

Adsorption of Parathion, Fenitrothion, Methyl Parathion, Aminoparathion and Paraoxon by Na⁺, Ca²⁺, and Fe³⁺ Montmorillonite Suspensions¹

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ABSTRACT

This study was conducted to investigate the influence of the saturating cation on the adsorption of parathion, methyl parathion, fenitrothion, aminoparathion, and paraoxon by montmorillonite suspensions. In all cases the saturating cation distinctly influenced the Freundlich-type adsorption, with adsorption decreasing in the following sequence: Fe³⁺ → Ca²⁺ → Na⁺-montmorillonite. Adsorption of parathion, methyl parathion, fenitrothion and aminoparathion at low concentrations varied inversely with their water solubilities in Na⁺- and Ca²⁺- montmorillonite suspensions, i.e. parathion > fenitrothion > methyl parathion > aminoparathion > fenitrothion > methyl parathion > aminoparathion adsorption. Paraoxon adsorption was slightly greater than the compound with the next lower solubility, aminoparathion. The water solubility of parathion at 20°C was 12.9 µg/ml. Aminoparathion was more than 99.9% adsorbed from solution by Fe³⁺-montmorillonite, suggesting the possibility of protonation of the -NH₂ group by the acidic clay surfaces. In Na⁺- and Ca²⁺-montmorillonite suspensions, there was some conversion of paraoxon to p-nitrophenol. Parathion adsorption-desorption exhibited greater hysteresis effects in Fe³⁺-montmorillonite than in Ca²⁺-montmorillonite. The desorption pathway was dependent only on the initial concentration. The volume of solution removed in each cycle did not alter the desorption pathway, but only the rate at which the desorption proceeded down the desorption isotherm.

Additional Index Words: desorption, isotherm, hysteresis, water solubility, water/methanol injection-GLC(AFID).

TWO PREVIOUS PAPERS (2,9) have extensively reviewed cation interactions with organic compounds, with specific reference to sulfoxide-containing compounds. There have been few reports in the literature of cation effects in soil on the adsorption of parathion or related compounds. Chopra et al. (4) found that parathion adsorption by homoionic soils followed the cationic sequence: H⁺ → Ca²⁺ → Mg²⁺ → K⁺ → Na⁺ - soil. They also found that the percentage of cation saturation in their soils followed the same decreasing sequence and concluded that parathion adsorption on homoionic soils depended directly on the saturation percentage of the various cations. Leenheer and Ahlrichs (10) have shown that H-saturated organic matter and a H-saturated cation exchange resin adsorbed more parathion than the respective Ca-saturated systems. They believed that the H-saturated adsorbents exhibited greater hydrophobic characteristics than the more hydrophilic Ca-adsorbents, thereby accounting for higher insecticide adsorption capacities.

Certain cations can complex with various organophosphorus insecticides. Anhydrous ZnCl₂ forms a 1:1 complex with the P → S group of parathion (3). Bidleman and Frei (1) demonstrated that palladium forms 1:1 complexes with the thiono sulfur of the phosphorodithioate insecticides azinphosmethyl, azinphosethyl, phosmet and dimephenthoate, and a 2:1 complex with the phosphorothioate insecticide, fenthion. They based their conclusions on frequency and intensity

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changes of the P → infrared absorption bands. Grice et al. (6) concluded in an adsorption study of some phosphonates and phosphothionates that the interlayer mineral cations coordinated with the P → O and P → S functional groups. Recently Saltzman and Yariv (13) showed that the interlayer cation in air-dried montmorillonite interacted with the nitro group of parathion via a water bridge mechanism. Mg²⁺- and Al³⁺-montmorillonites also bonded to the P→S group of parathion through a water-bridge mechanism.

The reversibility of the parathion adsorption process varies with the adsorbent. Leenheer and Ahlrichs (10) showed that parathion adsorption on organic matter extracted from soil was reversible whereas Saltzman et al. (12) found a hysteresis effect using natural soils with high organic matter content. After removal of the organic matter with H₂O₂, the adsorptive affinity for parathion decreased, but the hysteresis effect remained.

The objectives of this study were to: (i) examine the effect of the saturating cation on adsorption of parathion and related compounds by aqueous montmorillonite suspensions; (ii) determine if a solubility-adsorption relationship exists for these compounds; and (iii) examine the adsorption-desorption process in some detail using parathion as a model.

