

Enhanced Sorption of Trichloroethene by Smectite Clay Exchanged with Cs⁺

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Trichloroethene (TCE) is one of the most common pollutants in groundwater, and Cs⁺ can be a cocontaminant at nuclear facilities. Smectite clays have large surface areas, are common in soils, have high affinities for some organic contaminants, and hence can potentially influence the transport of organic pollutants entering soils and sediments. The exchangeable cations present near smectite clay surfaces can radically influence the sorption of organic pollutants by soil clays. This research was undertaken to determine the effect of Cs⁺, and other common interlayer cations, such as K⁺ and Ca²⁺, on the sorption of TCE by a reference smectite clay saponite. Cs-saturated clay sorbed the most TCE, up to 3500 mg/kg, while Ca-saturated smectite sorbed the least. We hypothesize that the stronger sorption of TCE by the Cs-smectite can be attributed to the lower hydration energy and hence smaller hydrated radius of Cs⁺, which expands the lateral clay surface domains available for sorption. Also, Cs-smectite interlayers are only one or two water layers thick, which may drive capillary condensation of TCE. Our results implicate enhanced retention of TCE in aquifer materials containing smectites accompanied by Cs⁺ cocontamination.

Introduction

Chlorinated solvents such as trichloroethene (TCE, C₂HCl₃) are environmental contaminants near thousands of governmental and private industry facilities: TCE contamination was identified at 852 of the 1416 sites proposed for the U.S. Environmental Protection Agency's (EPA) National Priority list (1). TCE is also one of the pollutants detected most frequently in water of industrial regions (2), and U.S. drinking water sources tested in 1997 showed a wide range of TCE contamination (3). The EPA drinking water standard for TCE is 0.005 mg L⁻¹ (4), while the water solubility of TCE is 1100 mg L⁻¹ at 25 °C (5), so even small amounts of TCE can pollute a large water volume. TCE is persistent in subsurface environments (6), so there is a need to accurately predict the long-term fate and movement of TCE.

Sorption by soils and sediments is a major process that controls the transport, bioavailability, degradation, and fate of organic contaminants in the environment (7–10). Clay minerals and soil organic carbon (OC) are typically the two most important components in controlling sorption of

organic chemicals that enter soils and sediments. Most research in the last two decades has focused on OC as the primary sorptive phase for the uptake of nonpolar or slightly polar organic contaminants (11–17). However, clay minerals and especially the smectites (18) are abundant in soils and aquifer materials, have large surface areas, and thus are potential sorbents of organic compounds. Several previous studies (20–22) attempted to identify the critical mass ratio of clay minerals to OC at which sorption by the mineral phase plays a dominant role: some estimates for this ratio are 30 for simazine (21), 62 for atrazine (20), and 84 for alachlor (20).

Adsorption of TCE has been studied by a number of researchers, but most such studies are limited to organo-clays (22, 23), zeolites (6, 24–26), and carbon materials (24, 27). Only a few studies on the interactions of clays with volatile, hydrophobic, low molecular weight halocarbons such as TCE have been conducted to date (19, 28–30). Ong and Lion (15) and Pignatello (31) observed that the mineral fraction of whole soil plays a significant role in the sorption of TCE. Results from the few previous studies on smectites are inconsistent. For example, Farrell and Reinhard (19) reported that montmorillonite sorbed 1300 mg kg⁻¹ TCE from the gas phase at 100% relative humidity, while Estes et al. (28) observed little or no TCE sorption by a smectite-rich soil but measured 5400 mg kg⁻¹ tetrachloroethene (PCE) sorption from water to a smectite. Rogers and McFarlane (29) reported that adsorption of TCE was variable, ranging from zero for Ca-montmorillonite to 17% of the TCE added to Al-montmorillonite.

