Journal of Soil Contamination, 3(3): (1994)

Slow Vapor-Phase Desorption of Toluene from Several Ion-Exchanged Montmorillonites

Spencer Steinberg

Department of Chemistry, University of Nevada, Las Vegas, NV 89154-1017

Jerry P. Fairley, Jr.

Department of Geoscience, University of Nevada, Las Vegas, NV 89154-4029

David K. Kreamer

Department of Geoscience and Water Resource Management Program,
University of Nevada, Las Vegas, NV 89154-4029

ABSTRACT: The sorption and desorption of volatile compounds from soils and clays exhibit a wide range of kinetics. While much of the sorptive interaction is very rapid, a certain fraction of volatile compounds that enter soil and clays are only slowly desorbed. It is generally believed that the formation of this recalcitrant or slowly desorbing fraction of volatile organic compounds (VOCs) in soils is due to the diffusion of compounds to poorly accessible sorption sites. However, the exact nature of these sites is in doubt. In montmorillonite, there are two likely possibilities for formation of the recalcitrant fraction: sites between the clay lamella and sites within clay particle aggregates. Because montmorillonite may be an important fraction of many soils, we have explored the formation of slowly desorbing toluene on a montmorillonite clay that was ion exchanged with five different ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, and Fe^{3+}) to form mineralogically similar clays with varying interlamellar spacing. The recalcitrant fraction was quantified for varying sorption and desorption times. The type of ion exchanged into the clay appears to have an important influence on the formation of a recalcitrant fraction.

KEY WORDS: toluene, montmorillonite, sorption, desorption.

I. INTRODUCTION AND BACKGROUND

When soils are exposed to volatile organic compounds (VOCs) from leaking fuel tanks or during soil fumigation, a residual concentration remains in the soil long after the majority of contaminant has volatilized or decomposed. This residual fraction has been called “recalcitrant”, “firmly bound”, or a “slowly desorbing” fraction. We refer to this fraction as the “slowly desorbing fraction” (SDF) through the remainder of this manuscript. One of the important implications for VOCs held in the SDF is that they may not be easily analyzed by the standard dynamic headspace concentration procedure. Sawhney et al. (1988) found that standard techniques for estimating VOC concentrations in soils (EPA Method 8240) underestimated the quantities of 1,2-dibromoethane (EDB) in fumigated soils by up to 89%. Similarly, Steinberg (1992) demonstrated that soil contaminated in the laboratory with various solvents contained a persistent residual fraction or SDF that was consistently underestimated by dynamic headspace concentration. Paviostathis and Jagial (1991) investigated the desorptive behavior of trichloroethylene in a contaminated soil and documented the existence of a slowly desorbing fraction. Thus, in the environment, this SDF may continue to desorb from soil to groundwater over a period of years, possibly providing a long-term health hazard.

Previous studies on soils and clays have indicated that the SDF may be associated with molecules trapped in micropores or within organic matter (humic substances) (Steinberg et al., 1987; Ball and Roberts, 1991a, b; Paviostathis and Jagial, 1991; Pignatello, 1990; Grathwohl and Reinhard, 1993). Slow diffusion through the highly tortuous pathway associated with the micropore or soil organic matter would then lead to the observed slow desorption kinetics (Sawhney and Gent, 1990; Pignatello, 1989; Wu and Gschwend, 1986).

In this work, we consider the potential role that montmorillonite could play in the formation of firmly bound organic compounds. The interaction of organic compounds with clays was recently reviewed by Ortego *et al.* (1991). Montmorillonite is a mineral composed of continuous two-dimensional aluminosilicate sheets. These sheets have a permanent negative charge that is balanced by cations in the interlamellar region (Brown, 1984; Velde, 1992). These interlayer cations can affect organic compounds in a variety of ways. Isaacson and Sawhney (1983) showed that the presence of transition metal cations catalyzed the decomposition and polymerization of phenols. Soma *et al.* (1984, 1985) found evidence for the polymerization of benzene and monosubstituted benzenes in transition metal ion-exchanged montmorillonites. Johnston *et al.* (1992) demonstrated a single electron transfer reaction between Cu^{2+} and xylene in the interlamellar region of montmorillonite. Sawhney and Gent (1990) performed vapor-phase sorption experiments that indicated that slowly desorbing VOCs were principally held in clay aggregates. Thus, with montmorillonite, there are two probable sites for the storage of persistent contamination: between the clay lamella (interlamellar) and within clay particle aggregates.

Several studies support the notion that VOCs and other organic compounds may become associated with physically inaccessible sites within soil and clay structures. Steinberg *et al.* (1987) studied soils from Connecticut tobacco fields that had been treated with EDB. Soils last fumigated with EDB up to 19 years previously were found to retain concentrations of EDB at levels of up to 200 ng/g. Steinberg *et al.* (1987) also found that EDB in the SDF could be released by grinding the soil. Similarly, Ball and Roberts (1991a) demonstrated that the long times required for equilibration of an aquifer material with VOCs could be drastically reduced by grinding. In both studies, the grinding of the soils either reduced the diffusive path length or exposed additional surfaces from within the soil particles. In similar studies, Rogers *et al.* (1980) reported that benzene sorbed to soil and montmorillonite from aqueous solution tended to resist desorption, and Estes *et al.* (1988) reported that perchloroethylene (PCE) was irreversibly sorbed to montmorillonite from solution.

