in the spectrum of the clay are evident in the $\nu(\text{CH})$ and in the CH_2 deformation regions. The $\nu(\text{CH})_{\text{asym}}$ and $\nu(\text{CH})_{\text{sym}}$ bands at 2919 and 2850 cm^{-1} have almost no intensity in the SWy-2 clay without DODA⁺. These bands grow in intensity and shift position with increasing surface coverage of DODA⁺ (Figure 4A). At low surface coverage of $0.6 \times \text{CEC}$, the positions of the $\nu_{as}(\text{CH})$ and $\nu_s(\text{CH})$ bands were 2925 and 2850 cm^{-1} , respectively. Upon increasing the surface coverage of DODA⁺, the $\nu_{as}(\text{CH})$ band shifted to lower frequency (2918.3 cm^{-1} at $2 \times \text{CEC}$) and the position of the $\nu_s(\text{CH})$ increased in frequency slightly to 2850.6 cm^{-1} , in agreement with earlier work.⁶⁰ The position of the CH_2 rocking band at 720 cm^{-1} also shifts to lower energy and narrows with increasing surface coverage of DODA⁺ (Figure 4B). The changes in the $\nu(\text{CH})$ and CH_2 rocking band regions indicate that the alkyl chains become more ordered with increasing surface coverage. Before the clay is fully expanded (i.e., at maximum interlayer distance), the intercalated DODA⁺ molecules are kinked and disordered, extending away from the siloxane surfaces, but perhaps also interacting with the siloxane surfaces, especially at low loading. As DODA⁺ saturates and exceeds the CEC, the clay is fully expanded, and the alkyl chains adopt a more linear “unkinked” structure.

Sorption of Hydrophobic Organic Solutes on DODA⁺ Organoclay

Prior sorption studies with DODA-smectites in aqueous suspension included pentachlorophenol,⁴⁰ 2-chlorophenol,⁴⁵ and *p*-nitrophenol.⁴⁹ All of these solutes have aqueous solubilities $>20 \text{ mg/L}$. A goal of this study was to characterize sorption of the hydrophobic probe molecule, dibenzo-*p*-dioxin (DD) by DODA–SWy-2 and to compare to sorption of DD by other well-known sorbents. The aqueous solubility of DD is $<1 \text{ mg/L}$. The sorption data were fit using the Freundlich model expressed as

$$C_s = K_f C_e^{1/n} \quad (1)$$

where C_s is the mg of DD sorbed per kg of geosorbent (mg kg^{-1}), C_e is the equilibrium DD concentration in the aqueous phase (mg dm^{-3}), and K_f ($\text{dm}^3 \text{ kg}^{-1}$) and n are the Freundlich sorption coefficient and the sorption nonlinearity constant, respectively. The Freundlich adsorption parameters along with standard errors are given in Table 1. Pair wise comparisons of the sorption isotherm data at 95% confidence interval indicated that sorption of DD on the selected geosorbents was significantly different from each other (P -value <0.0001).

The sorption affinities of DD decreased in the following order: GAC > DODA-SWy-2 > muck > K-saponite, with $\log K_f$ values of 5.44, 4.36, 3.11, and 2.39, respectively (Figure 5). The sorption of DD by DODA-SWy-2 is intermediate between GAC and the muck soil with a $\log K_f$ value of 4.37. Because the isotherm obtained when using DODA-SWy-2 is linear with a $1/n$ value of 0.99, the $\log K$ value is constant over the concentration range used. Sorption data were also fit to eq 1 with $1/n$ set at a value of 1 (K_L – linear fit) to facilitate comparison of sorption on a unit mass of organic matter. The $\log K_{om}$ ($K_{om} = K_L/f_{om}$) value for DD on DODA-SWy-2 was 4.68, and for the muck soil $\log K_{om}$ was 3.32 (Table 1). We compared the sorption efficiency of the organic matter of the muck soil and of DODA-SWy-2 to that of octanol (utilizing the octanol–water partition coefficient, K_{ow} of DD: $\log K_{OM} - \log K_{OW}$) in Table 1. A partition-like process is thought to occur between the DD molecule and the organic phases of DODA-SWy-2 and the amorphous organic matter of the muck soil.^{3,39} As shown in Table 1, the K_{OM} of DD by DODA-SWy-2 was 22 times greater the K_{om} value of DD for the muck soil demonstrating that the DODA-derived organic phase found on SWy-2 was ~20 times more effective than natural soil organic matter as a sorbent (or partition phase) for DD. Compared to 1-octanol, DD shows a greater affinity for the DODA phase formed on SWy-2 than for octanol. In contrast DD shows a higher affinity for octanol than for the natural organic matter of the muck soil (Table 1). The much greater effectiveness of the organic phase of DODA-SWy-2 (> 20×) compared to natural soil organic matter (muck soil) as a partition/sorption phase for DD is a reflection of the composition/polarity of the respective “partition phases”. The agglomeration of the C-18 alkyl chains of DODA, in DODA-SWy-2 forms a highly nonpolar lipophilic phase in the clay interlayer.³ In comparison natural soil organic matter is moderately lipophilic, having an oxygen content between 30 and 40% and a preponderance of polar functional groups such as –OH and –COOH. The less polar, more lipophilic phase in DODA-SWy-2 renders it a much more effective DD sorbent than the muck soil, compared on a unit mass C basis. These trends are consistent with prior work utilizing smaller, more water-soluble organic solutes, and organoclays formed using smaller cations such as HDTMA.^{3,39} That the K_{om} value for DD is significantly greater for the DODA-derived organic phase in DODA-SWy-2 compared to octanol (i.e., $K_{om} > K_{ow}$) indicates that the low polarity of the DODA⁺ phase combined with its low density (ca. 0.5) renders it a more effective partition phase than octanol.

