Effect of Fulvic Acid on Adsorption of Methyl Parathion and Parathion by Ca^{2+}- and Fe^{3+} - Montmorillonite Suspensions. [1]

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ABSTRACT

A study was conducted to examine the effect of fulvic acid (FA) on the adsorption of methyl parathion and parathion by Ca^{2+}- and Fe^{3+}-montmorillonite suspensions, and to determine whether FA in solution could alter the water solubility of these insecticides. FA, in the 10- to 100-mg/liter range, did not affect the water solubility of the two insecticides. In Ca^{2+}-montmorillonite suspensions, increasing FA concentrations first enhanced methyl parathion adsorption, followed by adsorption decrease at higher FA levels. Methyl parathion adsorption in Fe^{3+}-montmorillonite suspensions decreased, with increasing FA levels. Parathion adsorption was not significantly altered in either clay suspension. The order in which the FA, clay, and insecticide were mixed affected methyl parathion adsorption. The greatest effects were observed where FA was adsorbed by the clay before the insecticide solutions were added. FA adsorption by Ca^{2+}-montmorillonite fitted the Freundlich isotherm, whereas the much greater adsorption by Fe^{3+}-montmorillonite fitted the Langmuir isotherm. Although both $CaCl_2$ and $FeCl_3$ solutions greatly enhanced FA removal by their respective clay suspensions (even at low concentrations), parathion adsorption was not affected. The presence of FA in the $FeCl_3$-Fe^{3+}-montmorillonite suspensions appeared to prevent parathion degradation.

Additional Index Words: solubility, isotherm.

THE CLAY AND ORGANIC MATTER fractions of soil are two prime factors influencing pesticide adsorption (1). Although there have been numerous published studies of herbicide adsorption by clays (7,9,12,20,25,34) and by organic matter (8,9,16,24,30,31) there are relatively few reported studies of insecticide adsorption by clays (3,5,9,23,37,42) and by organic matter (9,27,35). These laboratory adsorption studies have provided valuable information about the relative affinity of pesticides for clays and organic matter, but as with any model system, only a limited amount of extrapolation is possible to pesticide behavior in natural soil systems.

The next logical step is to expand the model system to include clay-organic matter adsorbents. There has been considerable recent activity in investigating the nature of organo-clay associations, both natural and artificial (17,18,38). The role of cations in organic matter associations has received particular emphasis (14,19,39,40). Most of the studies employing organo-clay adsorbents investigated the adsorption of phenols or 2,4-D (2,4-dichlorophenoxy acetic acid) (11,28,29,36,41). Miller and Faust (28,29) used as their adsorbents, a number of organic cations and benzyl or aliphatic amines adsorbed to a Wyoming bentonite. They found that organo-clays adsorbed considerably greater amounts of 2,4-D, or phenols than did the clay alone. Organo-clays using an organic amine having both an aromatic and long aliphatic component were more effective adsorbers of 2,4-D than were those clays with only an aromatic or aliphatic component (28). Wang et al (43) studied the adsorption of parathion by montmorillonite and kaolinite clays in the presence of a secondary organic adsorbate (rhodamine B, methylene blue, or phenol). Parathion adsorption was enhanced two-to fourfold by the presence of rhodamine B, while methylene blue and phenol had little or no effect. However, some of their results appear suspect because of low centrifugation speeds (1,500 x g) which were incapable of removing fine clay from equilibrium solutions. This would allow some of the parathion adsorbed to fine clay to be analyzed as being in the equilibrium solution.

Khan (26) used a fulvic acid (FA)-clay adsorbent while studying adsorption of 2,4-D from aqueous solution. He prepared a high ratio FA/Na-montmorillonite adsorbent (62% clay, 37% FA) and dried it prior to the adsorption process. Khan observed that the FA-montmorillonite complex adsorbed less 2,4-D than Haque and Sexton (21) reported for a humic acid (HA) adsorbent, but greater than for the clay alone.