Previous research with montmorillonite indicates that interlamellar regions are generally considered inaccessible to volatile sorbates (Smith and Jaffé, 1991). It has been demonstrated that when the exchangeable cations on montmorillonite are replaced with alkylammonium ions, the extent of sorption of volatile organic compounds by the clay is greatly increased (Smith *et al.*, 1990; Smith and Jaffé, 1991). Similarly, Hermosin *et al.* (1993) have shown that cationic monobutyltin species can be adsorbed into the interlamellar region of expandable clays. After sorption of the charged monobutyltin species, neutral monobutyltin complexes, which become associated with the lipophilic environment, could penetrate into the interlamellar region. Apparently, the large organic cations force open the interlamellar spaces and increase the amount of surface area available for sorption. In addition, the larger organic cations should be less hydrated than inorganic cations. Thus, with organic cations in the interlamellar region, there will be fewer water molecules competing with volatile organic compounds for sorption sites. One possibility is that the interlamellar region is much less available for sorption of organic compounds when inorganic cations occupy the ion-exchange sites, but that a small amount of sorbate does penetrate to this region, where it may then experience very long diffusion times and behave as a slowly desorbing fraction.

The specific objective of this study was to investigate the formation of SDF toluene in several different ion-exchanged montmorillonites. Our goal was to examine the potential of montmorillonite clay in soils to contribute to slow desorption kinetics for volatile organic compounds. Several different ion-exchanged montmorillonites (K^+, Na^+, Ca^{2+}, Mg^{2+}, and Fe^{3+}) were investigated to determine if the formation of slowly desorbing toluene was related to interlamellar spacing. These soils were either inoculated with an organic compound (toluene) or exposed to saturated toluene vapor. During the course of this study, we also examined the effects of moisture on the formation of slowly desorbing toluene.

II. EXPERIMENTAL

All of the inorganic reagents, including NaCl, KCl, $MgCl_2$, $CaCl_2$, and $FeCl_3$, were analytical reagent grade and purchased from Mallinckrodt Chemical Works. Toluene and acetonitrile were purchased from American Burdick and Jackson. All salt solutions and the chromatographic mobile phase were prepared with 18 MΩ-cm resistivity water (Nanopure).

A. **Preparation of Ion-Exchanged Clays**

Montmorillonite #26 (Clay Spur, WY) was obtained from Ward's Scientific Establishment. The clay was treated exhaustively with a 1.0 *N* solution of one of the following: NaCl, KCl, $CaCl_2$, $MgCl_2$, or $FeCl_3$. The clay was then rinsed with distilled H_2O until excess salt was removed. The ion-exchanged clay was then dried at 75°C for neat toluene incubation experiments or at 105°C for toluene vapor experiments. The dried clay was then pulverized and sieved (#80) before use in experiments. Clays were characterized by X-ray diffraction using standard powder methods. The percent H_2O for the clay samples was determined by drying the clay at 105°C and measuring the weight loss. However, drying at 105°C would not be sufficient to remove the interlamellar water associated with the hydration of the exchangeable cations (Velde, 1992). The results of this analysis are reported in Table 1.

B. **Incubation Experiments**

As mentioned above, two different types of incubation experiments were performed. All incubation experiments were performed at ambient laboratory temperatures of 25 ± 3°C. In the first set of experiments, clays were treated with 10 µl of neat toluene. Before exposing a 1.0-g aliquot of ion-exchanged clay to toluene, a measured amount of water (0, 1, or 10%, w/w) was added. The clay was allowed to equilibrate with the water for 72 h and the ion-exchange clay then inoculated with 10 µl of toluene. The test tubes were shaken to mix the toluene into the clay and then incubated at 30°C for 24 h.

The second set of sorption experiments involved exposing the clay to toluene in the vapor phase. A measured amount of clay (1.0 g) was placed in a screw-cap culture tube (16 × 100 mm). The clay was dried at 105°C and then incubated for 72 h in a desiccator with a controlled relative humidity. After 72 h, an open beaker

TABLE 1
Characteristics of Montmorillonite Clays After Drying at 75°C

Ion	d(001)	Number of H_2O layers	% H_2O
K^+	12.63	1	1.8
Na^+	12.63	1	8.7
Mg^{2+}	14.98	2	7.0
Ca^{2+}	15.50	2	8.7
Fe^{3+}	16.67	2–3	13.2

of toluene was placed inside the desiccator, and incubation was continued for an additional 24 to 260 h. Humidity control in these experiments was achieved using an open beaker filled with either $CaSO_4$ (0% relative humidity) or an open beaker filled with saturated sodium chloride (70% relative humidity).

After incubation in both types of incubation experiments, the toluene-exposed clay was allowed to desorb for 0 to 160 h at ambient room temperature (25 ± 3°C) in a laboratory fume hood. The SDF was then measured. For the 0-h desorption measurements for the vapor-phase treatments, the clay was incubated in an Erlenmeyer flask (25 ml) with a screw-top cap equipped with a Teflon® slider valve (Alltech Mininert® Valve). The silicone septum from the valve was removed so that when the valve was opened, the contents of the vial could equilibrate with the toluene vapor present. The Mininert® valve could be easily and immediately closed after opening the desiccator, so that the amount of toluene sorbed onto the clay before any desorption could be directly measured. Methanol was injected into the sample through the Mininert® valve. The toluene extracted into the methanol was then quantified as described below. The toluene measurements were corrected for vapor-phase toluene using an empty vessel.