The DD sorption coefficient for smectite exchanged with K⁺ was about 200 times smaller than for DODA-SWy-2. In related studies, we have shown that sorption of certain nonionic organic contaminants, including DD, is greater when the exchangeable cations are weakly hydrated alkali metal cations on smectites dominated by tetrahedral substitution.⁶¹ This is especially evident for Cs⁺-exchanged saponite.^{54,55} The use of K-saponite was included in this study to evaluate the role of mineral-only surfaces. Although significant, the overall sorption affinity of DD for K-saponite is several orders of magnitude less than that for DODA-SWy-2 or GAC.

Of the geosorbents evaluated here, DD showed the highest affinity for GAC. In contrast to DODA-type organoclays, GAC functions as a high surface area adsorbent, and loosely resembles the “end member” of a group of carbonaceous geosorbents found in soils and

sediments. These materials, usually present in low amounts in soil, are condensed, rigid, aromatic structures, with high carbon contents (approaching 100% OC) and are in the same general structural family as black carbon, kerogen, coal, char, and carbon nanotubes.^{62–64} The GAC is a high surface area (1050 m²/g), porous material that has an intrinsically high affinity for nonpolar aromatic compounds but this does not result from a partitioning process. Rather, the high affinity is due to strong van der Waals forces combined with pore-filling processes that occur in macro-mesopores and in micropores.^{63,64} Importantly GAC is more sensitive to interference from competing colloids and macromolecules (e.g., humic acids, oils that block pores and occupy surface area (sometimes called fouling). Competitive effects among similar solutes (e.g., DD and PAHs) is also expected to reduce uptake by GAC

The enhanced uptake of DD by DODA–SWy-2 over the muck soil and 1-octanol is attributed to the presence of multiple long alkyl chains which induce greater expansion and hence greater access for the target organic contaminant. The sorptive phase found is also highly lipophilic and nonpolar, and the presence of multiple large (e.g., C-18) alkyl chains increases the total organic carbon content of the organoclay. These two factors combined with greater layer expansion maximize the sequestration of poorly water-soluble organic solutes such as DD. The low-density organophilic phase in the organoclay interlayer likely contributed to the enhanced affinity of the organoclay for the hydrophobic contaminant due to loose packing of the alkyl chains.

ENVIRONMENTAL APPLICATIONS

The results presented here suggest that smectites exchanged with quaternary ammonium compounds containing two large alkyl chains, such as DODA⁺, are a good choice for use in solidification/stabilization of soils, sediments, and sludge containing NOCs. The multiple large alkyl chains manifest optimal properties that optimize the effectiveness of the resultant organoclay by providing a maximal organic C content that is highly lipophilic, and hence highly effective as a partition phase. Because sequestration of such contaminants by these organoclays is not related to, or dependent on, high surface areas, they should be less subject to fouling, as compared to GAC for instance. Also because partitioning involves dissolution of NOCs into the DODA⁺ derived partition phase, sorption of target contaminants should not be suppressed by the presence of other organic solutes including cocontaminants. In contrast, NOC sorption by GAC is dependent on available surface area hence surface fouling and competitive effects in multisolute systems could diminish sequestration of the target contaminants.⁶⁵ Commercially produced organoclays, similar to DODA–SWy-2, are currently being recommended as an integral part of remediation plans in at least two Superfund sites contaminated by PCDDs/PCDFs and/or PCBs. This emphasizes the need for quantitative mechanistic knowledge of their interactions with organic contaminants. In addition, surface modification of clay minerals using cationic surfactants is attractive because they are relatively inexpensive. The use of organoclays such as DODA-smectite in combination with GAC may be advantageous due to their distinct operative sorptive mechanisms, affinities for specific contaminants, and susceptibility to interferences. For example, removal of large petroleum related hydrocarbons and dissolved organic matter by organoclays should plausibly increase the efficacy and longevity of GAC which has also