MATERIALS AND METHODS

Preparation of Clay

The < 2µm fraction of montmorillonite No. 25, a Wyoming bentonite, was saturated with Na⁺, Ca²⁺, or Fe³⁺ as described elsewhere (2). After washing the clay free of chlorides, it was freeze dried, passed through a 50-mesh sieve and stored over anhydrous P₂O₅.

Purity of Compounds

The purity of parathion and fenitrothion, obtained commercially, was 98.9%. Aminoparathion hydrochloride was purified as follows: after extracting impurities from the hydrochloride salt with hexane, it was dissolved in water and made alkaline with NaOH. Aminoparathion was extracted with CHCl₃, and passed through anhydrous Na₂SO₄ to dry the product. CHCl₃ was subsequently removed. Paranitrophenol was extracted from the paraoxon prior to its use. Technical methyl parathion (approximate analysis - 80% methyl parathion, 16% xylene, 4% other impurities) was used in preliminary work. Purified methyl parathion was obtained by recrystallization (3 times) from methanol at -20°C. This product was used for all adsorption data shown herein. No GLC (ECD or AFID) responses of impurities were found in any of the five compounds.

Table 1- Chemical designations of compounds mentioned in

Compound	Registered trademark	Chemical designation
Aminoparathion		O,O-diethyl O-p-aminophenyl phosphorothioate
Azinphosethyl	Ethyl Guthion®	O,O-diethyl S-(4-oxobenzotriazino-3-methyl)phosphorodithioate
Azinphosmethyl	Guthion®	O,O-dimethyl S-(4-oxobenzotriazino-3-methyl)phosphorodithioate
Dimephenthoate	Cidial®	O,Odimethyl S-[a-(ethoxycarbonyl)benzyl] phosphorodithioate
Fenitrothion		O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate
Fensulfothion	Dasanit®	O,O-diethyl O-[p-(methyl sulfinyl)phenyl] phosphorothioate
Fenthion	Baytex®	O,O-dimethyl 3-methyl-4-methylthiophenyl phosphorothioate
Methyl parathion		O,O-dimethyl O-p-nitrophenyl phosphorothioate
Paraoxon		O,O-diethyl O-p-nitrophenyl phosphate
Parathion		O,O-diethyl O-p-nitrophenyl phosphorothioate
Phosmet	Imidan®	O,Odimethyl S-phthalimidomethyl phosphorodithioate

Generation of Adsorption-Desorption Isotherm Data

For adsorption isotherms aqueous 30-ml aliquots of the appropriate insecticide solution (five concentrations) were added to glass bottles (tin-foil lined screw caps) containing 450-mg freeze-dried montmorillonite clay saturated with Na⁺, Ca²⁺, or Fe³⁺ cations. Each concentration was prepared in triplicate. Samples were tumbled overnight at 20± 1.5°C, and centrifuged for 0.5 hour at 34,800 x g. Appropriate aliquots of the supernatant were taken for GLC analysis.

Desorption studies used the same quantities of aqueous solution and clay as above, but in 150-ml Corex centrifuge tubes with tin-foil lined screw caps. Samples (in triplicate) were shaken for at least 6 hours, and then centrifuged at 6000 x g for 0.5 hour. (Equilibration was attained in < 6 hours.) Twenty or twenty-five milliliter aliquots were transferred from the Corex tubes to 50-ml stainless steel centrifuge tubes and centrifuged again for 15 min, at 34,800 x g. Appropriate aliquots were removed for GLC analysis. Twenty or twenty-five milliliter aliquots of distilled water were added to the samples in the Corex tubes and the samples again shaken for at least six hours. Five desorption cycles were completed.

The second centrifugation step removed traces of clay which could not be separated at the slower speeds to which the Corex tubes were restricted. At the end of the study the clay remaining in each bottle was freeze dried and the amount of clay lost during the experiment accounted for in calculating the x/m values. Generally, < 5% of the clay was lost through the five desorption steps.