In certain instances there appears to be an inverse relationship between pesticide solubility and adsorption (5,9). Wershaw et al. (44) found that the soluble salts of HA lowered the surface tension of water thereby increasing DDT [1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane] solubility by 20-fold (for 0.5% Na-humate). However, the solubility measurements of DDT reported by Wershaw were near 40 ng/m for filtered samples, 33 times greater than the widely accepted value of 1.2 ng/ml reported by Bowman et al (6). It is not known whether this discrepancy was consistent throughout the study for the measurement of DDT solubility in the presence of 0.5% Na humate. It is difficult to ascertain the practical significance of these results since dissolved organic matter in natural waters does not tend to exceed 80-100 mg/liter (33) compared with 5000 mg/liter (0.5%) in this study. Ballard (2) has also reported that DDT in forest soils was solubilized by HA when the soils were fertilized with urea. The urea appeared to disperse the HA.

It was the purpose of this study to investigate (i) the possible influence of FA on the water solubility *of* parathion and methyl parathion, (ii) the role *of* FA on the adsorption of parathion and methyl parathion by montmorillonite suspensions, and (iii) possible salt effects ($CaCl_2$, $FeCl_3$) in the FA-montmorillonite-parathion adsorption systems.

MATERIALS AND METHODS
Clay Preparation
The <2 µm fraction of montmorillonite no. 25, a Wyoming bentonite, obtained from Ward's Natural Science Establishment, Rochester, N.Y., was used in this study. The clay was saturated with either Fe^{3+} or Ca^{2+} using the batch technique (3), freeze-dried, and stored over anhydrous P_2O_5.

Insecticide Purity
Recrystallized methyl parathion and commercially available parathion (98.9% purity), as used in an earlier study (5), were used.

Fulvic Acid (FA)
The FA, from a Podzol soil, was kindly supplied by Dr. D. S. Gamble, Soil Research Institute, Canada Agriculture, Ottawa, Ontario. The preparation and characterization of the FA has been previously reported (13). The freeze-dried preparation was stored over anhydrous P_2O_5.

Solubility Studies
To aqueous solutions of FA (0,10,20,50, and 100 mg/ml) were added methyl parathion or parathion at rates approximately five fold in excess of their respective solubilities at 20ºC (5). The pH was governed by the FA concentration in solution (for zero FA system ≈ pH 6, for 100 mg FA/ml ≈ pH 3-3.5). Samples were tumbled for several days at 20ºC. Periodic sampling and analyses performed on each sample until no further changes in concentrations occurred. Samples were centrifuged at 34,800 x g for 3 hours prior to taking supernatant aliquots for gas-liquid chromatography (GLC) analysis. Samples were injected directly as a 1:1 water to methanol mixture as previously reported (5). An alkali flame ionization detector (AFID) with a rubidium sulfate pellet was used to detect both insecticides.

Adsorption Studies
(A) FA-INSECTICIDE-CLAY
The effect of FA on insecticide adsorption by Fe^{3+}- and Ca^{2+}-montmorillonite suspensions was examined using the following four methods of preparation (each in triplicate) to determine whether the order of addition of FA and insecticide to the clay suspension affected the adsorption of the insecticide. The tumbling time required to attain sample equilibrium was < 12 hours. Tumbling times were varied from 18 to 48 hours to accommodate physical requirements of the experiments such as two-step adsorption procedures. The pH of the systems was governed by the saturating cation and the FA content (in supernatants pH ranged from 4.85 for zero FA to 3.65 for Fe^{3+}-montmorillonite suspension).

Method 1— To each of 12 bottles, add: 450 mg of clay; 0, 5, 10, or 20 mg of FA; and 15 ml distilled water. Tumble for 24 hours. Fifteen-milliliter aliquots of 40 µg/ml methyl parathion or 10 µg/ml parathion solutions were added to the 15-ml FA-clay suspensions and tumbled for 18 hours (20ºC).

Method II— To each of 12 bottles. 450 mg of clay and 30-ml aliquots of either 20 µg/ml methyl parathion or 5 µg/ml parathion solutions were added and tumbled for 24 hours. Fulvic acid was then weighed into these samples at the following rates: 0, 5, 10, or 20 mg/bottle. Samples were then tumbled for an additional 18 hours (20ºC).

Method III — To each of 12 bottles, add: 450 mg clay; 0, 5, 10, or 20mg of FA; and 30 ml of either 20 µg/ml methyl parathion or 5 µg/ml parathion solutions. Tumble for18 hours (20ºC).