Thus, there are some indications that the sorption of chlorinated solvents by smectites is cation-dependent. One effect of changing the interlayer cations in smectites is to change the layer spacing of the clay. Farrell et al. (32) indicated that TCE adsorption is energetically most favorable in pores that are just large enough to accommodate a TCE molecule. The theory of capillary phase separation says that sorption of a hydrophobic molecule into a slit-pore should become more favorable in materials with small mesopores or micropores (33). We therefore hypothesize that TCE should most effectively compete with water for sorption sites in smectite clay interlayers when the smectite layer spacing is ~12.5 Å, as these clay interlayers are just large enough to accommodate TCE molecules. Cs⁺-saturated smectites generally equilibrate with ~12.5 Å layer spacings at 100% humidity and even in aqueous suspensions (34). Thus, a priori, Cs-smectites appear to possess optimal properties for TCE sorption. By the same reasoning, TCE should not be able to compete as effectively for sorption sites on Ca-smectites because the strongly hydrated Ca²⁺ ions ($\Delta G_{\text{hyd}} \text{Ca}^{2+} = -1593 \text{ kJ/mol}$, while $\Delta G_{\text{hyd}} \text{Cs}^{+} = -284 \text{ kJ/mol}$, ref 35) cause greater swelling of the clay interlayers to *d* spacings of at least 18 Å, so Ca-smectites are expected to sorb less TCE than Cs-smectites.

This hypothesis is of environmental interest, since TCE and Cs⁺ cocontamination has been reported in groundwater plumes at a number of U.S. Department of Energy (DOE) sites (36–39). As one example, mixed liquid waste containing both Cs⁺ and TCE was injected through a single well into the Snake River Plain aquifer at Idaho National Engineering and Environmental Laboratory from 1953 to 1972 (40).

On the basis of these hypotheses and observations, this study was initiated to study the adsorption of TCE by saponite, a 2:1 trioctahedral clay, saturated with different exchangeable cations (K⁺, Cs⁺, and Ca²⁺). K⁺ and Ca²⁺ were selected, as they are common exchangeable cations in the soil environ-

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ment. Cs^+ was selected primarily because TCE and Cs^+ cocontamination has been reported and because Cs-smectites should present a more favorable interlayer environment for TCE sorption as hypothesized above.

Materials and Methods

Clays. The saponite SapCa-2, a reference smectite with CEC of 95 cmol kg^{-1} (41) used in the adsorption study, was purchased from the Clay Minerals Society Source Clay Repository (Department of Agronomy, Purdue University, West Lafayette, IN). The $<2 \mu\text{m}$ clay-sized particles were separated by wet sedimentation and then exchanged with K^+ , Cs^+ , and Ca^{2+} to prepare homoionic clays. To do so, 25 g of clay was dispersed in a 0.1 M chloride solution (500 mL) of the respective cation. The clay suspensions were shaken for 24 h, and fresh chloride salt solutions were used to replace the original solutions after centrifugation. This process was repeated four times to ensure complete cation saturation. The excess chlorides were removed by repeatedly washing with Milli-Q water until Cl^- was determined negative by reacting with AgNO_3 solution. The clay suspensions were then quick-frozen, freeze-dried, and stored in a closed container for later use.

Solute. Analytical grade TCE used in the adsorption experiment was purchased from Aldrich Chemical Co. (Milwaukee, WI) with a purity of $>99\%$ and used as received. The selected physicochemical properties of TCE are as follows: molecular weight, 131.4 g mol^{-1} ; vapor pressure at 30°C , 12.5 kPa; boiling point, 87°C ; density, 1.45 g cm^{-3} ; log K_{ow} at 25°C , 2.53; dipole moment, 0.9 D; molar volume, $89.87 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C ; average molecular diameter, 6.8 Å (19).