Paraoxon was partially degraded to p-nitrophenol in some clay suspensions. For GLC evaluation, the p-nitrophenol was methylated according to a modified (R. A. Chapman, personal communication) methylation procedure of Schlenk and Gellerman (15). Three traps with O-ring sealed delivery tube caps were connected in series with O-ring seal joints to form a sequential glass generator. Nitrogen gas was swept through the unit, entering the first trap containing ethyl ether for

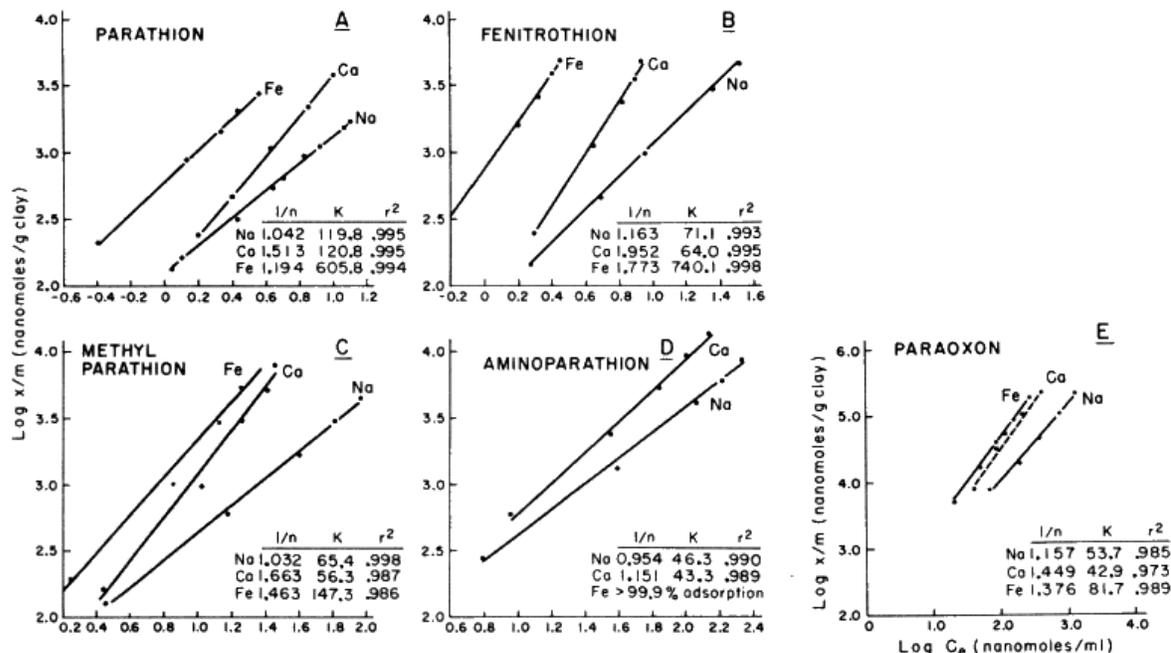


Fig. 1— (A to E) Adsorption isotherms of the five compounds in Na⁺, Ca²⁺, Fe³⁺-montmorillonite suspensions, plotted in Freundlich log-log form.

ether saturation, then bubbled into a second trap containing ethyl ether over 40% aqueous KOH to which N-nitroso-methyl urea was added when diazomethane was required. The diazomethane was swept into the third trap containing ethyl ether over KOH pellets, then into the reaction receptacle. Evolution of diazomethane was allowed to continue until a yellow color persisted in the reaction receptacle (about 2 to 3 min).

An automated GLC system (autosampler, computing integrator) with an alkali flame ionization detector (AFID) injected triplicate samples three times each and the average value was used. Injections giving responses which varied > 3% were rejected and the sample was reinjected. Standards were interspaced among the samples and were also injected in triplicate. All data shown herein were well within the analytical working range of the instrument. With exception of paraoxon, the following procedure was adopted: aqueous supernatant samples and respective standards were diluted with aqueous methanol giving solutions ranging from 40 to 70% methanol in water. The methanol percentage (in samples and standards) was fixed for each compound and was chosen on the basis of the analytical working range on the GLC for each compound. This aqueous methanol mixture was injected directly into the GLC-AFID system. Lower sensitivity and the instability of paraoxon in aqueous methanol solutions necessitated use of the conventional CHCl₃ extraction subsequent removal of CHCl₃, and concentration in hexane. GLC operating parameters were: column, Pyrex glass 183 cm by 2 mm inside Diameter (6.35 mm out-side Diameter); packing, 6% DC-200 and 100/120 mesh Chromosorb 750; column temperature, 190°C; detector, AFID (Rb₂SO₄).

