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Desorption hysteresis in five ion exchanged montmorillonites

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Abstract

It is generally believed that the formation of recalcitrant (slowly desorbing) fractions of volatile organic compounds (VOCs) in soils is due to diffusion of compounds to sorption sites inaccessible to bulk fluid. The exact nature of these sites, however, is not well understood. In clay minerals, researchers favor two probable areas for the storage of persistent contamination; sites between the clay lamella, or sites within clay particle aggregates.

To test the hypothesis that recalcitrant fractions are formed in interlamellar spaces, a Na/Ca Montmorillonite (Smectite) was ion exchanged with five different cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}) to form mineralogically similar clays with varying interlamellar environments. These soils were inoculated with an organic compound (toluene), incubated for 24 hours, and the recalcitrant fraction quantified for varying desorption times. The results did not show a clear correlation between persistent contamination and the interlamellar environment. Instead, evidence appears to support the conclusion that persistent contamination may be stored in clay particle microaggregates.

Keywords: sorption/desorption, persistent contamination, VOCs, interlamellar environment.

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ii

Table of Contents

List of Tables

List of Figures

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Purpose

When soils are exposed to volatile organic compounds (VOCs), whether accidentally, as in leaking fuel tanks, or purposely, as in soil fumigation, a residual remains behind in the soil long after the majority of contaminant has volatilized or been decomposed by soil bacteria. The presence of these compounds may go undetected by standard methods of estimating organic compounds in soils. Sawhney, et al. (1988) found that standard techniques for estimating VOCs in soils (EPA Method 8240) underestimated quantities of 1,2 dibromoethane (EDB) in fumigated soils by greater than or equal to 89%. This "persistent fraction" will continue to desorb over a period of many years, possibly providing a long term health hazard.

Persistent contamination can have other effects as well. In discussing experiments done on sediments from the Borden, Ontario landfill, Ball and Roberts (1991) point out that slow desorption kinetics can hinder remediation efforts and complicate accurate transport modeling. Additionally, while held in a sorbed state, these compounds are probably unavailable to microorganisms for biodegradation (Steen et al., 1980; Ogram et al., 1985), reducing the effectiveness of bioremediation programs. Clearly, knowledge of persistent contamination is necessary in order to understand the true

impact of our actions on the environment. This study undertakes to determine where the persistent fraction resides within one component of soil (clay), and what factors may effect formation of a fraction resistant to desorption.

Introduction

When soils are exposed to VOCs, a certain amount of
compound becomes sorbed to sites on and within the soil. The
relationship between vapor phase VOC concentration and VOCs
attached to the sorbent at a given temperature defines a graph
known as a sorption isotherm (Fig 1). Sorption isotherms are
most frequently described using the Freundlich equation,
although other models are also used (for a review see Ruthven,
1984). The Freundlich equation is stated:

$$S = K_d C^n$$

where:

S = sorbed concentration of sorbate (M/M)

C = sorbate in vapor phase (M/M)

K_d = distribution coefficient (dimensionless)

n = empirical "order" of reaction
(dimensionless)

For low concentrations of many sorbates the value of "n" is
usually found to be equal to 1.0.

Ideally, sorption equilibrium would be instantaneous.
Practically speaking; however, equilibration appears to
proceed in two phases. The first is characterized by rapid
rate kinetics: a graph of sorbate uptake vs. time exhibits a
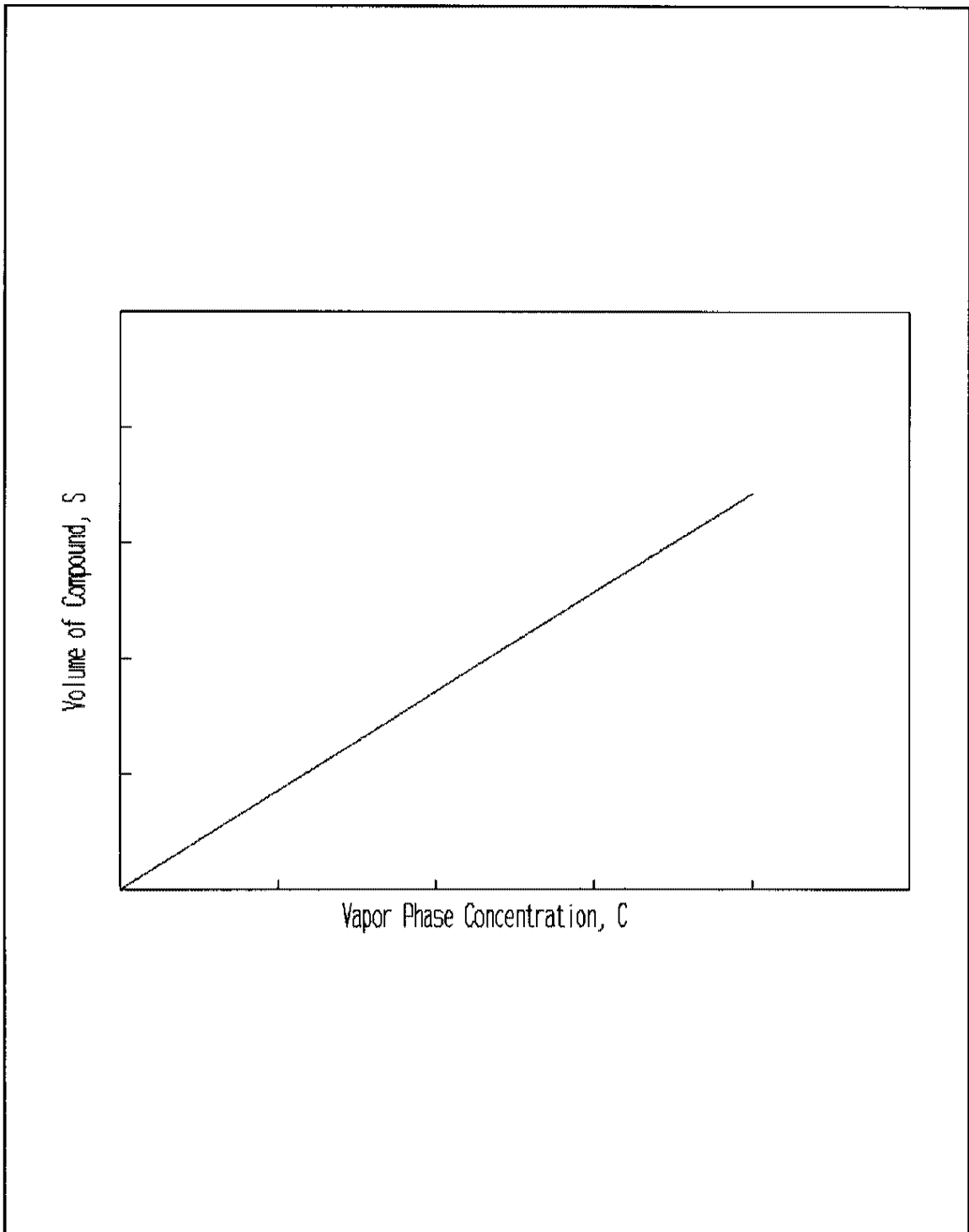
Figure 1: Conceptualized Freundlich adsorption isotherm, of the form $S = K_d C^n$, where: S = volume of adsorbed compound, C = vapor phase concentration of sorbate, K_d and n are constants.