Determination of Henry's Law Constant. The equilibrium headspace technique was used to determine the Henry's law constant of TCE in different electrolytes, which is similar to the method reported in refs 42 and 43. Determinations of the Henry's law constant as well as sorption isotherms were conducted using 20 mL capacity glass headspace GC vials. The bottle volume was determined by weight by filling to capacity with water at room temperature ($23 \pm 2^\circ\text{C}$). Three different TCE concentrations were prepared in 0.1 M KCl or CsCl, or 0.05 M CaCl_2 . The same volume (25 μL) of stock TCE solution (prepared immediately prior to their use) (500 mg L^{-1}) was injected into the vials containing different volumes of each electrolyte solution to create different concentrations. Vials were capped immediately with Teflon-lined silicone septa and aluminum crimp caps to minimize volatile loss of TCE. The vials were then shaken reciprocally overnight at 40 rpm at room temperature ($23 \pm 2^\circ\text{C}$); preliminary studies showed that equilibrium was achieved within this time period. The TCE concentration in the headspace of each vial was determined using a Varian 3700 gas chromatograph with flame ionization detector (GC-FID) connected with an HP 19395A headspace autosampler. The dimensionless Henry's law constant (H_c) was calculated (43) as

$$H_c = \frac{C_{g2}V_{l2} - C_{g1}V_{l1}}{C_{g1}V_{g1} - C_{g2}V_{g2}} \quad (1)$$

where C_{g1} and C_{g2} are the TCE concentrations in the gas phase of vials 1 and 2, V_{g1} and V_{g2} are the gas volumes in vials 1 and 2, and V_{l1} and V_{l2} are the solution volumes in vials 1 and 2. The experiment was performed in triplicate, and at least duplicate results are presented. We used these values of the Henry's law constant to calculate the distribution of TCE in the sorption experiments, as Henry's law was dependent on the cation in solution.

Sorption Isotherm Measurement. TCE sorption isotherms were determined using a batch equilibrium headspace

technique (42). Freeze-dried clay (0.1–0.6 g) was suspended in 5.0 mL of electrolyte solution (0.1 M for CsCl and KCl and 0.05 M for CaCl_2). A series of initial TCE concentrations (0.5, 1.0, 2.0, 5.0, 10, 20, 40, 70, and 100 mg L^{-1}) were prepared by injecting different volumes of stock TCE solution (500 mg L^{-1}) (prepared immediately prior to their use in respective electrolyte solution) into vials using a syringe. The vials were capped immediately with Teflon-lined silicone septa and aluminum crimp caps to minimize volatile losses of TCE. The vials were then shaken reciprocally overnight at 40 rpm at room temperature ($23 \pm 2^\circ\text{C}$); preliminary studies showed that equilibrium was achieved within this time. The TCE concentration in the headspace of the vials was determined using a Varian 3700 GC-FID as above. All isotherm experiments were performed in triplicate, and at least duplicate results are presented.

After reaching partitioning equilibria, TCE distributions in air, solution, and clay were determined by comparing two systems, viz., systems containing clay and systems without clay. The same solution volume (V_l), gas volume (V_g), and total mass of TCE (M_T) was applied to both systems. Under such circumstances, sorption equilibria were evaluated using the following relationships.

(a) System without clay (at equilibrium):

$$M_T = C_{l1}V_l + C_{g1}V_g \quad (2)$$

(b) System with clay (at equilibrium):

$$M_T = C_{l2}V_l + C_{g2}V_g + C_{\text{clay}}M_{\text{clay}} \quad (3)$$

where C_{l1} and C_{l2} are the equilibrium TCE concentrations in the solution phase of systems without and with clay, respectively, C_{g1} and C_{g2} are the equilibrium TCE concentrations in the gas phase of systems without and with clay, respectively, C_{clay} is the TCE concentration in the clay phase, and M_{clay} is the mass of clay (g) added to the system. Since the same amounts of TCE were added into both systems, eqs 2 and 3 are equal, thus:

$$C_{l1}V_l + C_{g1}V_g = C_{l2}V_l + C_{g2}V_g + C_{\text{clay}}M_{\text{clay}} \quad (4)$$

From Henry's law, we know that

$$C_l = \frac{C_g}{H_c} \quad (5)$$

and we determined H_c for each electrolyte using eq 1 as described above. Substituting C_l from eq 5 into eq 4, we get

$$\frac{C_{g1}}{H_c}V_l + C_{g1}V_g = \frac{C_{g2}}{H_c}V_l + C_{g2}V_g + C_{\text{clay}}M_{\text{clay}} \quad (6)$$

From eq 6 the amount of TCE sorbed on the clay (C_{clay}) can be determined as

$$C_{\text{clay}} = \frac{(C_{g1} - C_{g2})[(V_l/H_c) + V_g]}{M_{\text{clay}}} \quad (7)$$

C_{g1} and C_{g2} are determined using a Varian 3700 GC-FID. The TCE concentrations in aqueous solution and clay phases were calculated using eqs 5 and 7, respectively.

