

Table I. Effect of Preincubation of Methylparathion or Soil with Some Clay Minerals on Soil Methylparathion Hydrolyzing Activity

Clay mineral	Preincubation of methylparathion, <sup>a</sup> act., nmol of PNP/h per g of soil		Preincubation of soil, <sup>b</sup> act., nmol of PNP/h per g of soil	
	1 g of clay	2 g of clay	1 g of clay	2 g of clay
Control <sup>c</sup>	56	56	56	56
Kaolinite	54	46	38	36
Bentonite	49	34	34	32
Vermiculite	34	23	32	23
Illite	47	33	33	29
Attapulgite			44	30

<sup>a</sup> Sterilized clay minerals were preincubated with methylparathion for 10 h before addition of the soil. Methylparathion hydrolyzing activity was assayed as described under Materials and Methods. <sup>b</sup> Sterilized clay minerals were preincubated with soil for 10 h before addition of methylparathion. Methylparathion hydrolyzing activity was assayed as described under Materials and Methods. <sup>c</sup> Controls were carried out by incubation of methylparathion and soil without addition of clays.

minerals with soil for 10 h before the addition of methylparathion on its hydrolysis is shown in Table I. Controls of sterilized clays and methylparathion showed no activity. The effect of sterilized clay minerals in reducing or inhibiting methylparathion hydrolyzing activity is in harmony with the results of McLaren and Peterson (1967) and Galstyan et al. (1968). Aomine and Kobayashi (1964) found that aliphatic clay inhibited protease, amylase, and cellulase. Clays were found to inhibit glucose oxidase and invertase (Zviaginstev and Velikanov, 1968). Galstyan et al. (1968) reported that the most active fractions of soil particles in fixing added enzymes were silts and clays. In this study kaolinite had the smallest effect which might be attributed to its smaller surface area. Methylparathion is known to have a dipole with cationic

and anionic nature (Yaron and Saltzman, 1972). It may be suggested that both the clay and substrate compete for the same active sites of the enzyme. Since it is highly unlikely that the enzyme was transferred from soil to clay, the probable explanation is that adsorption of the substrate on the clay reduced the reaction rate. The nature of the substance in soil that hydrolyzes methylparathion to yield *p*-nitrophenol is under investigation. Its biotic nature, however, is suggested by the fact that neither sterilized pure clays nor autoclaved soil exhibited the capacity to hydrolyze methylparathion. Enzymes are a possible explanation for the biotic substances which could be derived from decaying vegetation or microorganisms.

The results of the present investigation suggest that methylparathion hydrolyzing activity might be attributed to soil enzymes; however, the possibility of nonenzymatic activity cannot be completely ruled out.

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## Studies on the Adsorption and Interaction of 1,2-Dibromo-3-chloropropane. I. With Montmorillonites

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The adsorptive behavior of 1,2-dibromo-3-chloropropane on montmorillonite suspensions as affected by saturating cations yielded H class isotherms. Rapid initial adsorption pointed to chemisorption. The data agreed with the Langmuir equation. No desorption of the pesticide occurred on treatment of the complex with organic salts suggesting a strong nonionic electrostatic binding of the chemical to the clay surface. Electrical conductivity and pH observations were in accordance with the formation of an ion-dipole complex. X-ray diffraction showed a maximum interlamellar expansion of 6.42 Å, confirming an upright monomolecular ion-dipole bonded adsorption of the chemical with penetration and swelling of the substrate micropores by the solute.

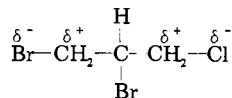
While the adsorption and interaction of ionic polar pesticides (Nearpass, 1971; Weber, 1970) with clay minerals have been extensively studied in recent years, relatively little work has been done on the mechanism of adsorption of nonionic insecticides. A study of the adsorption and

interaction of pesticides with clays and soils is of great importance, because processes such as effective pesticidal action, the persistence, the chemical and biodegradation, the leachability and translocation, and the toxicity of a pesticide depend to a great extent upon the nature of adsorption of the organic chemical by the silicates (Singhal and Singh, 1974; Bailey and White, 1970), although soil organic matter also has a profound influence on these factors. Montmorillonite is an important constituent of

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basaltic vertisol soils which occur so widely all over the world. The mineral possesses a high cation exchange capacity and has been known to provide heterogeneous chemically reactive spots on its surface in the form of exchangeable cations, sorbed water around cations, hydroxyl groups, and lattice surface oxygens.

Nemagon or 1,2-dibromo-3-chloropropane is an important pesticide and is used on a large scale for control of nematode and fungus diseases in soils. It is a nonionic dipolar molecule. Its structure can be represented as follows.



The primary objective of this work was to investigate the mechanism of adsorption of nemagon, a typical nematocide, on suspended montmorillonite particles in their acid and base saturated forms.

#### EXPERIMENTAL SECTION

Montmorillonite, a Mississippi bentonite, obtained from Ward's Natural Science Establishment, Rochester, N.Y., was used in this study. The <2- $\mu$  fraction, obtained by removal of organic matter and repeated sedimentation, was saturated in separate portions, with the chloride salts of Na<sup>+</sup> and Ca<sup>2+</sup> cations. The hydrogen montmorillonite was prepared by passing a part of the dilute Na-clay suspension through H-Dowex-50W-X8 cation exchange resin (Aldrich and Buchanan, 1958) just prior to use. The other portions of the 2 N salt-saturated clay were washed with distilled water until the conductivity of the Na- and Ca-montmorillonite suspensions became constant and no chloride was detected with AgNO<sub>3</sub> solution. The concentration of all the clay suspensions varied from 8.2 to 11.4 g of clay per l. of suspension.