steep positive slope. In the second, or slow rate kinetics phase, sorption continues, but at a reduced rate. True equilibrium may not be reached for many days (Fig. 2). Kahn (1973) observed biphasic kinetics in the uptake of 2,4-D [(2,4-dichlorophenoxy)acetic acid] by humic acids. Equilibrium was not reached even after 48 hours. Karickhoff (1980) reported two phase uptake of pyrene, phenanthrene and naphthalene by soils from aqueous solution. An empirical kinetic model was devised consisting of a fast sorbing compartment and a slow sorbing compartment. Fast sorbing sites were postulated to reach equilibrium within minutes, while slow sites may require days or weeks to equilibrate. Karickhoff and Morris (1985) concluded that up to half the sorption to a natural soil may be held in slowly sorbing sites. Similar results have prompted other researchers to propose two-site models to describe desorption processes. McCall and Agin (1985) describe desorption kinetics of picloram (4-amino-3,5,6-trichloropicolinic acid) utilizing a two-site model. In this study researchers defined fast sites as those desorbing in less than two minutes and slow sites as those desorbing in more than two minutes. Picloram desorbed within this time limit was believed to correspond to that portion of the sorbed compound readily leached from soil on a field situation. The investigators found an increase in the amount of firmly held picloram with increasing incubation times, and noted apparent hysteresis between equilibrium
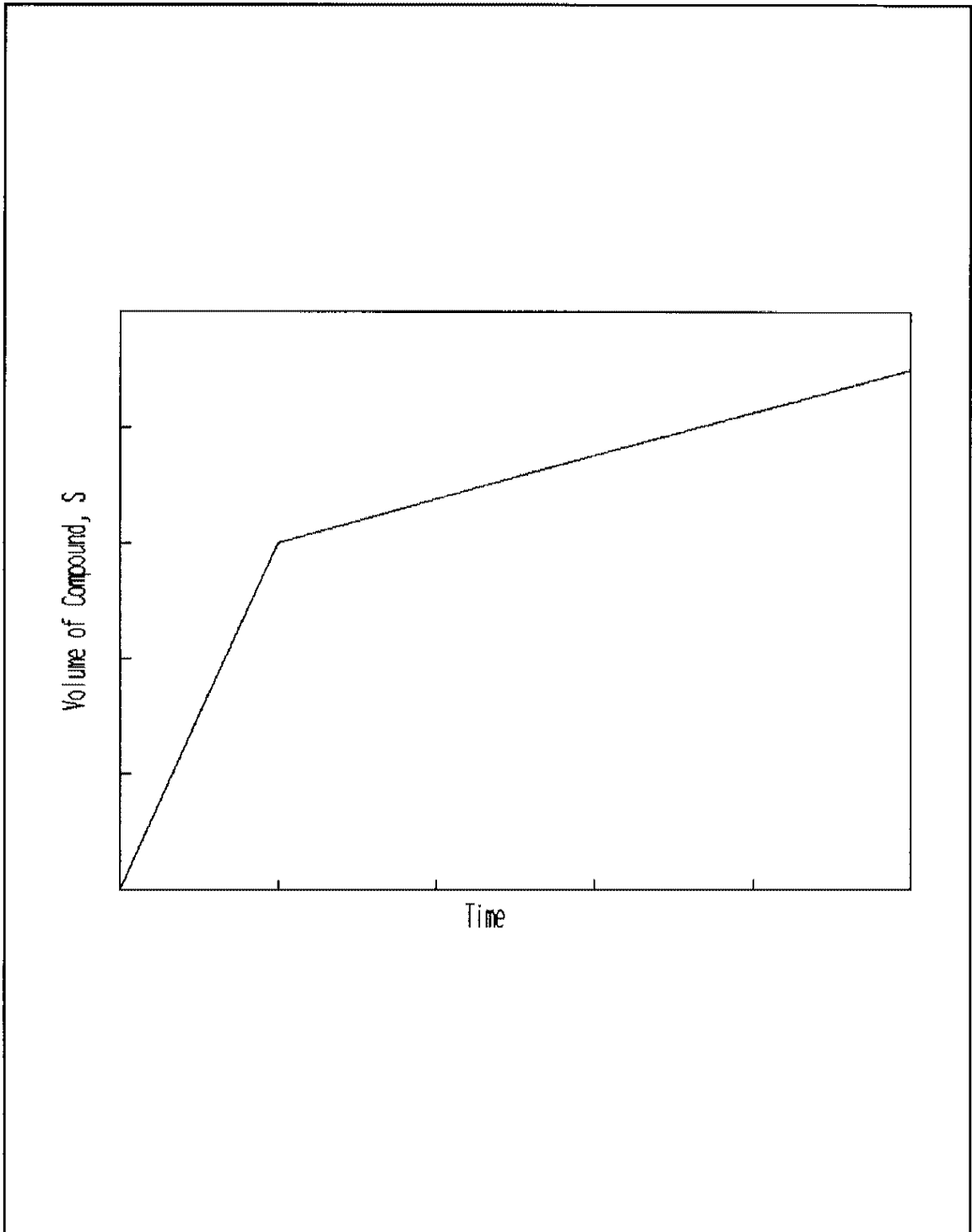
Figure 2: Conceptualized graph of uptake of some volatile organic compound by natural soul. Note two distinct phases, rapid (steep slope) and slow (mild slope) rate kinetics.

coefficients for adsorption and desorption.

Hysteresis is a phenomena in which the apparent equilibrium distribution coefficient is different depending on whether it is approached from the adsorptive or desorptive direction. This phenomena has been reported by several researchers (for a review, see Pignatello, 1989). The Kelvin equation (Thompson, 1871), which is a mathematical relationship between equilibrium vapor pressure of a curved surface to the equilibrium vapor pressure of a plane surface predicts that condensation and evaporation will proceed at different rates for pores of different sizes. This provides a theoretical model which has been used to provide a thermodynamic explanation for hysteresis (for a review, see Lowell and Shields, 1991). A more difficult problem is the presence of VOC's in the soil even though the vapor (or aqueous) phase concentration is negligible. The sorbate present under such conditions is known as a "recalcitrant" or "persistent" fraction; that is, the quantity of compound which remains sorbed in quasi-equilibrium (Figure 3).