been proposed as an in situ amendment to sequester organic contaminants such as PCDD/Fs.⁶⁶ Detailed knowledge of cationic surfactant interactions with clay minerals, such as presented herein, may also advance an alternate strategy of incorporating additional chemical functionality (e.g., metal or oxyanion chelators) within the clay interlayers such that they are capable of multi-contaminant (e.g., inorganic and organic) attenuation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

X-ray diffraction patterns of Na-SWy-2 smectite treated with varying fractions of DODA⁺ relative to the cation exchange capacity of the clay. Samples were run as oriented deposits on glass slides. Labels correspond to *d*-spacing values in nm.

Figure 2.

Change in d -spacing of the Na-SWy-2 and DODA-SWy-2 complexes plotted as a function of the initial DODA^+ that was added relative to the cation exchange capacity. For the higher concentrations of DODA^+ , the d -spacing was derived from the 002 and 003 reflections (A). Also included in (A) is an illustration of the expanded DODA-SWy-2 complex with a d -spacing of 4.2 nm. In the lower figure, the organic carbon content of the Na-SWy-2 and DODA-SWy-2 complexes derived from TGA measurements are plotted as a function of the initial amount of DODA^+ added relative to the cation exchange capacity of the Na-SWy-2 smectite. Values are expressed as % organic carbon (B).⁶⁷

Figure 3.

Thermal analysis of the Na-SWy-2 and DODA-SWy-2 complexes. The first derivatives of the TGA curves (DTG) are plotted in the upper figure (A). Differential scanning calorimeter results for the DODA-SWy-2 complex treated with 150% initial surface loading of DODA⁺ are shown in B. The sample was initially heated to a temperature of 75 °C and the sample was cooled to a temperature of -50 °C at a rate of 5 °C/min. The sample was then heated at a rate of 5 °C/min to a temperature of 200 °C. The downscan (75 to -20 °C) thermogram is represented by a dashed line. The upscan thermogram (-20 to 200 °C) is represented by a solid line. The top upscan thermogram from 20 to 200 °C represented by a dotted line is that of crystalline DODA-Br. Samples were run in Al pans (sealed with a hole) and the reference was an empty Al pan.

Figure 4.

$\nu(\text{CH})$ region of the DODA-SWy-2 clay complexes with varying surface coverages of DODA^+ plotted on the left side of the figure (A). The 2919 cm^{-1} and 2850 cm^{-1} bands correspond to the $\nu_{\text{as}}(\text{CH})$ and $\nu_{\text{s}}(\text{CH})$ bands of the alkyl chains, respectively. The CH_2 rocking at $\sim 720 \text{ cm}^{-1}$ is plotted on the right side of the figure (B).

Figure 5.

Aqueous sorption of dibenzo-*p*-dioxin on DODA-SWy-2 (150% of CEC), granular activated carbon (GAC), a Houghton muck soil, and a K-exchanged saponite. The amount of dibenzo-*p*-dioxin (DD) sorbed is expressed as mg of DD/kg of sorbent. The *x*-axis corresponds to the equilibrium solution concentration of DD after equilibration in mg/dm³.

Table 1Freundlich (K_f) and Linear (K_L) Sorption Coefficients

geosorbents	f_{OM}	$\text{Log } K_f \pm \text{SE}$	$1/n \pm \text{SE}$	$\text{Log } K_L$	$K_{OM} = K_L/f_{OM}$	$\text{Log } K_{OM}$	$\text{Log } K_{om} - \text{Log } K_{ow}$
GAC	1.00	5.44 ± 0.15	0.93 ± 0.08	5.55	359019	5.56	
DODA-Swy-2	0.50	4.36 ± 0.11	0.99 ± 0.08	4.37	47440	4.68	0.37
muck	0.74	3.11 ± 0.03	0.35 ± 0.03	3.19	2106	3.32	-0.98
K- Saponite		2.39 ± 0.05	0.81 ± 0.08	2.46			