C. **Mechanical Disruption Experiments**

Simultaneous mechanical disruption and ion exchange of clay aggregates was performed as follows. Experiments were performed by inundating toluene-inoculated montmorillonites with ion-exchange solutions in an effort to cause shock desorption of recalcitrant toluene. Screw-cap test tubes containing toluene-treated clay samples were completely filled with either water or a 1.0 *N* solution containing NaCl, $MgCl_2$, or $CaCl_2$. The sample was vigorously agitated using a laboratory vortex mixer (Vortex Genie, Fisher Scientific) for 3 min and then immediately centrifuged. Our experiments indicated that the amount of toluene released reach a plateau after 3 min of mixing; however, we have not tried to quantify the extent of clay particle disruption. The supernatant liquid was analyzed for toluene is as described below.

D. **Analysis**

Toluene remaining on the clay samples was measured using the following procedure. The residual toluene was first extracted using the method outlined in Sawhney et al. (1987). Five milliliters of glass-distilled methanol was added to the clay sample. The sample was capped with a teflon-lined screw cap and then heated for 24 h at 70°C in a constant-temperature aluminum block.

Toluene was measured by using high-performance liquid chromatography (HPLC). The HPLC consisted of a Milton-Roy minipump, a Reodyne 7410 injector with 20-µl sample loop, and a Kratos Spectroflow Model 747 ultraviolet/visible detector. The methanol or aqueous (mechanical disruption) extracts (20 µl) were injected directly into the HPLC with no additional sample processing. Toluene was separated from interfering compounds on a 5µ C_{18} analytical column (25 × 0.46 cm). The analysis was performed isocratically, with the column eluted with 80% methanol/water at a flow rate of 1 ml/min. The column effluent was monitored at 254 nm. Peak areas were measured with an HP 3390 integrator. The instrument was calibrated with external standards.

III. **RESULTS**

In most of the experiments when neat toluene was added, clays were incubated for 24 h prior to desorption. When clays were exposed to toluene vapors, exposure was generally for 120 h. The results of experiments where clays were treated with neat toluene are summarized in Figure 1A. We found that increased incubation times did not increase the concentration of the SDF for montmorillonite. The results with dried montmorillonite indicate that SDF toluene formation is sensitive to the nature of the exchangeable cation, and, with the exception of K-montmorillonite, concentration levels generally showed a slight decrease with increasing desorption times. Clearly, for the dry samples at 24 h desorption, Mg-montmorillonite has the highest affinity for toluene, followed by K-montmorillonite (Mg > K > Na > Ca > Fe). The toluene concentration in the K-montmorillonite decreased with increasing desorption time, and the loss rate can be fit to first-order kinetics.

The sensitivity of the formation of the SDF to water is demonstrated in Figure 1B. In this figure, all of the clay samples were preequilibrated with 10% added water vapor before addition of the toluene. The amounts of SDF toluene for all of these montmorillonite samples were clearly much lower than in the dried clay samples. This decrease in SDF toluene is consistent with the previous observation of equilibrium sorption of volatile compounds on clays and soils (Rhue *et al.*, 1988; Rao *et al.*, 1989; Ong and Lion, 1991). The particularly large decrease in SDF toluene for Mg-montmorillonite is especially noteworthy. In this series of experiments, Fe(III) montmorillonite initially had the highest concentrations of SDF toluene, although this toluene was lost more rapidly than SDF toluene in the other clay preparations. At 24 h, the concentrations of SDF toluene in the various ion-exchanged montmorillonites follow the order Fe(III) > Ca^{2+} > Mg^{2+} > Na^{1+}. SDF in K-montmorillonite was not measured during these experiments.

The information in Figures 1A and B for 0 and 10% additions of water (w/w) indicate that water has a major influence on the formation of the SDF. Figure 2 summarizes the observed concentrations of SDF toluene after 24 h for all of the ion-exchanged clays that were treated with neat toluene. In this figure, the SDF concentrations are plotted on logarithmic concentration axes, against bulk moisture (determined by drying at 105°C). There is a good correlation of log (SDF) with