It has been shown that up to 15% of sorbed tetrachloroethene (PCE) can remain as recalcitrant fraction after 7 days of desorption to infinite dilution (Pignatello, 1990b). Polychlorinated biphenyl (PCB) contaminated lake sediments have shown a similar pattern of initial rapid
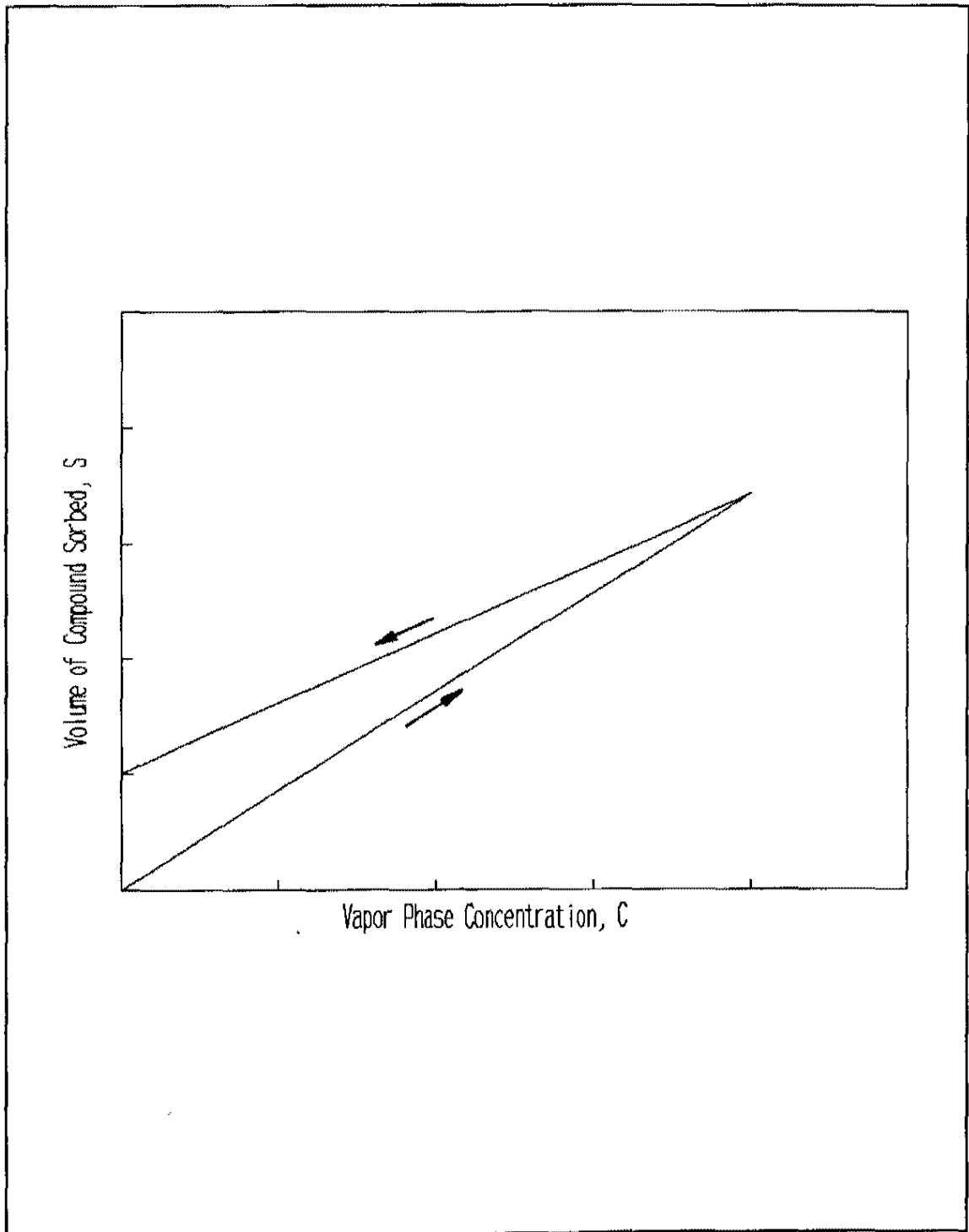
Figure 3: Freundlich isotherm showing desorption hysteresis. Note $S|_{C=0}$ can be non-zero. This non-zero amount is equal to the recalcitrant fraction.

desorption followed by a slower release of up to half the total amount sorbed (Dunnivant, 1988). Evidence indicates recalcitrant fractions may persist for years. Steinberg et al. (1987) showed that fractions of 1,2 dibromoethane (EDB) have resisted desorption from soil for up to 19 years after application as a nematicide.

Researchers describing hysteresis in soils agree on the basic outline of the two phase model. The rapid rate kinetics phase is attributable to sorption sites accessible to bulk fluid. In this phase, sorption is dominated by sites on mineral and organic surfaces. Uptake of sorbent is rapid and readily reversible.

The slow rate kinetics phase, however, arises from sorption to sites physically remote from the surface of the sorbent. Because these sites are not accessible to bulk fluid, sorption is diffusion limited. Sorption\desorption kinetics result from diffusion transport of sorbate to (or from) remote locations within the structure of the sorbent. Sorption to remote sites is not readily reversible.

Several studies support the belief that sorbate may be stored in physically inaccessible sites within the soil structure. Steinberg et. al. (1987) studied soils from Connecticut tobacco fields which had been treated with EDB.

These soils clearly showed evidence for a slow rate kinetics phase: soils last fumigated with EDB up to 19 years previously were found to retain concentrations of EDB at levels up to 200 ng/g. The presence of a recalcitrant fraction in these soils is particularly surprising given the physical properties of EDB, which is highly volatile (vapor pressure of 13.8 mmHg and estimated Henry's law constant 8.2×10^{-4} atm m^3/mol @ $25°C$)(Rathbun and Tai, 1987) and has a low affinity for soils (Steinberg et al., 1987). The investigators found that soils fumigated with EDB retained a fraction of compound highly resistant to further desorption by volatilization (dry N_2 gas passed through soil samples at a rate of 30 volumes of gas per volume of soil per minute for 3.5 days only removed 8% of the recalcitrant fraction of one soil) and unavailable for microbial degradation.

Another interesting aspects of the Steinberg, et al. experiments was the response of the recalcitrant fraction to mechanical shock. When a ball mill was used to physically break apart soil particles, the percentage of recalcitrant EDB released to a dry stream of N_2 gas increased from 8% to 40%. This led the investigators to postulate entrapment of EDB in soil "micropores" inaccessible to bulk fluids (Steinberg et al., 1987).