Method IV — Fulvic acid-clay adsorption complexes were prepared in sufficient quantities for both methyl parathion and parathion adsorption studies (in triplicate). The following ratios were maintained during preparation (similar to Methods I to III): 450 mg clay: 0, 5, 10, 20, or 30 mg FA: 30 ml volume. These FA-clay suspensions were tumbled for 48 hours (20ºC), then centrifuged to remove the supernatant. The FA-clay complexes were freeze-dried, crushed to pass a 40 mesh sieve, and stored over anhydrous P_2O_5. Thirty-milliliter aliquots of 20 µg/ml methyl parathion or 5 µg/ml parathion solutions were added to 450 mg samples of the five FA-clay complexes (0, 5, 10, 20, 30 mg FA/450 mg clay) and tumbled for 18 hours (20ºC). The supernatant FA solutions from the centrifuged FA-clay suspension, during the preparation procedure, were analyzed by ultraviolet (UV) spectroscopy (465 nm) to estimate, by difference, the amount of FA adsorbed by the clay.

(B) SALT-FA-PARATHION-CLAY ADSORPTION.
The effect of dilute $FeCl_3$ and $CaCl_2$ solutions on the behavior of the FA-parathion-clay system was examined. $FeCl_3$ and $CaCl_2$ solutions were used only with Fe^{3+}- and Ca^{2+}-montmorillonite suspensions, respectively. The following ratios were maintained: 450 mg clay:10 mg FA:30 ml of salt solution (0, 0.005, 0.05, 0.1M) containing 5 µg/ml parathion. These samples (in triplicate) were tumbled for 18 hours.

After tumbling, samples from all of the above methods were centrifuged for 20 min at 34,800 x g, and supernatant aliquots were taken for GLC-AFID analysis as outlined previously (5).

RESULTS AND DISCUSSION
Solubility Studies
Fulvic acid, in the 10–100 mg/liter range, appeared to have no significant effect on water solubility of either methyl parathion or parathion. This range of FA concentrations encompassed the naturally occurring FA content of river water (33). The concentration of FA in this study was probably insufficient, or not in the appropriate form (i.e. Na^+-form), to affect the surface tension of the solution as Wershaw reported (44). The possible effect of humic acid, in this concentration range, on insecticide solubility has not yet been reported. Thus, it seems unlikely that FA would affect the adsorption of methyl parathion or parathion to clays by formation of soluble complexes which might possess different affinities for clay surfaces.

Adsorption Studies
(A) FA-CLAY ADSORPTION STUDIES
The adsorption of FA by Ca^{2+}- and Fe^{3+}-montmorillonite suspensions was investigated in connection with the preparation of FA-clay complexes used in Method IV, Part B of this discussion. The amount of FA adsorbed by the two clays was determined spectrophotometrically (465 nm) obtaining the difference between the absorbance of the original FA solution and the supernatant equilibrium solution. Implicit in this method was the assumption that the UV spectrum (in the 465 nm region) of the equilibrium FA solution was the same as that of the original FA, from which the analytical standards were made. Should certain UV absorbing fractions of FA be preferentially adsorbed, errors would be introduced into the resulting adsorption isotherms (Fig. 1).
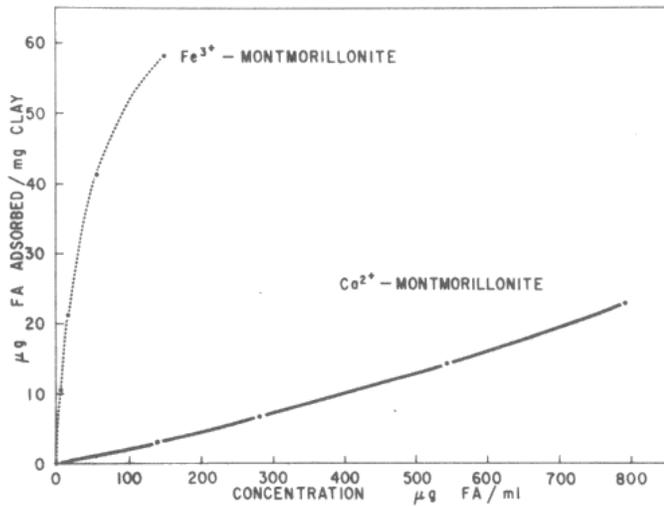
Fig. 1 — Adsorption isotherms of FA in Ca^{2+}- and Fe^{3+}-montmorillonite suspensions.