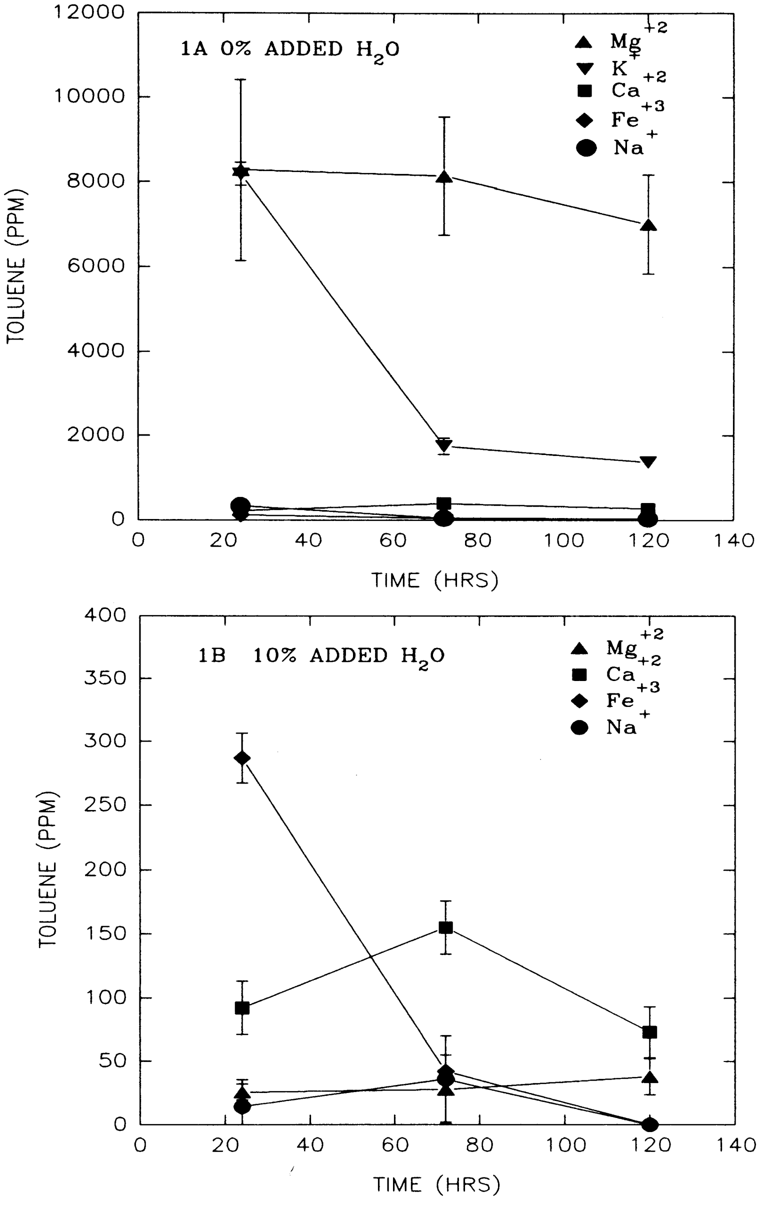

FIGURE 1. (A) Clay samples were dried at 75°C and then incubated with 10 μl of toluene for 24 h in a closed screw-cap test tube. The toluene concentration remaining in the clay is reported as a function of desorption time (hours). The correlation coefficients for the first-order loss of toluene from the K^+-, Na^+, and Ca^{2+}-exchanged clays are 0.98, 0.98, and 0.93, respectively. (B) Dried clay was rehydrated with 10% (w/w) water and then incubated with toluene as described above. The toluene concentration remaining in the clay is reported as a function of desorption time (hours).

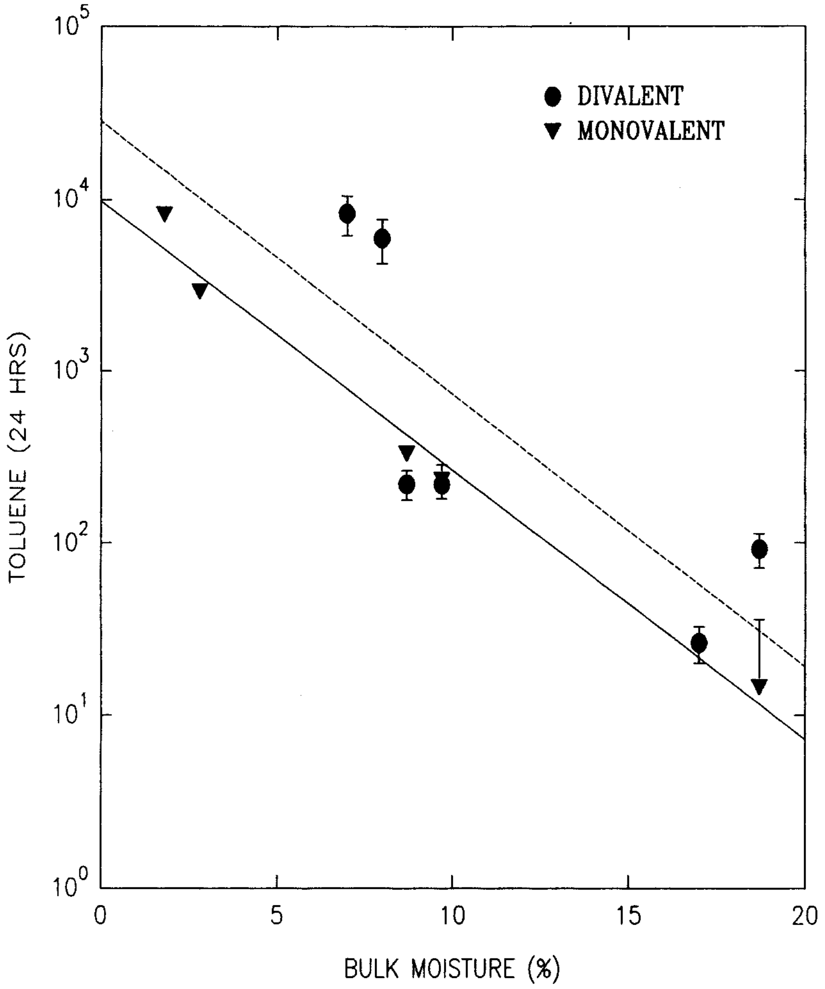

FIGURE 2. SDF toluene concentrations after 24 h of desorption are presented for clay samples that were incubated with 10 μl of toluene as a function of water content (percent moisture) in the clay. A best-fit line (least squares) is shown for monovalent (dotted) and divalent (solid) cation-exchanged clays.

percent moisture. When the data for monovalent and divalent cation-exchanged clays are pooled, the correlation coefficient is 0.75. The correlation coefficient for monovalent cation-exchanged clays is 0.98. For divalent cation-exchanged clay, the correlation coefficient is only 0.68, but the trend is still clear. As for equilibrium sorption of volatile compounds, water apparently plays a major role in moderating the formation of the SDF.