Further evidence for soil micropores was found by Aochi

et al. (1992), who used Infrared Spectroscopy to examine sorption of EDB on clay surfaces. Clays exposed to EDB vapor for a sorption period of 22 hours demonstrated spectra consistent with the formation of a liquid phase on the clay surfaces. Following a 24 hour desorption period the clays were again examined and the clay surfaces found to be depleted of EDB. This is consistent with the rapid rate kinetics phase of desorption. Further experiments, however, discovered EDB slowly diffusing onto the clay surfaces, presumably from areas of the clay inaccessible to the infrared beam. This evidence led the investigators to infer the presence of EDB in a liquid phase "accumulating in micropores of the clay that limit subsequent diffusion to the surface.".

Because it is not possible at this time to directly examine VOC's sorbed within soils, the exact structure of micropores is highly speculative. In soils containing significant percentages of organic material, sorption may be dominated by diffusion of sorbate directly into soil organic gels, particularly in situations where the sorbent is saturated with water. In this case, competition for surface sites between sorbate and water is intense, and partitioning of sorbate into organic matter is driven by hydrophobic processes (Pignatello, 1989). However, soils with low organic contents can clearly form resistant fractions as well (Steinberg, 1992).

Pignatello suggests that soil particles can aggregate to form larger, microaggregate particles with considerable porosity. These pores, with effective diameters of 100 to 1000 nm, exclude advection of bulk fluids, limiting sorbate transport within the pores to diffusion (Pignatello, 1989). This model of micropores agrees well with the release of EDB upon mechanical grinding of soils found by Steinberg et al., who concluded that "EDB in inaccessible regions becomes available as these region are exposed by pulverization" (Steinberg et al., 1987).

Another possible reservoir for a persistent fraction is the interlamellar space of clay minerals. Clays are minerals composed of continuous two-dimensional tetrahedral sheets based on the composition T_2O_5 (T=Si, Al, Fe^{3+},...). One or two tetrahedral sheets are associated with one octahedral sheet, which co-ordinate to form a layer. These layers can be electrically neutral, as is the case with pyrophyllite; in other cases the layers carry charges due to substitutions in octahedral and/or tetrahedral layers. The result is that interlayer cations are absorbed into the interlamellar region to maintain neutrality (Brown, 1984). These interlayer cations can effect VOC's in a variety of ways. Isaacson and Sawhney (1983) showed that the presence of transition metal cations catalyzed the production of transformation products of parent phenols. The modification of the compounds was

dependant on the exchangeable cation, and followed the order Fe-> Al-> Cu-> Ca-exchanged clay. Soma et al. (1984, 1985) found evidence for the polymerization of benzenes and monosubstituted benzenes in transition metal ion exchanged montmorillonites. In addition, 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 conformer sorbed to slow kinetic sites. This behavior hints at the possibility of dipole moment interactions with interlayer material or dielectric effects arising from the clay structure itself.

Water also exists in the interlamellar region. Ormerod and Newman (1983) studied water sorption on a Ca-montmorillonite and concluded that "the interlamellar and external surfaces of Ca-montmorillonite have distinctly different characteristics for water sorption." When water is present in the interlamellar spaces it forms a film which varies from a single molecule (known as a "single sheet complex") to many molecules in thickness. Depending on the moisture content of the clay, water exists between the clay lamella in one, two or three sheet complexes. Norrish (1954) found Na-montmorillonite interlayer spacing to increase in steps beginning with 9.6 Å (representing a completely dehydrated state) and going to 12.4, 15.4 and 19.0 Å for one, two, and three sheet complexes, respectively. Similar results

have been duplicated by others (Tennakoon et al., 1983, Fukushima, 1984).

Regardless of interlayer water or exchangeable cations, it is apparent that organic chemicals can and do penetrate the interlayer region of clay minerals. Whether or not organic compounds in the interlamellar region are hindered from leaving during desorption is presently unclear; however, the d-spacing, or separation distance of the lamella is of a size comparable to the effective diameter of the micropores postulated by Pignatello (1989), and is similarly exclusive of advective bulk fluids (d-spacing commonly varies from 100 to 200 nm).

Materials and Methods

The sorbent used in this experiment was Smectite (Montmorillonite No. 26, Clay Spur, Wyoming) obtained from Ward's Natural Science Establishment, Inc.. Smectite is a 2:1 phyllosilicate clay with low layer charge; a typical cation exchange capacity (CEC) is approximately 0.8 meq/g (Weber and Weed, 1968).

To insure uniform displacement of the native ions (Na^+, Ca^{2+}) exchange sites were repeatedly inundated with an excess of target ions. A 1.0 N solution of an appropriate compound ($NaCl$, $CaCl_2$, $FeCl_3$, KCl, $MgCl_2$) was prepared, and each lot of soil was washed three times. The soils were centrifuged between each wash and the supernate decanted. The washes were followed by three rinses using glass distilled, de-ionized water to remove excess ions. The ion exchange procedure followed generally accepted laboratory methods (see Isaacson and Sawhney (1983)). The exchanged clays were dried at 75°C, pulverized in an agate mortar and pestle, and passed through a number 80 (180 μm) sieve. Drying at 75°C was believed to be preferable to drying at 100°C in light of work done by Bush and Jenkins (1970), who noted changes in character in clays dried by normal methods used for moisture determinations. Other precautions taken throughout the experiments to insure reproducible results included the use of blanks, sample

replications, and comparison of experimental results with known standards.

Two of the five soil varieties were analyzed for complete mineralogy by X-ray diffraction analysis (XRD). This verified the identity of the clay mineral, and ensured no changes were taking place in the structure of the clay during cation exchange. In addition, d(001) spacing was measured for all five clays.

Two experiments were performed on the clays. The first experiment was designated the desorption to infinite dilution experiment, because samples were desorbed to the atmosphere. 1.00 gram samples of exchanged clays were placed in glass culture tubes sealed with teflon lined screw-caps (Baxter Scientific, Inc., Cat #20802938). Moisture content was varied in three regimes: no added moisture, 1% added moisture and 10% added moisture (by weight). After the addition of moisture, the samples were allowed to equilibrate in a 30°C incubator for approximately one week. Actual moisture contents of the clays were determined gravimetrically. A complete listing of sample variables can be viewed in the Appendix.

Following this initial equilibration period, each sample was inoculated with 10 μl of toluene and incubated for a

period of 24 hours at a temperature of $30^\circ C$. Samples were then desorbed by leaving the culture tubes uncapped in the incubator for periods of 24, 72, or 120 hours. The ventilated incubator was placed under a fume hood to insure a constant flow of air around the samples. These conditions were designed to be similar to those encountered by a field soil during fumigation or exposure to leaky tanks. For the sake of reproducibility, however, temperatures were kept constant rather than including diurnal variations. In addition, the conditions closely parallel experiments done by other investigators doing similar work (for instance, see Steinberg 1991).