The FA isotherm for Ca^{2+}-montmorillonite was best characterized by the linearized logarithmic form of the Freundlich equation

$$\log x/m = \log K + \log C. \tag{1}$$

where

x/m = µg FA adsorbed per mg clay;
C = equilibrium FA concentration, µg/ml;
$\log K$ = intercept at $\log C = 0$, $C = 1$ µg/ml; and
$1/n$ = slope of log isotherm.
The data took the form

$$\log x/m = -1.86 + 1.11 \log C \text{ and} \tag{2}$$
$$r^2 = 0.998.$$

FA was much more strongly adsorbed by Fe^{3+}-montmorillonite, producing an isotherm concave toward the x/m axis. The linearized logarithmic Freundlich equation for this isotherm was

$$\log x/m = 0.583 + 0.564 \log C \text{ and} \tag{3}$$
$$r^2 = 0.959.$$

However, a much better fit of this data was produced by the Langmuir adsorption equation for monolayer adsorption on a surface

$$1/x/m = (1/ab)(1/C) + 1/b, \tag{4}$$

where x/m and C are the same as in Eq. [1], b = monolayer capacity of FA on the clay, and a = adsorption energy-related constant. The data took the form

$$1/x/m = 0.648/C + 0.0115, \tag{5}$$

Table 1 — Amounts of FA adsorbed by Ca^{2+}- and Fe^{3+}-montmorillonite suspensions, relative tothe amounts added. †

Suspension	mg FA added/450 mg clay			
	5	10	20	30
	mg adsorbed/450 mg clay			
Ca^{2+}-montmorillonite	1.5	3.0	6.45	10.17
Fe^{3+}-montmorillonite	4.82	9.59	18.63	26.2

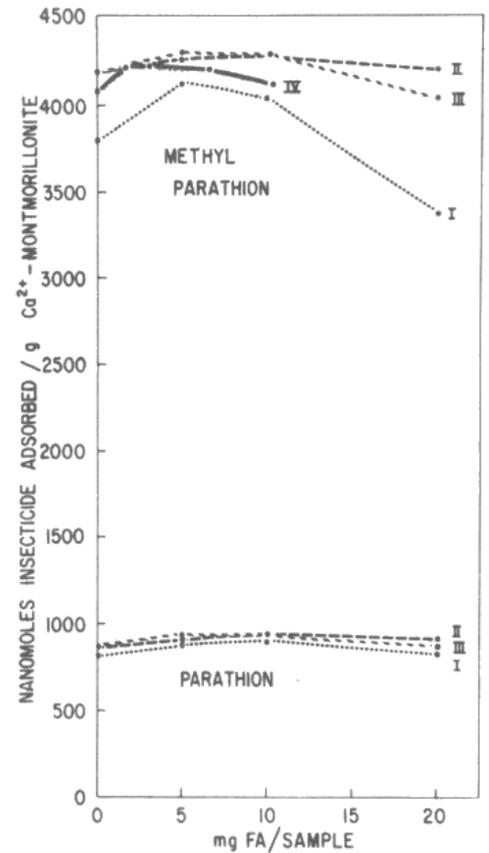† FA-clay samples freeze-dried for use in Method IV.

Fig. 2— Effect of FA and preparation methods (I - IV) on methyl parathion and parathion adsorption by Ca^{2+}-montmorillonite suspensions.
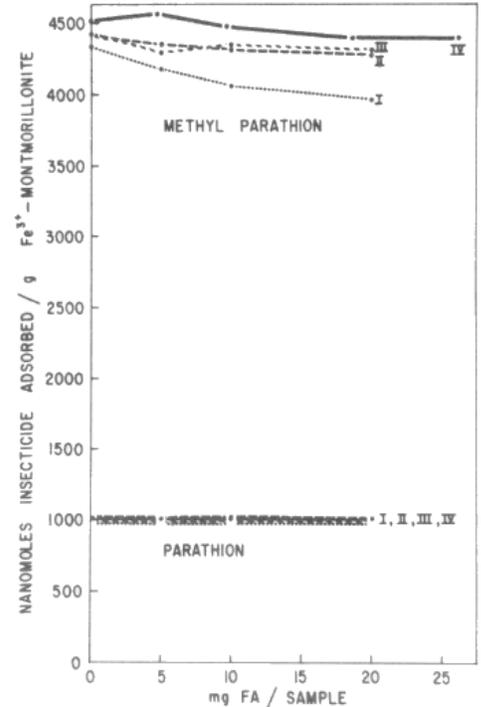

Fig. 3— Effect of FA and preparation methods (I - IV) on methyl parathion and parathion adsorption by Fe^{3+}-montmorillonite suspensions.