X-ray Diffraction. Clays were mixed with water to form suspensions, which were used to prepare clay films for X-ray diffraction analysis. The suspensions were dropped onto glass slides and air-dried overnight at ambient conditions to obtain oriented clay films. The clay films were then allowed to equilibrate with water vapor for 2 days in a closed container containing distilled water to expose the clay films at 100% relative humidity. X-ray diffraction patterns were recorded

using Cu K α radiation and a Philips APD 3720 automated X-ray diffractometer, fitted with an APD 3521 goniometer and a θ -compensating slit, a 0.2 mm receiving slit, and a diffracted beam graphite monochromator. Diffraction patterns were recorded from 5.5° to 16.0° 2 θ at a step of 0.005° 2 θ with 4 s/step.

Results and Discussion

The Henry's law constant of TCE was found to be different in the three different electrolyte solutions used for the sorption study. The values (and standard deviations) of the dimensionless Henry's law constant for TCE were determined to be 0.61 (\pm 0.09) for 0.1 M KCl, 0.74 (\pm 0.15) for 0.05 M CaCl₂, and 0.92 (\pm 0.16) for 0.1 M CsCl, which are all significantly larger than the 0.47 (\pm 0.04) value that we determined for the pure TCE–water–air system. Our latter measurement for TCE is somewhat larger than typical literature values of 0.40 (5, 42), 0.42 (43), and 0.37 (44). Nielsen et al. (65) reviewed the available Henry's law coefficients for TCE and observed that those obtained by equilibrium headspace techniques were generally larger than other literature values obtained by batch air-stripping methods. They cited potential systematic errors caused by gas-phase adsorption to vessels and/or septa and more random errors due to difficulties in adding volatile solutes and collecting headspace gas samples. A further concern is that air–water equilibrium be truly reached and maintained during sampling (45).

One expects the Henry's law constant to increase as ionic strength increases (45), as the presence of salt makes the aqueous solution less favorable for the dissolution of TCE. For example, Henry's law coefficients for various organic compounds are higher by a factor of 1.2–1.8 in seawater than they are in pure water (45). Gabarini and Lion (42) estimated activities of TCE in NaCl solutions of various ionic strengths: extrapolation of their data would imply that the ratios of H_c in our ionic solutions to H_c in pure water should be 1.06, 1.06, and 1.09 for TCE in 0.1 M KCl, 0.1 M CsCl, and 0.05 M CaCl₂, respectively. For comparison, our reported Henry's law constants for TCE in the salt solutions were factors of 1.3–2.0 times our value in pure water, so our methods have again apparently overpredicted the expected values of H_c . We have no explanation why our measurements are so much higher than literature values. Nonetheless, since the Henry's law constant plays a significant role in the calculation of sorption (eqs 5 and 7) and since our Henry's law coefficients were gathered using the same equipment as our sorption experiments, we used our salt-dependent coefficients to calculate the aqueous and sorbed TCE concentrations from the gas-phase concentrations in our experiments.