Water Solubility Determinations

An excess of the appropriate compound was weighed into a large glass bottle, distilled water added, and the bottle tumbled at 20 ± 1.5°C for 2 days. For purified methyl parathion, which was the only solid, maximum solubility was attained after shaking for 20 days at 20 ± 1.5°C. Samples were centrifuged in stainless steel tubes at 34,800 x g for 2 hours and suitable aliquots taken for GLC analysis.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms of the five compounds in Na⁺, Ca²⁺, and Fe³⁺-montmorillonite suspensions. The adsorption data fit the Freundlich adsorption equation

$$x/m = KC_e^{1/n} \quad [1]$$

or the linearized logarithmic form

$$\log x/m = \log K + 1/n \log C_e \quad [2]$$

where

x/m = nanomoles of compound adsorbed/g clay,

C_e = equilibrium concentration of compound (nanomoles/ml),

$1/n$ = slope of the log Freundlich equation, and

K = constant, intercept of log equation where $x/m = K$ at $\log C_e = 0$, $C_e = 1$ nanomole/ml.

The adsorption isotherm points were selected so as to cover the solubility range of each compound. This produced isotherm data having an overall range in excess of 3,100-fold. In order to present the data on a uniform scale so that comparisons

could be easily made, the data are presented in the logarithmic form. The coefficient of determination, r^2 , was > 0.973 (Fig. 1) for all transformed isotherm data (log form) indicating a good fit of the data to the linear regression equation (Eq. [2]). All amounts and concentrations involving the five compounds are expressed in molar units (nmoles) to facilitate comparing the adsorption of these compounds on a common basis. The molecular weight of each compound is shown in Table 2.

The saturating cation exhibited a very distinct influence on the adsorption of the compounds (Fig. 1) as it did in an earlier study of fensulfothion adsorption by homoionic Na^+ , Ca^{2+} , and Fe^{3+} -montmorillonite suspensions (2). The adsorption capacity of the montmorillonite decreased in the following saturating cation sequence: $\text{Fe}^{3+} > \text{Ca}^{2+} > \text{Na}^+$.

With exception of the Na-aminoparathion system ($1/n = 0.954$) all slopes of the isotherms were greater than unity, indicating that the normal isotherm was curved upward. Similar, but more pronounced curvatures were exhibited by the various fensulfothion-montmorillonite systems (2).

Often Freundlich isotherm data are compared by ranking the K values for the various adsorbent-adsorbate combinations (7,8,11,14). This practice is quite satisfactory providing either (i) the slopes of the isotherms are similar or (ii) the comparison is to be confined to equilibrium concentrations near 1 nanomole/ml (where $\log C_e = 0$, $C_e = 1$, and $x/m = K$) in which case the slope does not contribute to the x/m value in the Freundlich equation. Had only K been used to rank relative adsorption in the present study, adsorption in the Na-systems would have appeared to have been equal to or greater than that in the respective Ca-systems (Fig. 1). However, the greater slopes of the Ca-systems clearly indicated greater adsorption than in the respective Na-systems at higher equilibrium concentrations, suggesting that the isotherms of the two systems had converged or crossed at low equilibrium concentrations. The example of methyl parathion is shown in Fig. 2.

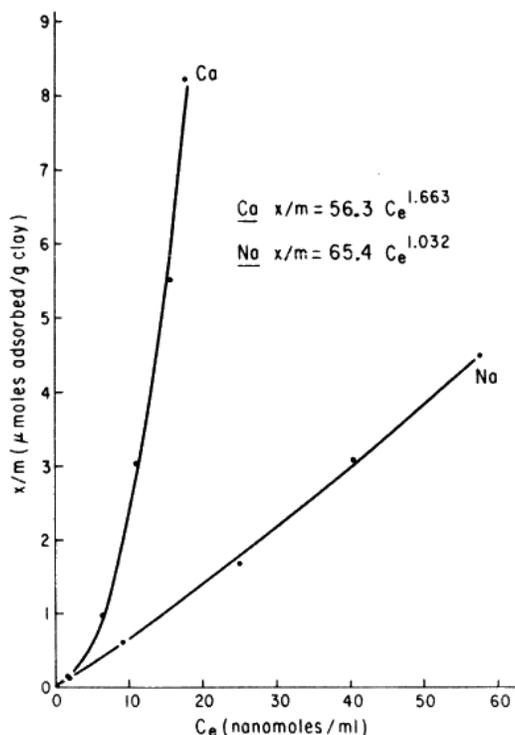


Fig. 2—Adsorption isotherms of methyl parathion in Na^+ - and Ca^{2+} -montmorillonite suspensions.