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Table 2— Largest calculated least significant difference [lsd (0.051] values for each insecticide-clay-FA system.

System	Largest lsd (0.05), nmoles/g
Ca-mont.-parathion-FA	86
Fe-mont.-parathion-FA	18
Ca-mont.-Me-parathion-FA	124
Fe-mont.-Me-parathion-FA	129

b = 86.96 µg/g = monolayer capacity,
a = 0.0178, and
r^2 = 0.992.

According to the isotherm classification of Giles et al. (15), FA adsorption by Ca^{2+}-montmorillonite produced an S-type isotherm, suggesting that FA molecules associated with each other, thereby increasing the adsorption tendency with increasing concentration.

They also suggested that the adsorbing molecules usually packed vertically in S-type isotherms. Fulvic acid adsorption by Fe^{3+}-montmorillonite produced the L-type isotherm, where the adsorbed molecules were most probably adsorbed flat on the clay surface, or where there was no strong competition from the solvent for adsorption sites. X-ray diffraction analysis of the Ca^{2+}- and Fe^{3+}-montmorillonite-FA samples of Method IV, under a dry N_2 atmosphere (3), indicated that there was no interlamellar adsorption of the FA at any of the levels examined. The great differences in FA adsorption between the two clays must be attributed to the nature of the two saturating cations, and their effect on aggregation of the colloidal clay particles. It is known that the saturation of montmorillonite by Fe^{3+} creates ferric hydroxy interlayer compounds (10, 22). These complexes could conceivably coat some of the external surfaces of the clay as well, thereby modifying their adsorption characteristics for organic compounds. Table 1 shows the relative amounts of FA adsorbed by Ca^{2+}- and Fe^{3+}-montmorillonite used in Method IV, in relation to the amounts of FA added per sample (450 mg). These amounts are plotted on the abcissa of Fig. 2 and 3 for Method IV. It should be also noted that these adsorption values also approximated the amount of FA adsorbed by the two clay suspensions in Methods II and III.

(B) FA-INSECTICIDE-Clay Adsorption Studies

Figures 2 and 3 show the effects that FA and the method of preparation had on methyl parathion and parathion adsorption by Ca^{2+}- and Fe^{3+}-montmorillonite suspensions. FA appeared to slightly enhance adsorption of both insecticides in the Ca^{2+}-montmorillonite suspensions at the lowest FA level (5 mg/450 mg clay, Fig. 2). However the lsd (0.05) values of Table 2 suggest that this increase was significant for only Methods I and IV for methyl parathion. There was a significant increase in adsorption in Methods II and III at higher FA levels (relative to the zero FA level). At higher FA levels, there was a decrease in adsorption, especially for Methods I, III, and IV which could be ascribed to competitive effects between FA and methyl parathion. Throughout the study, Method I always gave the lowest insecticide adsorption at the zero FA level. Similar observations were made in earlier studies of fensulfothion adsorption by clay suspensions (3,4) where greater adsorption occurred when the insecticide solution was added to dry clay than to clay suspensions.