TCE sorption isotherms are shown in Figure 1. Ca-saturated saponite sorbed the least TCE, K-saturated saponite sorbed roughly twice that amount (Figure 1a), and the greatest sorption of TCE was observed for Cs-saturated saponite (Figure 1b). Also, in Figure 1b we illustrate the dependence of our isotherms on the Henry's law coefficient used to convert gas-phase TCE concentrations to aqueous and sorbed phase concentrations according to eqs 5 and 7. The TCE–Cs isotherm (Figure 1b) illustrates the extreme case since our largest H_c (and our largest deviation from literature H_c estimates) was for the Cs system. Deviations between isotherms based on our H_c measurements versus literature estimates were similar for the TCE–K and TCE–Ca systems (graphs not shown) but smaller in magnitude than the deviations for the TCE–Cs system (Figure 1b). The effect of our larger H_c values (relative to previous estimates) was to overpredict sorption of TCE at low aqueous concentrations while underpredicting the sorption maxima, without sig-

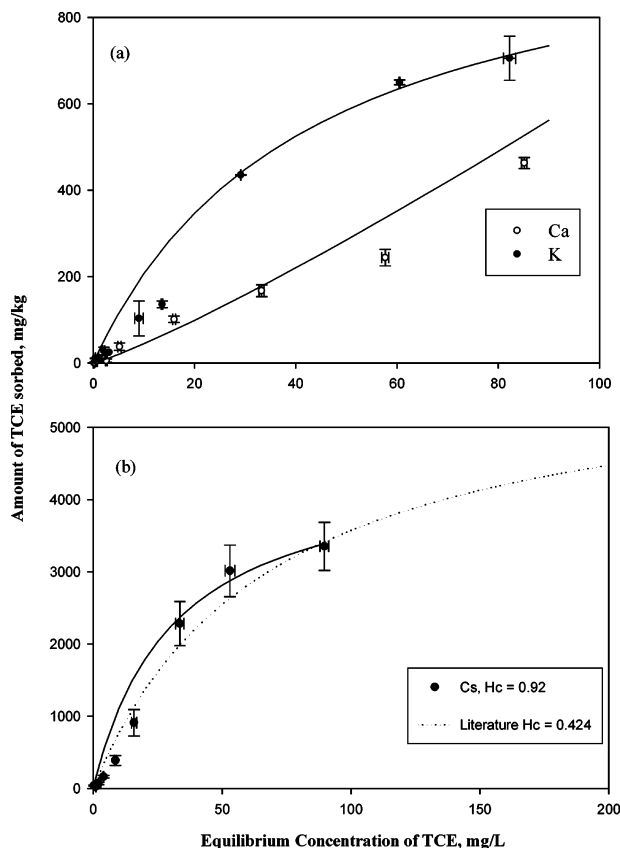


FIGURE 1. Sorption isotherms representing trichloroethene uptake from water by reference saponite (SapCa-2) clay saturated with (a) calcium and potassium and (b) cesium. The data points show average values, the error bars show standard deviations, and the solid lines are isotherm equation fits (Langmuir for Cs- and K-saponite and Freundlich for Ca-saponite). The dotted line in the lower graph shows the Langmuir fit for TCE sorption by Cs-SapCa-2 when a typical estimate from the literature (i.e., 0.42, see text) is used for the Henry's law coefficient rather than the 0.92 value determined in this study. The same gas-phase TCE concentrations were used to derive both isotherms pictured for the Cs-saponite.

nificantly altering any of our general conclusions from this study.

The sorption of 0.34% (w/w) TCE by the Cs-smectite at an equilibrium concentration of 90 mg L⁻¹ is the largest TCE sorption we found reported for any clay mineral. Previously, Farrell and Reinhard (19) reported a maximum of 0.13% (w/w) TCE sorption by a montmorillonite, while low-charged zeolites have been found to sorb 20% (25) and even 50% (26) TCE by weight. Figure 1 shows that there might be significant sorption of TCE to aquifer smectites, especially if Cs⁺ is a cocontaminant in the plume. Furthermore, since our data and the findings of Nielsen et al. (65) seem to indicate that Henry's law coefficients are overestimated by equilibrium headspace techniques, the maximum TCE sorption by each clay may be even larger than we report because smaller Henry's law coefficients correspond to larger sorption maxima (Figure 1b).