The results of experiments where clays were treated with vapor-phase toluene for 260 h are summarized in Figures 3A and B. The results presented in Figure 3A indicate that loss of toluene for clays incubated at 0% relative humidity followed

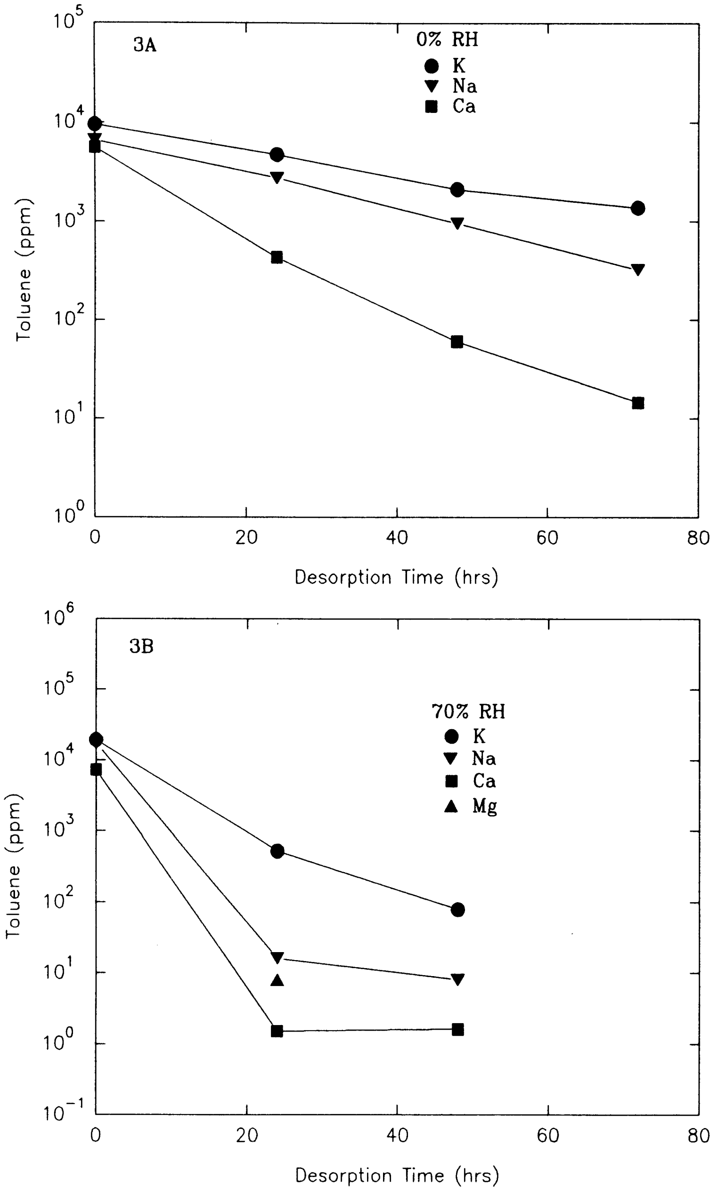

FIGURE 3. (A) Clay samples were dried at 105°C and then incubated with saturated toluene vapor for 260 h. The SDF toluene concentration remaining in the clay is reported as a function of desorption time (hours). (B) The dried clay was preequilibrated with a 70% relative humidity atmosphere for 72 h prior to a 260-h incubation with saturated toluene vapor. The SDF toluene concentration remaining in the clay is reported as a function of desorption time (hours).

approximately first-order kinetics from time zero. The SDF concentration results for the ion-changed montmorillonites investigated are K-montmorillonite > Na-montmorillonite > Ca-montmorillonite at both 0 and 70% relative humidity. Results for a similar experiment conducted at 70% relative humidity are summarized in Figure 3B. At 70% relative humidity, a single Mg-montmorillonite sample was examined and found to retain more toluene than the Ca-montmorillonite, but much less than the K- or Na-montmorillonite. Note that the initial (0 h) concentration of toluene sorbed onto the clay was not greatly altered by the presence of moisture. However, the results do show that during the first 24 h, a large fraction (95 to 99%) was lost from samples incubated at 70% relative humidity. This can be compared with the 0% relative humidity results, where for the K-montmorillonite, only about 40% of the sorbed toluene was lost during the first 24 h.

The effects of mechanical disruption (treatment) are summarized in Figures 4 and 5A and B. In Figure 4, the clay samples dried at 75°C were treated with neat toluene for 24 h, while in Figure 5, the samples were dried at 105°C and treated for 260 h with toluene vapor. The concentration of SDF toluene (after a 24-h desorption) as determined by the methanol extraction procedure is plotted in both figures. The results for Mg-montmorillonite incubated with neat toluene (Figure 4) indicate that, although mechanical disruption of the clay particles released toluene, the effect of the ion-exchange medium was negligible. It may be that Na^+ was unable to displace the divalent Mg^{2+} and disturb the interlamellar structure of the clay. However, because Ca^{2+} has a much higher affinity for the montmorillonite, the $CaCl_2$ should have induced substantial ion exchange, which would have disturbed the interlamellar region. Therefore, we conclude that for this set of experiments, disturbance of the interlamellar region by ion exchange did not result in increased desorption of toluene.

For Na- and Ca-montmorillonite exposed to toluene in the vapor phase (Figures 5A and B), there were notable differences in toluene desorption when using the various desorbing solutions. For example, NaCl and $MgCl_2$ solutions desorbed significantly more toluene from the Ca-montmorillonite than water alone. While water was able to desorb 60% of the methanol extraction value of SDF toluene from the Na-montmorillonite, treatment with $CaCl_2$ gave toluene SDF concentrations approximately 20% higher than methanol extractions. This result could imply that the ion exchange released toluene that was not extracted by the methanol extraction procedure. Therefore, for the Na- and Ca-montmorillonite, disturbance of the interlamellar region by ion exchange had an effect on the desorption of SDF toluene. Apparently, some of the SDF toluene became associated with the interlamellar regions of the clay when the clay was exposed to toluene vapor.