FA appeared to have no effect on parathion adsorption in Fe^{3+}-montmorillonite suspensions over the concentration ranges examined (Fig. 3). In general, increasing FA concentration tended to decrease methyl parathion adsorption by Fe^{3+}-montmorillonite suspensions (Fig. 2) with one exception in Method IV, where there was a slight enhancement at the lowest FA level. The lsd (0.05) value (Table 2) suggests that: (i) there was no significant difference between Methods II and III, and (ii) only the adsorption values at the highest FA level, in Methods II and III, were significantly less than their respective zero FA adsorption levels. In both Ca^{2+}- and Fe^{3+}-systems, Method I produced the greatest FA effect on methyl parathion adsorption, suggesting that the introduction of FA to the clay suspension before the insecticide resulted in a different, and/or greater interaction than if it was introduced simultaneously or after the insecticide. There was no effect of FA upon parathion adsorption by both clays using Method IV. The results were the same as those shown for parathion by the other preparation methods. The process of drying FA on the clay surfaces, at the levels examined, did not essentially alter the properties of the surface for parathion adsorption. It should be noted that one possible reason that methyl parathion, and not parathion, was affected by FA was because the concentration of methyl parathion was four times that of parathion (20 vs. 5µg/ml). The experiments were set up so as to have both insecticides at levels approximating 50% of their water solubility. Perhaps a more equitable comparison would have been made using identical concentrations.

The nature of the methyl parathion interaction with FA and the montmorillonite suspensions is not clearly evident from these data. The only major difference in methyl parathion adsorption between the Ca^{2+}- and Fe^{3+}-montmorillonite-FA systems was the increase in adsorption at low FA levels in the Ca-system. This difference may be attributed to cation effects, and/or the presence of surface-adsorbed hydrous oxides on the Fe^{3+}-montmorillonite formed when the clay was saturated. The adsorption mechanism for methyl parathion by both clays is probably similar to the parathion adsorption mechanism proposed by Saltzman and Yariv (37), namely H-bonding through hydration water molecules of the saturating cation to functional groups of the insecticide i.e. P→S group. They did not consider the possible effects that surface-adsorbed hydrous Al or Fe oxides might have had on adsorption.

Although insecticide adsorption by montmorillonite occurs via the above mechanism at low concentrations, the nature of the adsorption isotherms (Freundlich slope > 1.0)(5) suggests a "secondary" adsorption mechanism involving cooperative adsorption at higher concentrations. One could visualize incoming insecticide molecules being attracted by those molecules already held to the clay by H-bonding. In advanced stages of this process, thin films of liquid insecticide would tend to coalesce on and between the clay particles in a fashion somewhat analogous to capillary condensation phenomena. In the Ca^{2+}-montmorillonite system, adsorbed FA molecules (at low concentrations) may have enhanced methyl parathion adsorption via the "secondary" adsorption mechanism.
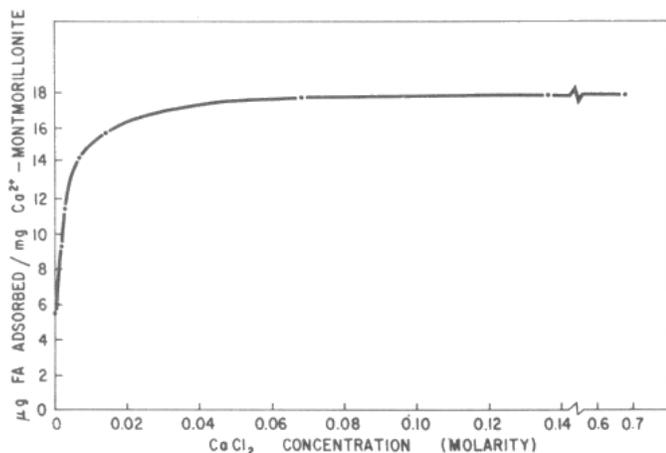
Fig. 4— Effect of CaCl$_2$ on FA removal in Ca^{2+}-montmorillonite suspensions.

The upward curve of the FA isotherm on Ca^{2+}-montmorillonite (Fig. 1) also supports this notion of a cooperative adsorption mechanism for FA. However in the Fe-system FA seemed to be much more strongly adsorbed than in the CA-system (Fig. 1). Consequently FA would compete much more strongly for adsorption sites with methyl parathion than in the Ca-system. At low FA concentrations, FA molecules may have assumed a nonfavorable orientation for "secondary" adsorption of methyl parathion as proposed for the Ca-system, and therefore no enhancement of methyl parathion adsorption was observed. In fact, just the opposite occurred and less methyl parathion adsorption occurred relative to the Fe^{3+}-montmorillonite alone. At higher FA levels in both Ca- and Fe-systems, methyl parathion adsorption may have been suppressed through competitive effects of the FA molecules, or alternately a rearrangement of surface-adsorbed FA molecules which was less favorable for methyl parathion adsorption.