Our data (Figure 1) are thus consistent with the hypothesis introduced earlier, that exchangeable cations exert a substantial influence on TCE sorption through their influence on lateral (that is, parallel to the smectite basal surfaces) interlayer sorption domains (Figure 3A and/or B) interlayer swelling (that is, vertical domains perpendicular to the basal surfaces, Figure 3B). Regarding lateral domains, the fewer water molecules associated with exchangeable Cs⁺ (smaller hydrated radius, Figure 3) should obscure a smaller fraction of the clay surface than those associated with Ca²⁺, resulting

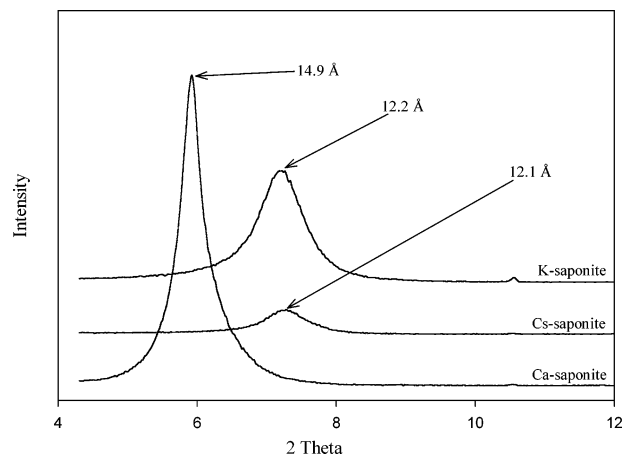


FIGURE 2. X-ray diffraction patterns of reference saponite (SapCa-2) clay in oriented clay films as a function of exchangeable cation at 100% humidity.

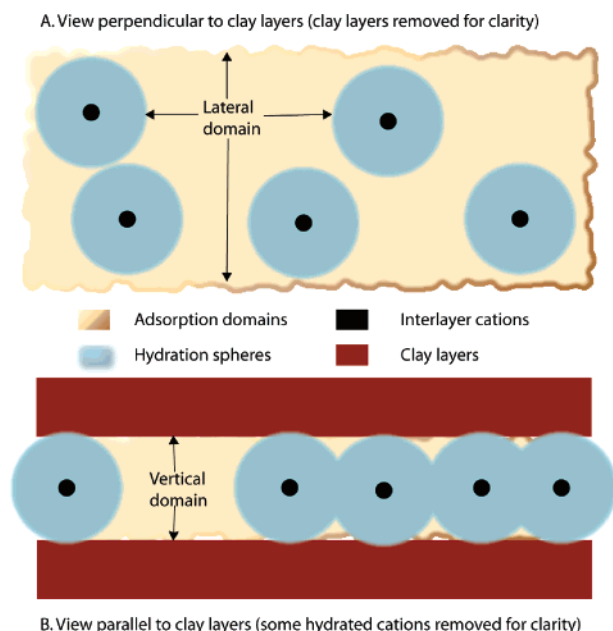


FIGURE 3. Schematic diagram of TCE adsorption domains in smectite clay mineral interlayers. We hypothesize that adsorption domains for TCE are regions in which adsorbed water is held less strongly than in the primary hydration spheres of interlayer cations, and therefore organic solutes have an improved chance of adsorbing by displacing interlayer water.

in larger adsorptive domains for Cs^+ -saturated clays. Zhu et al. (46) reported high sorption of polycyclic aromatic hydrocarbons (PAHs) by Cs-saturated clays and hypothesized that relatively weak hydration of Cs^+ resulted in stronger cation- π interactions and consequent higher sorption of PAHs, while bivalent cations such as Ca^{2+} with high hydration energies resulted in weak cation- π interactions and therefore low sorption.