The final step in the desorption to infinite dilution experiment was the extraction of residual sorbate. This was accomplished by the method outlined in Sawhney et al. (1988); after the designated desorption time (24, 72, or 120 hours) each culture tube received a 5 ml aliquot of methanol. In the case of the Na^+ exchanged clays, methanol saturated with $CaCl_2$ was utilized to avoid problems with swelling of the clays. After the addition of methanol, the culture tubes were resealed and placed in an oven at $65^\circ C$ for a 24 hour period. Analysis of the Fe^{3+} exchanged clay was facilitated with the addition of 2 ml of sodium hydroxide solution to each sample to precipitate iron ions in solution.

The second set of experiments examined the effects of the addition of various ionic solutions on desorption of the recalcitrant fraction, and were therefore designated the desorption to solution experiments. In these experiments, 1.00 gram samples of Mg^{2+} exchanged soils were weighed into glass culture tubes and inoculated with 10 1 of toluene for each sample. After a 24 hour sorption period at 30°C all culture tubes were uncapped and replaced in the incubator to desorb for 24 hours. At this point, 4 samples were extracted by the method of Sawhney et al. (1988) to determine the total toluene concentration present on the soil. The remaining samples were inundated with either 13.4 ml de-ionized water or a 1.0 N ion exchange solution (NaCl, $CaCl_2$, $MgCl_2$, KCl). This amount of solution completely filled the culture tubes, preventing partitioning of toluene into a headspace. Each sample was agitated for 3 minutes and centrifuged prior to analysis; the concentration of toluene desorbed to solution was analyzed directly by High Pressure Liquid Chromatograph (HPLC).

All samples were analyzed by HPLC, consisting of a Milton Roy mini-pump, Spectroflow 757 HPLC detector, SSI pulse dampener, and Reodyne model 710 injector with a 20 μl loop. A 250 mm Econosphere C18 5 column was used with a 1 ml/min flow rate. The wavelength for analysis was 254 nanometers; filter rise time was 0.5 seconds, and sensitivity range was

0.05 absorption units. Two eluents were used on the HPLC: a 60%/40% acetonitrile/de-ionized water mix, or an 80%/20% methanol/de-ionized water mix. All analyses were done isocratically, and chemicals used throughout the experiment were spectrophotometric grade. The detection limit was approximatly 5 ppm.

Results and Discussion

Desorption to infinite dilution. In the desorption to
infinite dilution experiments, samples were inoculated and
incubated for 24 hours, after which they were desorbed into a
ventilated space. Remaining toluene was quantified by
methanol extraction, and statistical tests applied to the
results.

One factor which may be correlated to persistent
contamination is sample moisture condition. Researchers have
reported an inverse correlation between moisture and sorption
equilibrium coefficients (for example, see Houston et al.
1989). Sensitivity to moisture is attributed to
water/sorbate competition for binding sites. Steinberg
(1992), however, concluded that formation of persistent
fractions may have a low dependence on moisture content in
natural soils when the sorbing compound is present in
concentrations comparable to the concentration of water
present in the sample. Whether or not moisture effects
persistent retention of contaminants in clays, however, is
unknown.

Bulk moisture assessments do not reveal the condition of
interlamellar water, which can, however, be accurately
determined by X-ray diffraction. Variations in d(001) spacing

and number of sheet complexes cause fluctuations in the dielectric constant of clay media. A strong negative correlation of persistent toluene with basal water (as measured by d(001) spacing or the number of sheet complexes) would be expected if the recalcitrant fraction was being held in the interlamellar space by dielectric field interaction. Alternatively, inverse correlation with bulk moisture and independence from basal water suggests sites other than those in the interlamellar region control persistent sorption.

Basal spacing of the clay lamella in this experiment were measured by X-ray diffraction. The results can be viewed in Table 1. It is worth noting that the d(001) spacings measured compare closely with those found by Norrish (1954). Differences are attributable to averaging (the basal spacing measured represents average basal spacing over the sample). The relationship of basal spacing (or the inferred number of sheet complexes) to residual concentration was examined using a contingency table and Chi-squared test for independence (see Table 2). The null hypothesis was that residual concentration was independent of basal spacing. In this case, it proved impossible to reject the null hypothesis at the 5% significance level. This implies that dielectric fields contribute little to the formation of a recalcitrant fraction.

Better agreement was obtained by testing the relationship

Table 1: Variation in separation of the clay lamella, as measured by X-ray diffraction. These values represent a mean value of d(001) spacing over the sample. The different spacings correspond to the assumed sheet complexes (molecular water layers) in the various exchanged clays, as determined by Norrish (1954).

Ion Exchanged	d(001) Spacing (A)	Number of Sheets
K	12.63	1
Na	12.63	1
Mg	14.98	2
Ca	15.50	2
Fe	16.67	2-3

Table 2: Chi-squared test for independence of two variables, inferred number of sheet complexes vs. concentration of toluene remaining after 24 hours. The test could not reject the null hypothesis (H_0: Toluene remaining is independent of sheet complexes) at the 5% level of significance.

Concentration (ppm)		0-3999	4000-7999	8000-11999
Number of	1	10	0	3
sheets	2	8	2	2
Total	3	18	2	5

$$df=2 \qquad \chi^2=2.39 \qquad \chi^2_{0.05}=5.99147$$

between bulk moisture and residual concentration. In 7 out of 15 groups (groups were based on constant time and ion types) Chi-squared tests for independence concluded at the 5% significance level the two variables were, in fact, related (see Table 3). While less than half the groups showed dependency, the correlation between bulk moisture and toluene residual was more consistent than with any other variable. In addition, the R^2 (coefficient of determination) values are quite good (>0.80), indicating moderate to low scatter, and correlation appears to improve at longer desorption times. The fact that bulk moisture shows at least nominal correlation with residual toluene, while interlayer moisture correlations appear irrelevant, seems to indicate that water on surfaces other than the interlamellar surfaces is of greater relative importance.

It is particularly interesting to examine the reaction of the Fe-montmorillonite to moisture content in the light of work done by Isaacson and Sawhney (1983), Soma et al.(1984), Soma et al. (1985) and Moreale et al. (1985). Each of these experiments found that montmorillonites homoionically substituted with transition metal ions act as powerful catalysts for the polymerization of monosubstituted benzenes (Soma et al. 1984, 1985), aniline (Moreale et al., 1985), and phenols (Isaacson and Sawhney, 1983). The formation of ion-pair oxidants arising from decomposition of toluene on the Fe-

Table 3: Chi-squared test for independence of two variables, bulk moisture content (%) vs. remaining concentration of toluene. The test shown is for Na-montmorillonite after 24 hours desorption. Seven out of fifteen tests rejected the null hypothesis (H_0: Remaining toluene is independent of bulk moisture) at the 5% level of significance.