IV. DISCUSSION

The sorption of toluene to the interlamellar region could be driven by energetically favorable interactions, which may include ion-induced dipole interactions and

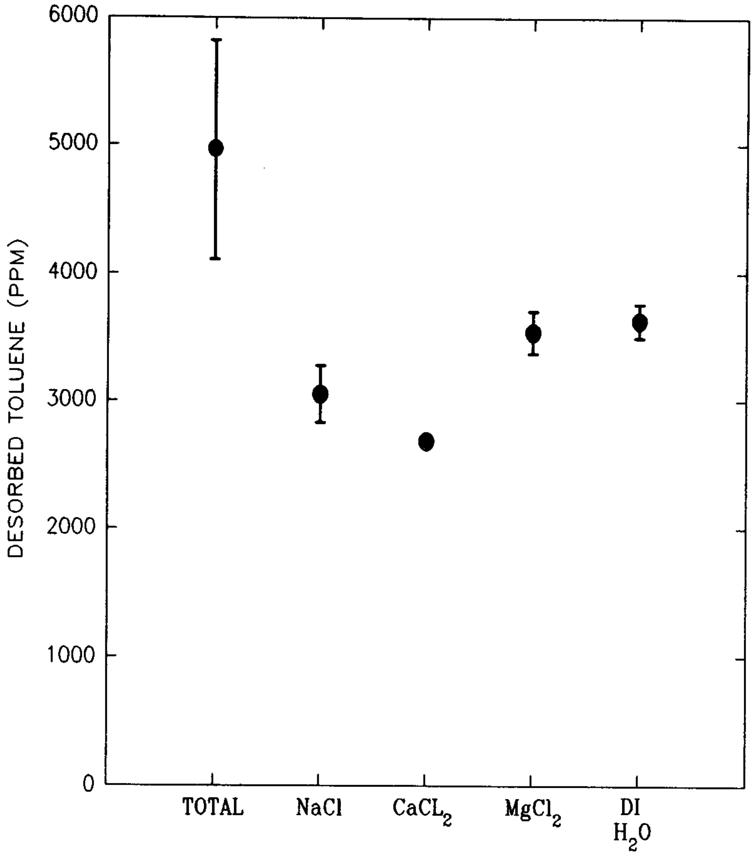

FIGURE 4. Mg-montmorillonite was dried at 75°C and then exposed to 10 µl of toluene for 24 h in a closed test tube. After desorption for 24 h, the clay was extracted with water or a 1.0 *N* solution of the various "ion exchange" media. The methanol extraction value is shown as the total concentration of SDF toluene.

dielectric field effects. For example, Aochi *et al.* (1992) found evidence that of the two EDB isomers (anti and gauche), the anti conformer is more labile, resulting in an enrichment of the gauche (higher dipole moment) conformer in persistently sorbed compounds. This behavior hints at the possibility of dipole moment interactions with interlamellar material or dielectric effects arising from the clay structure itself. If the concentration of SDF toluene was related to exchangeable ion-induced dipole interaction, a strong correlation between persistent toluene and ionic charge/radius^2 (z/r^2) would be expected. With montmorillonite treated with neat toluene, correlations with z/r^2 were indifferent to poor. With vapor-treated montmorillonite, divalent exchangeable cations gave lower concentrations of SDF