While “hydrated radii” are poorly defined, typical estimates of hydrated radii are 9.6 Å for Ca^{2+} , 5.3 Å for K^+ , and 3.6 Å for Cs^+ (35). Thus, the cross-sectional area of hydrated Ca^{2+} is about 290 Å², more than 7 times that of Cs^+ (40 Å²), so one hydrated Ca^{2+} takes up 3.5 times as much room in the clay interlayer as do the two Cs^+ ions that Ca^{2+} replaces. Using these hydrated radii along with an idealized smectite basal surface area of 750 m² g⁻¹ and the 95 cmol kg⁻¹ CEC of saponite SapCa-2, we compute that the hydrated radii of Ca^{2+} or K^+ must overlap in the interlayer regions of homoionic SapCa-2, meaning that the lateral adsorption domains (Figure

3A) are very small and TCE would have to compete with strongly bound water for interlayer sorption sites. On the other hand, Cs^+ and its hydration shells are projected to occupy only about 67% of the interlayer space. That is, about one-third of the surface area in the Cs-saponite may consist of lateral sorption domains (Figure 3A), implying that TCE has to compete only with weakly bound water in the Cs-smectite interlayers. This may explain why the Cs-smectite is a much more effective sorbent for TCE. This idea of lateral domains is supported by several observations (47–50) of an inverse relationship between the CEC of clays and the amount of the organic solute adsorbed, since fewer interlayer cations per unit surface area mean larger lateral adsorption domains available for organic solutes (Figure 3A).

Differences in the swelling behavior (vertical domains of Figure 3B) between Cs- and Ca-SapCa-2 may also contribute to their differential adsorption of organic compounds. Many Cs-smectites equilibrate with ~12.5 Å layer spacings (hydrate monolayer structures) at 100% humidity and even in aqueous suspension (34). All Ca-smectites, on the other hand, swell to more than 15 Å in suspension. Our results show that Cs-saturated saponite swells to 12.1 Å at 100% humidity (K-saturated saponite swells to 12.2 Å), while Ca-saturated saponite swells to 14.9 Å at 100% humidity (Figure 2). The thicknesses of 2:1 clay layers containing no cations (i.e., pyrophyllite and talc) are 9.1 to 9.5 Å, so the vertical adsorption domains (Figure 3B) in our Cs-, K-, and Ca-saponites are about 3, 3, and 6 Å, respectively. Of course, the *d* spacings of these clay films may be smaller than those of the smectites in aqueous suspension when the adsorption experiments were carried out, although the clay films were exposed to 100% RH.

Like many planar aromatic molecules, a TCE molecule is only about 3–3.5 Å thick, so it fits almost exactly into the vertical adsorption domains (Figure 3B) between two smectite layers at *d* spacings of 12–12.5 Å (52). Thus Cs-smectite, which can reasonably be expected to have a 12.5 Å *d* spacing even in aqueous suspension (52–57), may have the optimal slit-pore to maximize the energy of TCE condensation from solution (33), because if the interlayer region was any narrower than 12 Å, then TCE could no longer intercalate because it simply could not fit. In contrast, Ca-smectites exhibit vertical adsorption domains (Figure 3B) larger than 6 Å, and since these domains are much larger than the TCE thickness there is much less energetic incentive to drive adsorption (33).

We propose that in a system with a monolayer of water (K^+ - and Cs^+ -saturated clays near 12 Å *d* spacings as in Figure 2), TCE intercalates into clay interlayers and, coplanar with the clay basal surfaces, interacts with two opposing clay layers by full molecular contact via van der Waals and electrostatic forces. This hypothesis is consistent with simulation results (51) concluding that, for idealized siloxane surfaces, the most stable mode of TCE sorption occurs by full molecular contact, coplanar with the clay surface.

Given a 3 Å thick interlayer region, 33% of the basal surface not covered by Cs^+ hydration shells as described above, and the TCE molar volume cited above, we predict that the Cs-saponite might be able to sorb up to 10% TCE by weight if all interlayer volume (product of lateral and vertical adsorption domains, Figure 3) outside primary Cs^+ hydration shells were filled with TCE. Since we observed only 0.34% sorption (Figure 1), our assumptions may be simplistic in that (a) the kinetics of tortuous TCE diffusion to many interlayer sites may be slow, (b) TCE is not able to displace other interlayer water outside primary Cs^+ hydration shells, or (c) some Cs-saponite interlayers may be collapsed and unavailable for TCE sorption. In this regard, a tetrahedrally substituted clay may have been an inopportune choice in that tetrahedral charge is more localized on fewer surface oxygens (58) and