(C) SALT-FA-PARATHION-CLAY ADSORPTION STUDIES

Dilute CaCl$_2$ or FeCl$_3$ solutions were introduced to the FA-parathion-Ca^{2+}-, and Fe^{3+}-montmorillonite systems, respectively, to simulate naturally occurring soil solutions which often have total electrolyte concentrations in the 0.01M region (32). Figure 4 shows that FA removal by the Ca^{2+}-montmorillonite suspension increased very rapidly with increasing CaCl$_2$ concentration to a maximum near 0.1M. There was a 67% increase in FA removal (compared with distilled water) at the lowest CaCl$_2$ level examined (0.001M). At the naturally occurring soil solution electrolyte level (0.01M), there was a 2.83-fold increase in FA removal over the control. The FA removal was a combination of adsorption by Ca^{2+}-montmorillonite and a precipitation reaction due to decreased solubility of the Ca^{2+}-saturated FA. There is no data presently available indicating whether the precipitated FA formed a distinct separate phase, or whether it was intimately associated with clay surfaces i.e., surface coatings. In spite of this marked effect of CaCl$_2$ on FA removal by Ca^{2+}-montmorillonite suspensions, there was no significant effect on parathion adsorption. A series of controls of varying salt concentrations (no FA), used as a reference indicated that there was; (i) no salt effect on parathion adsorption by Ca^{2+}-montmorillonite, and (ii) slightly less parathion adsorption in the absence of FA, as was noted earlier from Fig. 1.

FeCl$_3$ solutions also appeared to cause markedly increased FA removal by Fe^{3+}-montmorillonite suspensions but unfortunately this could only be confirmed visually (color removal) since FeCl$_3$ solutions absorbed very strongly in the 465 nm region (CaCl$_2$ solutions did not absorb significantly at 465 nm) where the FA concentrations were determined. Essentially all color due to FA was removed by all FeCl$_3$ solutions examined. As noted with CaCl$_2$ solution, FeCl$_3$ solutions had no apparent effect on parathion adsorption (in the presence of FA) despite the great increase in FA adsorption. However, it was noted that in the control samples (no FA) that there was a rapid disappearance of parathion, directly related to the FeCl$_3$ concentration. Apparently the presence of the FA in solution inhibited the degradation, perhaps by complexing with the Fe^{3+} ions in solution. Parathion was rapidly converted to paraoxon with p-nitrophenol content gradually increasing with time.

In summary the following facts were observed in this study:

1. FA, in the 10 - 100 mg/liter range, had no effect on the water solubility of methyl parathion or parathion at 20ºC,
2. In the Ca^{2+}-montmorillonite suspensions, increasing FA concentrations first enhanced methyl parathion adsorption, followed by adsorption decreases at higher FA levels. Methyl parathion adsorption in Fe^{3+}- montmorillonite suspensions tended to decrease with increasing FA levels. FA did not significantly affect parathion adsorption in either Ca^{2+}- or Fe^{3+}-montmorillonite suspensions.
3. The order in which FA and methyl parathion were added to the Ca^{2+}- and Fe^{3+}-montmorillonite suspensions affected methyl parathion adsorption, but not parathion adsorption. Essentially the same amount of methyl parathion was adsorbed when parathion was adsorbed before FA, as when parathion and FA were added simultaneously to the clay suspension.
4. The adsorption of FA by Ca^{2+}-montmorillonite fitted the Freundlich isotherm, whereas the much greater adsorption by Fe^{3+}-montmorillonite fitted the Langmuir isotherm better.
5. Although both CaCl$_2$ and FeCl$_3$ solutions greatly enhanced FA removal by their respective clay suspensions, parathion adsorption was not affected. The removal of FA from those dilute salt solutions by the clay suspensions was believed to be a combination of adsorption by the clay and a precipitation reaction due to the formation of insoluble Ca^{2+}- and Fe^{3+}-FA complexes. Parathion was degraded quite rapidly in the FeCl$_3$ -montmorillonite suspension, but not when FA was present in the system.

The results of this study suggest that in certain instances, FA can increase or decrease insecticide adsorption by montmorillonite suspensions, depending on FA concentration, and the saturating cation. Further studies on insecticide-FA-soil component systems are currently in progress.

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