Toluene (ppm)		0-99	100-199	200-299	300-399	400-499
Bulk	8.7	0	0	0	5	1
Moisture	9.7	0	2	6	0	0
(%)	18.7	8	0	0	0	0
Totals		8	2	6	5	1

df=8 $\qquad$ $\chi^2=44$ $\qquad$ $\chi^2_{0.05}=15.5073$

montmorillonite probably accounts for the low toluene recovery (see data, Appendix). Of special interest, however, is the effect of increasing moisture content on toluene desorption. Alone among the homoionically exchanged montmorillonites in this study, the recovery of toluene from Fe-montmorillonite actually increased with increasing moisture content, as evidenced by the positive slopes of the best fit equations for moisture vs. recovered concentration (see Table 4, Figure 4). Although there is a lack of direct evidence, the natural inference is that water present in the interlayer spaces is limiting access, and subsequently limiting decomposition of toluene by Fe^{+3} ions within the interlamellar spaces.

Attempts were made to find correlation between the formation of a residual fraction and the ionic charge/radius^2 (z/r^2) with little success. It was believed that toluene residing in the interlayer space might be bonded by ion induced dipole interactions; however, multiple linear regressions performed on data using residual toluene in ppm (or the natural log of concentration) as the dependant variable and percent moisture and z/r^2 showed poor correlation (see Table 5).

Desorption to solution. The desorption to solution experiment was performed on the Mg-montmorillonite only. In this experiment Mg-montmorillonite was inoculated with

Table 4: Linear curve fits for plots of remaining toluene as a function of bulk moisture content in five ion-exchanged montmorillonites. The coefficients as listed apply to the equation $C=a+bM$; where: C= concentration of toluene remaining in sample (ppm), M= sample bulk moisture content, b= slope of curve and a= C-intercept.

Exchanged	Desorption	a	b
Na	24	539.7	-28.2
	72	27.4	0.6
	120	52.9	-2.7
Ca	24	948.8	-36.6
	72	419.5	-12.6
	120	397.0	-17.5
K	24	6744.5	-150.5
	72	1950.9	-166.5
	120	1508.4	-129.0
Mg	24	13278.5	-783.8
	72	129399	-764.3
	120	10839.6	-641.2
Fe	24	-100.1	17.4
	72	0.6	1.7
	120	0.3	0.1

Table 5: Results of multiple linear regressions using % moisture and z/r^2 as independent variables (where z= ionic charge and r= effective ionic radius in water in angstroms) and the natural log of remaining toluene concentration (in ppm) as the dependant variable. The coefficients are listed as they correspond to the equation: Ln $C = a + b(\%M) + c(z/r^2)$. R^2= Coefficient of determination.

Time (hours)	a	b	c	R^2
24	9.47	-0.30	3.43	0.63
72	15.66	-0.49	-91.72	0.49
120	17.01	-0.62	-100.92	0.64
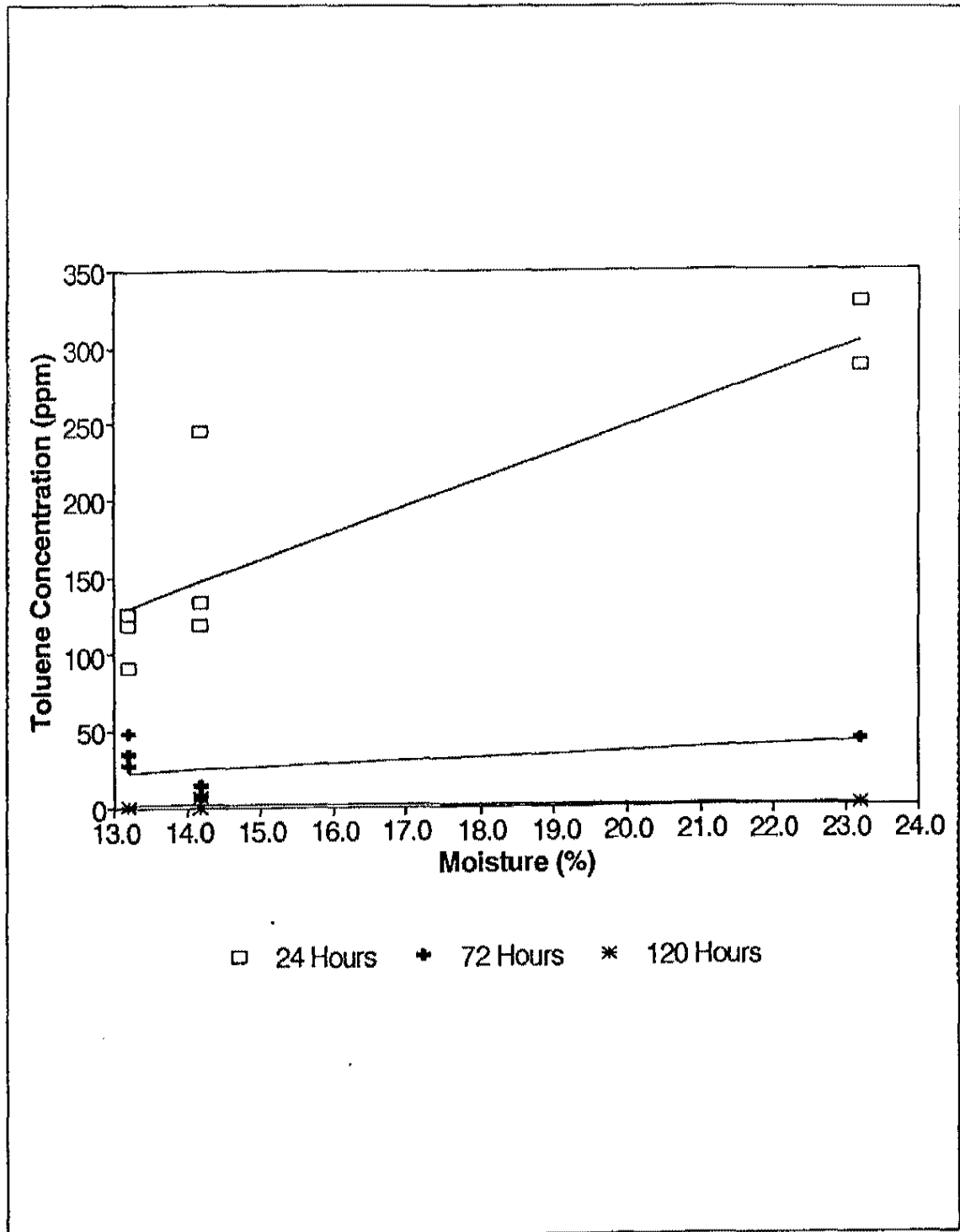
Figure 4: Moisture vs. recovered toluene in Fe-montmorillonite. Note positive slopes of best fit lines indicating increasing moisture.

toluene, incubated for 24 hours, and allowed to desorb for 24 hours. After extracting several samples for baseline use the remaining samples were inundated with a solution of either de-ionized water or a 1.0 N ion transfer solution. The object was to determine if an exchange of interlayer cations would cause "shock" desorption.