exchangeable cation ordering is only found in tetrahedrally substituted smectites (59). The exchangeable cations (at a given hydration state) can always approach tetrahedral sites more closely than octahedral sites (60) and thereby strengthen the hydrogen bonding of interlayer water to the siloxane surface itself (61). Thus, further work should be done to compare sorption of TCE by smectites with layer charge originating from octahedral versus tetrahedral substitution. Compared to smectites with negative charges from octahedral isomorphous substitution, the 2:1 smectites with negative charges from tetrahedral substitution exhibit less swelling of the interlayer space in water. The theory of capillary phase separation (33) thus implies that sorption of hydrophobic molecules from water should be more favorable in tetrahedrally versus octahedrally substituted smectites (for a given layer charge and interlayer cation, and assuming the interlayer does not dehydrate and collapse), and such behavior has been observed (47, 50) though not explained.

Sorption isotherms for TCE on Cs-, K-, and Ca-saturated saponites are nonlinear (Figure 1). This nonlinearity could be due to several possible causes: (1) the heterogeneous distribution of sorption sites on the clays, (2) equilibrium was not achieved during the course of the study, or (3) at least some of the postulates of a Langmuir-type sorption are satisfied, particularly the presence of a finite number of sorptive sites that, when fully occupied, constitute a "monolayer" of adsorbate coverage. Li and Werth (62) concluded that since sorbate molecules first occupy those sorption sites that have the highest adsorption potential, sorption isotherms of TCE on two different natural solids were nonlinear. Similarly, Estes et al. (28) and Hamaker and Thompson (63) did not observe equilibrium for sorption of organic on montmorillonite clay over a period of 30 days and concluded that slow changes in the clay surface that resulted in the continuous exposure of new adsorption sites were the primary reason for the failure to achieve equilibrium.

If our hypotheses about TCE sorption to the Cs-saponite are correct, then the smectite interlayer should behave very nearly like an ideal Langmuir system because the 12 Å *d* spacing allows only monolayer coverage in the interlayer and the lateral adsorption domains between hydrated cations are only a fraction of a finite smectite basal surface area. The best-fitting Langmuir parameters are a monolayer coverage of about 4500 mg kg⁻¹ and Langmuir *k* of about 0.032. This Langmuir function does not fit the data particularly well (Figure 1b) at low concentrations because of the upward curvature of the isotherm data, but the Freundlich curve is even worse for the same reason. Similarly, a Langmuir isotherm does not fit well for K-smectite at low concentrations but can be fit at high concentrations (Figure 1a). The Ca system on the other hand will never have a 12.5 Å layer spacing in suspension, so sorption of a simple monolayer of TCE is unlikely in the Ca-smectite interlayer. For the Ca system there was no evidence of an adsorption plateau, so there is no way to fit the Langmuir equation. Therefore, we report Freundlich parameters for our Ca system: *K_f* (mg^{1-N} L^N kg⁻¹), the Freundlich sorption coefficient is 3.11, and *N* (unitless) is 1.16. The *N* value > 1.0 for Ca-smectite is consistent with earlier results (47, 64) for hydrophobic compound sorption to Ca-smectites.

In summary, the sorption of TCE to homoionic saponite clays followed the order Cs-saponite >> K-saponite > Ca-saponite. These data are consistent with a hypothesis of hydrophobic condensation of TCE on neutral siloxane surfaces between charge sites on the clay. Sorption is perhaps strongest on the Cs-saponite because it possesses substantial lateral adsorption domains and an optimal vertical domain. The K-saponite may share the optimal vertical domain but sorbs less TCE because its lateral domains are much smaller and TCE apparently does not compete well with even

moderately bound interlayer water. Finally, it is reasonable that Ca-saponite sorbs the least TCE because it should have small lateral domains and a larger, less optimal vertical domain size.

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