isotherms crossed at $\log C_e$ (nmoles/ml) = 0.629 and -0.15, respectively. In order to quantitatively evaluate relative adsorption of curvilinear isotherms in relation to other factors such as water solubility, concentration values (C_e) were arbitrarily selected at which to evaluate adsorption (x/m): (i) $C_e = 1.0$ nmole/ml. and (ii) $C_e = 10$ nmoles/ml. At $C_e = 1.0$, $\log C_e = 0$, and $x/m = K$; at $C_e = 10$, $\log C_e = 1.0$ and $\log x/m = \log K + 1/n$. Thus the adsorption values required for evaluation were the already available log regression equation constants. In the Na- and Ca- systems at $C_e = 1.0$ nmole/ml, there was a distinct inverse relationship between water solubility and adsorption, with the exception of paraoxon, where the

Table 2—Molecular weight and water solubility of the five compounds.

Compound	Molecular weight	Solubility (20°C)	
		nmoles/ml	μg/ml
Aminoparathion	261.3	1,493.0	390.0
Fenitrothion	277.2	91.6	25.4
Methyl parathion-technical	263.2	212.8	56.0
-purified	263.2	171.0	45.0
Paraoxon	275.2	11,810.0	3,250.0
Parathion	291.3	44.3	12.9

Slopes of Ca-isotherms for the five compounds were greater than slopes of either the Na- or Fe-isotherms. In addition to the crossovers for the Na- and Ca-isotherms, the regression equations suggested the possibility of crossover in the Ca- and Fe-isotherms at high concentrations. Since this was not confirmed experimentally and because it would occur above practical concentration ranges, it was not considered further. In the concentration range of interest, the larger K values for the Fe-systems always positioned Fe-isotherms above Ca-isotherms.

Solubility of parathion in water was 12.9 μg/ml (44.3 nmoles/ml) at 20°C (Table 2) in contrast to the widely quoted value of 24 μg/ml at 25°C. Yaron and Saltzman (16) quoted a value of 4.3 μg/ml at 10°C. M. Yang³, using this value, calculated that the water solubilities should be 5.7, 7.2, and 8.6 μg/ml at 20, 30, and 40°C, respectively. The solubility value of Yaron and Saltzman (16) seems low, perhaps because only 1 hour was allowed to reach equilibrium at 10°C, where kinetic processes could be expected to be considerably retarded (relative to 20°C). The solubility for fenitrothion was about 15% < the 30 μg/ml quoted by Eto (5). The solubility of technical grade methyl parathion was essentially the same as that quoted by Eto (5) (56 μg/ml). However, the solubility of the purified methyl parathion was only 45 μg/ml. The presence of xylene or other unidentified impurities appear to have enhanced the water solubility of the technical product. Adsorption isotherms for the technical grade methyl parathion indicated that it was adsorbed less by the three montmorillonite systems than was purified methyl parathion. This is an example where sample purity affected two parameters (adsorption, solubility) commonly used to characterize insecticide behavior in soil systems.

Relative adsorption of the five compounds within each clay system is tabulated in Table 3. In the Ca- and Fe-systems, parathion and fenitrothion

adsorption was equal to or slightly greater than that for methyl parathion, although its solubility was 72 times greater. In the Fe-systems at $C_e = 1.0$, and all three cation-systems at $C_e = 10$ nmoles/ml, there was no consistent relationship between solubility and adsorption.

The only degradation observed in the adsorption studies was with paraoxon in the Na^+ - and Ca^{2+} -montmorillonite suspensions. Equilibrium solutions in these systems developed a yellowish color after overnight mixing, which was confirmed to be p-nitrophenol. Less than 2% of the paraoxon was converted to p-nitrophenol in the Na- and Ca-systems.

Only a trace of p-nitrophenol was detected in the Fe^{3+} -montmorillonite suspension, perhaps because of the greater acidity.