Initially the samples were analyzed without agitation; however, it quickly became apparent that any addition of mechanical energy to the soil/solution system resulted in increased release of toluene to solution. This increase peaked after approximately 3 minutes of agitation (see Figure 5). The data as compiled in the Appendix is reported as concentration released after three minutes agitation.

Amounts of toluene desorbed to solution were quantified by direct analysis of solution, and the results tabulated (see Table 6). A one-way analysis of variance was performed on the data to determine if the mean values varied or were substantially the same. A 5% level of significance was used. The analysis of variance, which can be viewed in Table 7, indicate that the amount of toluene desorbed to solution was independent of the ion exchange solution used.

These results are not consistent with the formation of a recalcitrant fraction in the interlamellar space, controlled
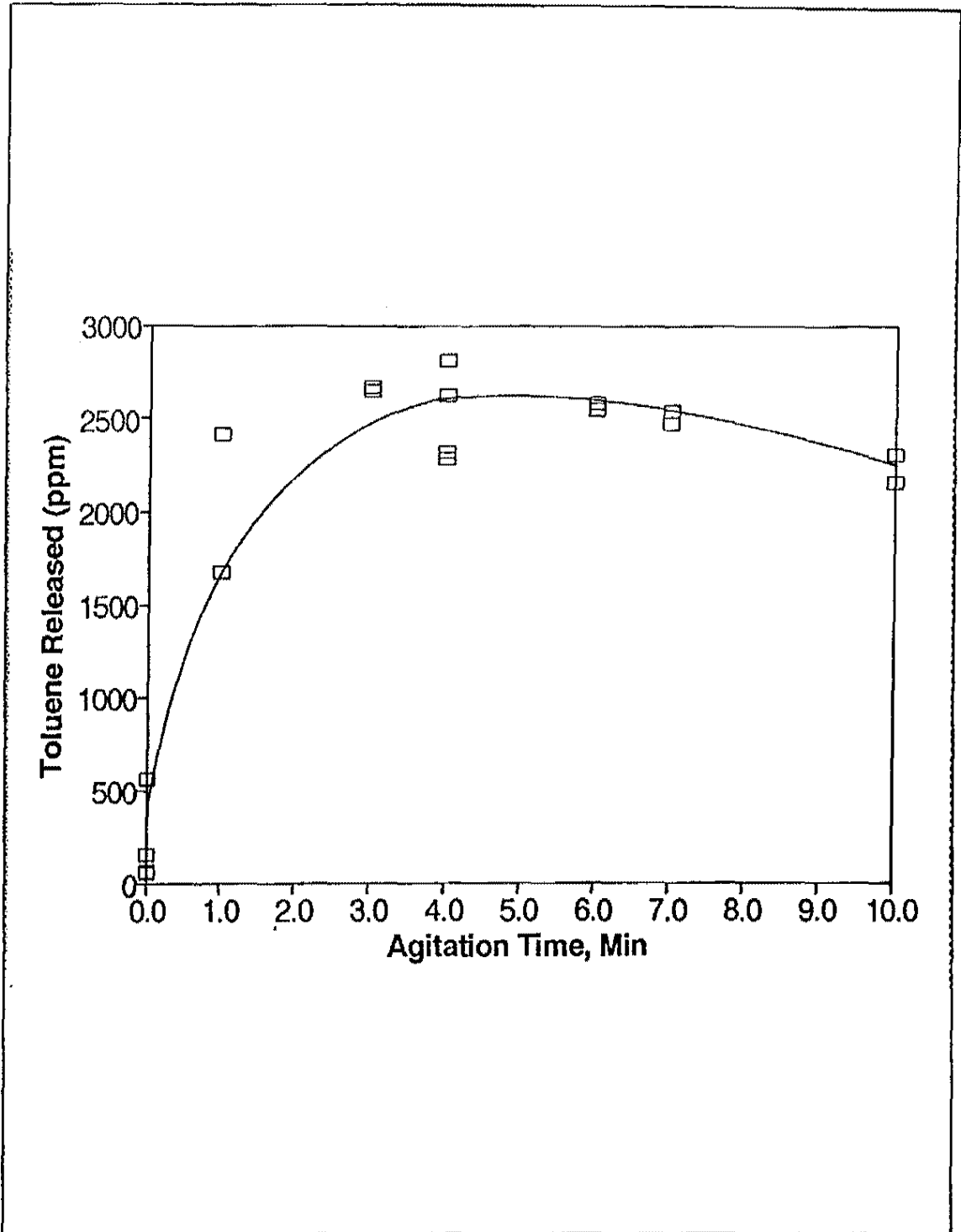
Figure 5: Concentration of toluene released to solution (ppm) vs. agitation time in minutes. Agitation was achieved with a Vortex-Genie laboratory agitator.

Table 6: Values of toluene released to solution after 3 minutes agitation time. A Mg-ion exchanged montmorillonite was allowed a 24 hour desorption time before the introduction of an ion exchange solution. The mean value of toluene retained by the samples as determined by the method of Sawhney et al. 91988) was 4975 ppm.

Ion exchange solution:	Ca	Na	Mg	DI-water
Experimental	2626	2801	710	3765
values	2814	3015	3698	3739
	2640	3350	3618	3605
	2667	6190	3310	3430
Mean:	2687	3839	2834	3635
Standard Deviation:	86.52	1583.5	1425.9	153.5
Sums of Xs:	10747	15356	11336	14539

Table 7: Table of analysis of variance in the mean amount of toluene released to solution by inundation of a contaminated Mg-montmorillonite with three ion-exchange solutions and de-ionized water. The null hypothesis (H_o: No difference in mean values for the four solutions) could not be rejected at the 5% level of significance. SS, df, MS, and F stand for sum of the squares, degrees of freedom, mean squares, and the test statistic, respectively (Crow, et al., 1960).

	SS	df	MS	F
Treatments	3941010	3	1313670	1.15
Error	13714945	12	1142912	
Totals	17655955	15	$F_{0.05}=$ 3.49	

by ionic variables. Such a model would require a considerable variation on the amount of toluene released among the different ionic solutions as the interlayer environment varied.