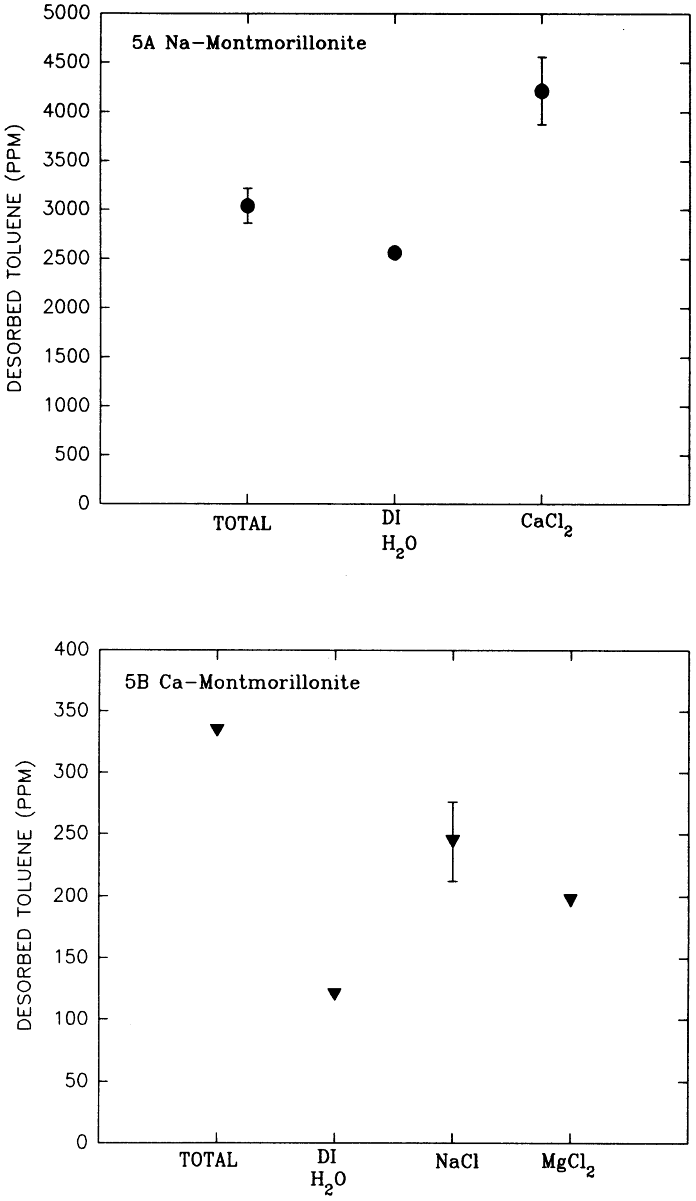

FIGURE 5. (A) Na-montmorillonite and (B) Ca-montmorillonite were oven dried at 105°C and then exposed to toluene vapor for 260 h. After desorption for 24 h, the remaining SDF toluene was extracted with water or a 1.0 *N* solution of the various “ion-exchange” media. The methanol extraction value is shown as the total concentration of SDF toluene.

toluene than the monovalent cations, again indicating that the exchangeable ions do not directly interact with the toluene.

Neither positive nor negative correlations between the SDF toluene concentration and interlamellar spacing are apparent for clays treated with neat toluene, but would be expected if toluene was associated with the interlamellar region of the clay. This apparent lack of a relationship with the interlayer environment argues for the association of the SDF with other types of sorption sites on the clays that were treated with neat toluene. With these samples, the added toluene was originally present as a nonaqueous-phase liquid (NAPL). Some of the NAPL should be drawn into capillaries in the clay matrix. During the incubation period, this liquid should be redistributed to the vapor phase and to sorption sites on the clay. From these experiments, we are unable to gauge the extent of this redistribution. Therefore, evaporation from these samples may have occurred from a NAPL or from sorption sites on the clay. The distribution between NAPL and clay may be difficult to reproduce experimentally and could have led to the lack of any pattern in the desorption results presented here. On the other hand, for vapor-treated montmorillonite, the K- and Na-montmorillonites, which have smaller interlamellar spacing as a result of reduced cation hydration, had significantly higher concentrations of SDF toluene. These results could imply that the interlamellar environment did play a role in the formation of SDF toluene for these clay samples. The lower extent of hydration of K- and Na-montmorillonites may allow toluene to compete for sorption sites in the interlamellar region. As noted above, Soma et al. (1984, 1985) found that aromatic hydrocarbons could enter the interlamellar region of dry clays, where they may become oxidized by transition metals. Similar experiments by Johnston et al. (1992) have demonstrated enhanced penetration of xylene into the interlamellar region of Co- and Cu-exchanged montmorillonite under extremely dry conditions.

As noted above, experiments were also performed by inundating toluene-exposed montmorillonites with ion-exchange solutions and then vigorously agitating in an effort to cause shock desorption of recalcitrant toluene. In all cases, the amount of SDF toluene desorbed increased with increasing agitation of up to 3 min. For the neat toluene-treated montmorillonite, the amount of toluene released was independent of the ion-exchange solution used. This strengthens the argument that toluene is not held in the interlamellar space. Furthermore, the amount of toluene released was directly proportional to the amount of agitation received by the sample (up to 3 min). These results are consistent with the microaggregate model of persistent fraction formation. In this model, residual toluene is held within water-stable and nonwater-stable microaggregates. Some of the toluene may be associated with NAPL held in pores between adjacent clay particles. The addition of solution (ionic or nonionic) causes decomposition of the nonwater-stable microstructure and subsequent release of toluene. Agitation results in further toluene desorption, as marginally water-stable structures also collapse. These findings are reminiscent of the Steinberg et al. (1987) experiments, where the addition of mechanical energy to the sample, by grinding, resulted in increased EDB desorption. In both cases, the result was a large increase in the amount of residual compound released, apparently through a loss of microstructure. For montmorillonite treated with toluene vapor, the nature of the desorbing medium was important and ion exchange enhanced the desorption of toluene from the clay. This result implies that interlamellar binding of toluene could also contribute to the SDF.

V. CONCLUSIONS

A slowly desorbing fraction of toluene was apparent on montmorillonite clay. The extent of formation of the slowly desorbing fraction (SDF) is apparently a function of ion exchange. The experimental results were a function of the exposure route (neat toluene or toluene vapor). Indeed, it is apparent from Figures 1 to 5 that the SDF toluene concentrations were much more reproducible for samples treated with vapor-phase toluene.

When toluene was added as a neat liquid, the SDF concentration did not correlate with interlamellar spacing. When toluene was added in the vapor phase, on the other hand, the concentration of the SDF did correspond to interlamellar spacing or extent of exchangeable cation hydration (K > Na > Mg > Ca). Water is a strong competitor for sorption in both types of incubation experiments.

The observation that toluene may be displaced during ion exchange and that mechanical disruption induced desorption of the SDF toluene indicates that toluene can be trapped in a combination of interaggregate and interlamellar sites. In the experimental results here, some of the differences in the two incubation experiments might be explained by the longer incubation used for vapor-phase exposure and that, for this experiment, the clay was dried at 105°C rather than the 75°C used with the neat toluene incubation experiment. For drier samples, toluene may more easily diffuse to the interlamellar region of the clay and can more easily compete for sorption sites that would otherwise be occupied by water. It is not clear whether toluene can penetrate to interlamellar sites when samples are incubated at 70% relative humidity.

It is clear that the nature of the clay-toluene association may be a function of the exposure route, relative humidity (moisture content), and duration of toluene exposure. It is also clear that the exchangeable cations exert some influence on toluene desorption kinetics by either changing the nature of the cross-linking between various particles or by their effect on interlamellar spacing and hydration.