It was noted in the introduction that parathion adsorption appears to be more reversible in some instances than in others. Figure 3 shows the desorption of parathion from Ca^{2+} - and Fe^{3+} -montmorillonite suspensions. Desorption curves for the Fe^{3+} -montmorillonite were obtained using 20-ml-removal aliquots in each cycle. Because of the high degree of adsorption (> 90%) the five desorption cycles removed only a limited amount of parathion. Consequently 25-ml-removal

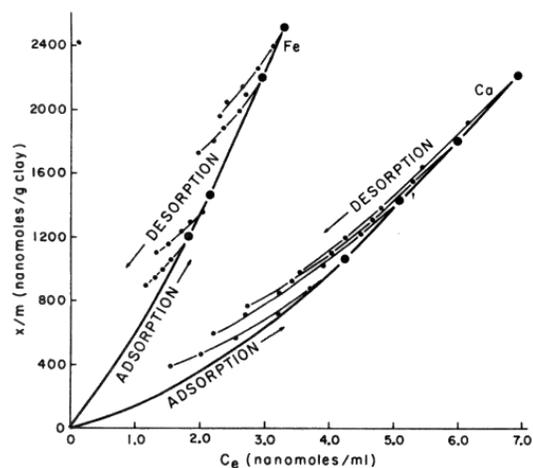


Fig. 3—Desorption isotherms of parathion in Ca^{2+} - and Fe^{3+} -montmorillonite suspensions.

rates were used when generating desorption curves in the Ca^{2+} -montmorillonite system. For comparison purposes it was confirmed that the desorption pathway was independent of the solution volume removed in each cycle (15, 20, 25-ml).

The desorption curves of parathion of Fe^{3+} -montmorillonite exhibited greater hysteresis effects than on Ca^{2+} -montmorillonite, although it is difficult to fully compare the systems because of the restricted range of the Fe^{3+} -montmorillonite curves. Initial desorption points in Ca-system tended to leave the adsorption curve in a somewhat asymptotic manner, thus exhibiting a minimal hysteresis effect until the second or third cycle. M. Yang³, in a parathion desorption study of two soils, generated one desorption point from each of four initial concentrations, and joined them to create a desorption curve. His data give the misleading impression that starting a desorption process with several different concentrations produces only one desorption isotherm (for a given temperature). Had this procedure been followed with the Ca^{2+} -montmorillonite in the present study, no significant hysteresis effect would have been observed. The Ca^{2+} -montmorillonite system exhibited its greatest hysteresis effect in the lower concentration range where the adsorption isotherm slope increased at the fastest rate. The adsorption isotherm in the Fe-system was not as curvilinear as in the Ca-system and the hysteresis effect seemed to occur more consistently over the concentration ranges studied. In general three points were observed: (i) the desorption path was dependent only on the initial concentration; (ii) the rate of removal in each cycle changed the desorption rate, but not the desorption pathway; and (iii) parathion exhibited greater hysteresis effects in Fe^{3+} -montmorillonite than in Ca^{2+} -montmorillonite suspensions.

In summary it has been found that parathion, and the four related compounds produced curvilinear adsorption isotherms fitting the Freundlich equation, but which required the use of both isotherm constants, K and $1/n$ to rank the adsorption of the compounds in the three clay systems. The compounds (excepting paraoxon) exhibited an inverse relationship between adsorption and solubility in the Na^+ - and Ca^{2+} -montmorillonite systems at $C_e = 1.0$ nmole/ml, but departed from this relationship in the other systems at $C_e = 1, 10$ nmoles/ml. The Fe^{3+} -montmorillonite suspension almost completely adsorbed aminoparathion from solution. It seems likely that the interaction occurred between the saturating Fe^{3+} cation (or hydrated cation) and the $-\text{NH}_2$ functional group, perhaps resulting in a protonated or H-bonded form. Parathion adsorption-desorption on Ca^{2+} - and Fe^{3+} -montmorillonite exhibited hysteresis effects, with the greater hysteresis in the Fe^{3+} -montmorillonite. Further in-depth studies are in progress on other aspects of organophosphorus insecticide adsorption in clay systems.

Table 3— Relative adsorption of the five compounds by Na^+ , Ca^{2+} , and Fe^{3+} -montmorillonite.†

<u>Na^+ - montmorillonite</u>	
Parathion > fenitrothion > Me-parathion > NH_2 -parathion paraoxon	
<u>Ca^{2+}-montmorillonite</u>	
Parathion > fenitrothion ($\log C_e < 0.629$)	
Fenitrothion > parathion ($\log C_e > 0.629$) > Me-parathion > paraoxon > NH_2 parathion	
<u>Fe^{3+}-montmorillonite</u>	
parathion > fenitrothion ($\log ce < -0.15$)	
NH_2 parathion » fenitrothion > parathion ($\log Ce > -0.15$) > Me-parathion > paraoxon	

† Relative adsorption comparisons were made only within the range of experimental data.

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