More in line with the experimental results is the microaggregate model of persistent fraction formation. In this model, the residual toluene is held in sites within water stable and non-water stable microaggregates. The addition of solution (ionic or non-ionic) causes a decomposition of the non-water stable microstructure and subsequent release of toluene to solution. The addition of mechanical energy (agitation) causes additional toluene release as marginally water stable structures also collapse. The addition of mechanical energy to the sample by agitation is analogous to the addition of mechanical energy by grinding in the experiments by Steinberg et al.(1987). In each case, the result was a large increase in the amount of residual compound released by the loss of microstructure.

Conclusions

The actions of the ion exchanged clays in the experiments are consistent with the formation of a recalcitrant fraction in microaggregate pores. This conclusion is supported by several lines of evidence.

If the recalcitrant fraction resided in the interlayer region, one would expect a strong correlation between the interlayer environment and the amount of toluene sorbed persistently. The desorption to infinite dilution data do not support this model.

The two most likely mechanisms for sorption of toluene to the interlayer region are ion induced dipole interactions and dielectric field effects. If the recalcitrant fraction was related to ion induced dipole interaction in the interlamellar space, a strong correlation between persistent toluene and ionic charge:radius^2 (z/r^2) would be expected. In reality, correlations with z/r^2 are indifferent to poor (see Table 5). Correlations between toluene and sheet complex or interlamellar spacing which would indicate sorption by dielectric field effects also were similarly untenable. The apparent lack of relationship to interlayer environment argues for the existence of the recalcitrant fraction in areas other than the interlamellar space.

These conclusions are also supported by the desorption to solution experiments. If a recalcitrant fraction were being held in the interlamellar space by ion induced dipole interactions, one would expect the amount of toluene released to solution during cation exchange to vary as a function of z/r^2. This was not the case, as all solutions were equally as effective in releasing toluene (see Table 7). Finally, the release of toluene by agitation, is strongly suggestive of toluene in the clay microaggregates.

These findings suggest that remediation efforts which disturb the structure of soils, such as bucket auger drilling combined with soil agitation, may be more effective than comparable methods that are non-disruptive of soil structure. It should be stressed that soil agitation may increase the mobility of the pollutant, so the findings must be applied to field situations with caution.

Although the modeling of sorption processes by dividing sorptive behavior into two types (rapid and slow rate kinetics) is popular and useful, it is apparent that this is an approximation of a system whose actual behavior is far more complex. It seems likely that, similar to clays, natural soils hold volatile organic compounds in multiple types of sites, each of which desorbs at a somewhat different rate and under different conditions. Interlamellar sites may be more

intermediate rate sites, while highly tortuous microaggregate pores fall into the slow rate category. Regardless, it is obvious that the sorption of VOC's to clays can only partly account for the complex interaction of similar compounds in natural soils.

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Appendix

Table of experimental variables for desorption to infinite
dilution experiments. Instrumental detection limit was
approximatly 1 ppm, the standard deveations of the results
varied from 85 to 1585 ppm.

Ion type	Moisture (%)	Desorption time (Hrs)
Na$^+$	8.7	24
		72
		120
		360
	9.7	24
		72
		120
	18.7	24
		72
		120
Ca^{2+}	8.7	24
		72
		120
		360
	9.7	24
		72
		120
	18.7	24
		72
		120
K$^+$	1.8	24
		72
		120
	2.8	24
		72
		120
	11.8	24
		72
		120
Mg^{2+}	7.0	24
		72
		120
	8.0	24

Fe^{3+}

		72
		120
17.0		24
		72
		120
13.2		24
		72
		120
14.2		24
		72
		120
23.2		24
		72
		120

Desorption to infinite dilution data: The following data is a
list of the results of the desorption to infinite dilution
experiments, given separated into groups by homoionic
montmorillonite type, moisture (% gravimetric), and desorption
time.

Na- montmorillonite

Moisture: 8.7%		Moisture: 9.7%		Moisture: 18.7%	
Desorp. Time (Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(hrs)	Conc. (ppm)
24	342	24	201	24	66
24	300	24	163	24	25
24	400	24	145	24	15
24	315	24	275	24	trace
24	335	24	260	24	5
24	300	24	280	24	trace
		24	285	24	trace
72	35	24	265	24	5
72	30				
72	50	72	64	72	83
		72	64	72	5
120	29	72	63	72	20
120	40				
120	trace	120	45	120	trace
		120	51	120	–
360	trace	120	trace	120	trace
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				

Ca-montmorillonite

Moisture: 8.7%		Moisture: 9.7%		Moisture: 18.7%	
Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)
24	1080	24	1560	24	660
24	1270	24	1570	24	680
24	1180	24	195	24	75
24	215	24	240	24	75
24	290	24	215	24	75
24	230	24	230	24	125
24	155			24	110
24	215	72	560		
		72	590	72	125
72	355	72	595	72	165
72	–			72	175
72	425	120	120		
72	–	120	215	120	90
72	–	120	240	120	45
				120	85
120	470				
120	195				
120	205				
120	205				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				
360	trace				

K-montmorillonite

Moisture: 1.8%		Moisture: 2.8%		Moisture: 11.8%	
Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)
24	3500	24	7930	24	7575
24	8985	24	2570	24	7750
24	9395	24	3230	24	105
24	8730				
		72	1355	72	-
72	1430	72	1300	72	-
72	1945	72	1585	72	-
72	1835	72	1270		
72	1780			120	-
		120	1395	120	-
120	1360	120	960	120	-
120	1380	120	930		
120	1150	120	875		
120	1600				

Mg-montmorillonite

Moisture: 7.0%		Moisture: 8.0%		Moisture: 17.0%	
Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)
24	7215	24	4215	24	20
24	10335	24	7615	24	25
24	10290			24	35
24	5295	72	4815		
		72	7225	72	20
72	10180	72	5985	72	-
72	6755			72	65
72	8670	120	5045		
72	6960	120	5195	120	55
		120	3930	120	40
120	7850			120	20
120	8155				
120	6890				
120	5175				

Fe-montmorillonite

Moisture: 13.2%		Moisture: 14.2%		Moisture: 23.3%	
Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)	Desorp. Time(Hrs)	Conc. (ppm)
24	91	24	133	24	287
24	119	24	119	24	329
24	126	24	245	24	287
72	28	72	7	72	42
72	49	72	7	72	42
72	35	72	14	72	42
120	trace	120	7	120	trace
120	trace	120	–	120	trace
120	trace			120	trace

Desorption to solution data: The following list is from the desorption to solution experiments, where a contaminated Mg-montmorillonite was inundated with an ion exchange solution and the quantity of toluene released as a result quantified.

Ionic solution	Toluene conc (ppm)
Na^+	2801
	3015
	3350
	6190
Ca^{+2}	2640
	2667
	2626
	2814
Mg^{+2}	710
	3698
	3618
	3310
De-ionized water	3765
	3739
	3605
	3430
Total concentrations in soil as determined by method of Sawhney, et al. (1988)	5685
	4600
	3745
	5870