REFERENCES

Aochi, Y. O., Farmer, W. J., and Sawhney, B. L. 1992. In-situ investigation of EDB sorption/desorption processes on clay mineral surfaces by diffuse reflectance infrared spectroscopy. *Environ. Sci. Technol.* **26:**329–335.

Ball, W. P. and Roberts, P. V. 1991a. Long-term sorption of halogenated organic chemicals by aquifer material. I. Equilibrium. *Environ. Sci. Technol.* **25:**1223–1236.

Ball, W. P. and Roberts, P. V. 1991b. Long-term sorption of halogenated organic chemicals by aquifer material. II. Intraparticle diffusion. *Environ. Sci. Technol.* **25:**1237–1249.

Brown, G. 1984. Crystal structures of clay minerals and related phyllosilicates. *Philos. Trans. R. Soc. London Ser.* A. **311:**21–240.

Estes, T. J., Shah, R., and Vilkner, V. 1988. Adsorption of low molecular weight halocarbons by montmorillonite. *Environ. Sci. Technol.* **22:**377–381.

Hermosin, M. C., Martin, P., and Cornejo, J. 1993. Adsorption mechanisms of monobutyltin in clay minerals. *Environ. Sci. Technol.* **27:**2606–2611.

Isaacson, P. J. and Sawhney, B. L. 1983. Sorption and transformation of phenols on clay surfaces: effect of exchangeable cations. *Clay Miner.* **18:**253–265.

Johnston, C. T., Tipton, T., Trabue, S. L., Erickson, C., and Stone, D. 1992. Vapor-phase sorption of p-xylene on Co- and Cu-exchanged SAz-1 montmorillonite. *Environ. Sci. Technol.* **26:**382–390.

Ortego, J. D., Kowalska, M., and Cocke, D. L. 1991. Interactions of montmorillonite with organic compounds — adsorptive and catalytic properties. *Chemosphere.* **22(8):**769–798.

Ong, S. K. and Lion, L. W. 1991. Mechanism for trichloroethylene vapor sorption onto soil minerals. *J. Environ. Qual.* **20:**180–188.

Paviostathis, S. G. and Jagial, K. 1991. Desorptive behavior of trichloroethylene in contaminated soil. *Environ. Sci. Technol.* **25:**274–279.

Pignatello, J. J. 1989. Sorption dynamics of organic compounds in soils and sediments. **In:** *Reactions and Movement of Organic Chemicals in Soils.* Special publication no. 22, Madison, WI, Soil Society of America and American Society of Agronomy.

Pignatello, J. J. 1990. Slowly reversible sorption of aliphatic halocarbons in soils. I. Formation of residual fractions. *Environ. Toxicol. Chem.* **9:**1107–1115.

Rao, P. S. C., Ogwada, R. A., and Rhue, R. D. 1989. Adsorption of volatile organic compounds on anhydrous and hydrated sorbents: equilibrium sorption and energetics. *Chemosphere.* **18:**2177–2191.

Rhue, R. D., Rao, P. S. C., and Smith, R. E. 1988. Vapor-phase adsorption of alkylbenzene and water on soil and clays. *Chemosphere.* **17:**727–741.

Rogers, R. D., McFarlane, J. C., and Cross, A. J. 1980. Adsorption and desorption of benzene in two soils and montmorillonite clay. *Environ. Sci. Technol.* **14:**457–460.

Sawhney, B. L., Pignatello, J. J., and Steinberg, S. M. 1988. Determination of 1,2-dibromoethane (EDB) in field soils: implications for volatile organic compounds. *J. Environ. Qual.* **17(1):**149–152.

Sawhney, B. L. and Gent, M. 1990. Hydrophobicity of clay surfaces: sorption of 1,2-dibromoethane and trichloroethene. *Clays Clay Miner.* **38:**14–20.

Smith, J. A. and Jaffé, P. R. 1991. Comparison of tetrachlormethane sorption to an alkylammonium-clay and alkyldiammonium-clay. *Environ. Sci. Technol.* **25:**2054–2058.

Smith, J. A., Jaffé, P. R., and Chiou, C. T. 1990. Effect of ten quaternary ammonium cations on tetrachloromethane sorption to clay from water. *Environ. Sci. Technol.* **24:**1167–1172.

Soma, Y., Soma, M., and Harada, I. 1984. The reaction of aromatic molecules in the interlayer of transition-metal ion exchanged montmorillonite studied by resonance Raman spectroscopy. I. Benzene and p-phenylenes. *J. Phys. Chem.* **88:**3034–3038.

Soma, Y., Soma, M., and Harada, I. 1985. Reactions of aromatic molecules in the interlayer of transition-metal ion-exchanged montmorillonite studied by resonance Raman spectroscopy. II. Monosubstituted benzenes and 4,4′-disubstituted biphenyls. *Phys. Chem.* **89:**738–742.

Steinberg, S. M. 1992. Persistence of several volatile aromatic and halogenated hydrocarbons in a low organic carbon calcareous soil. *Chemosphere.* **24(9):**1301–1315.

Steinberg, S. M., Pignatello, J. J., and Sawhney, B. L. 1987. Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. *Environ. Sci. Technol.* **21:**1201–1208.

Velde, B. 1992. *Introduction to Clay Minerals: Chemistry, Origins, Uses and Environmental Significance.* London, Chapman and Hall.

Wu, S.-C. and Gschwend, P. 1988. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Technol.* **20:**717–725.