Adsorption experiments were done by placing 5 ml each of the montmorillonite suspensions in a number of glass-stoppered tubes, adding varying concentrations of standard nemagon solution (2000  $\mu\text{g}/\text{ml}$ ), and adjusting the mixture to a constant volume of 25 ml with distilled water. The tubes were shaken for 3 h each day for 3 days at  $30 \pm 1^\circ\text{C}$  to attain equilibrium. The mixtures were then centrifuged and the supernatant liquids refluxed with alcoholic KOH. The pesticide was estimated as halide as per Volhard's silver thiocyanate-ferric aluminum method (Scott, 1939). All samples were run in duplicate. In all cases a clay blank was included. The adsorption of nemagon was obtained from the change in the concentration of the solution before and after contact with the clay. Adsorption isotherms were plotted between equilibrium concentration and millimoles of pesticide adsorbed per 100 g of montmorillonite (Figure 1). The pH and electrical conductivity of the equilibrium suspensions were also recorded in each case. The BEC of the montmorillonite determined as per Ganguli's (1951) method was 90 mequiv/100 g of clay.

Desorption of nemagon from the montmorillonites was attempted in all cases with deionized water and with varying concentrations of KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub> solutions, respectively, kept in contact with complexed montmorillonites for 3 days. Concentrations of these salts up to 5 times the base exchange capacity and repeated washing with distilled water did not desorb the pesticide from the clay surfaces.

The results obtained during the adsorption experiments were correlated with x-ray data of the samples. For the x-ray analysis less than 2  $\mu\text{m}$  of acid and base-saturated suspensions of montmorillonite were placed on glass slides

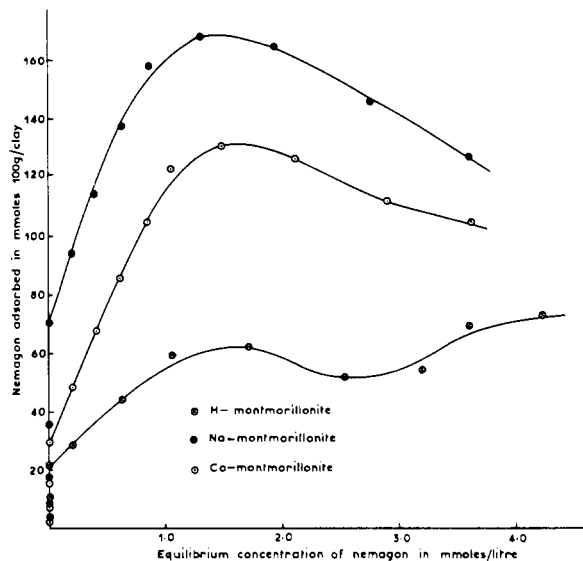


Figure 1. Adsorption of nemagon on acid- and base-saturated montmorillonites.

and allowed to dry to form a well-oriented layer. Similar samples of H-, Na-, and Ca-montmorillonite-nemagon complexes taken at the maxima of adsorption (61.9, 167.0, and 129.8 mmol per 100 g of clay, respectively) and at a subsequent minimum in adsorption (51.5, 127.7, and 104.8 mmol per 100 g of clay, respectively) were carefully oriented on microglass slides to get patterns at different adsorptive sites. Glycerine treatment was adopted in the case of Na-clay and its nemagon complexes. X-ray diffractograms were recorded both with the air-dry and heat-treated (at  $550^\circ\text{C}$  for 1 h) samples on a Philip's diffraction unit at a speed of  $2^\circ 2\theta$  per min using filtered Cu K $\alpha$  radiation. Basal spacings in angstroms are represented in Figure 3 and Table I.

#### RESULTS AND DISCUSSION

Adsorption of nemagon on H-, Na-, and Ca-saturated montmorillonite suspensions (0.82–1.14% w/v) in the equilibrium concentration range of 0.0 to 4.5 mmol of the fumigant per l. yielded isotherms as shown in Figure 1 (curves 1 to 3). An examination of the isotherms revealed that they were similar to class H and C isotherms as defined by Giles et al. (1960). Three clearly well-defined regions could be seen in all the isotherms. The initial H part was vertical indicating that nemagon had such a high affinity for the acid- and base-saturated montmorillonites that in dilute suspensions it was completely adsorbed until limiting values were reached (20.6, 70.5, and 29.7 mmol per 100 g of H<sup>+</sup>-, Na<sup>+</sup>-, and Ca<sup>2+</sup>-montmorillonites, respectively). Such initial, rapid, and steep rises in adsorption isotherms were certainly indicative of some form of chemisorption, occurring on the outer edges of montmorillonites with edge-to-edge ion attraction (Huang and Liao, 1970). Thereafter a change of slope occurred in the adsorption isotherms producing a linear rising portion (the C curve) of adsorption, until values of 61.9 mmol per 100 g of H-clay, 167.0 mmol of Na-clay, and 129.8 mmol of Ca-clay were reached. As represented by the linear (Giles et al., 1974) intermediate section of the curves, the second region was indicative of the creation of new adsorptive sites in the substrate with slow penetration of the solute in its micropores until they were filled up. Such linear isotherms were also obtained by Greenland et al. (1962) for the adsorption of amino acids on Ca-montmorillonite. They were able to show by x-ray measurements that the clay structure was steadily swelling as more and more of the solute was adsorbed. As these sites were saturated, a third

**Table I.** Basal Spacings of H-, Na-, Ca-, Nemagon-, Glycerine-, and Heat-Treated Samples of Montmorillonite

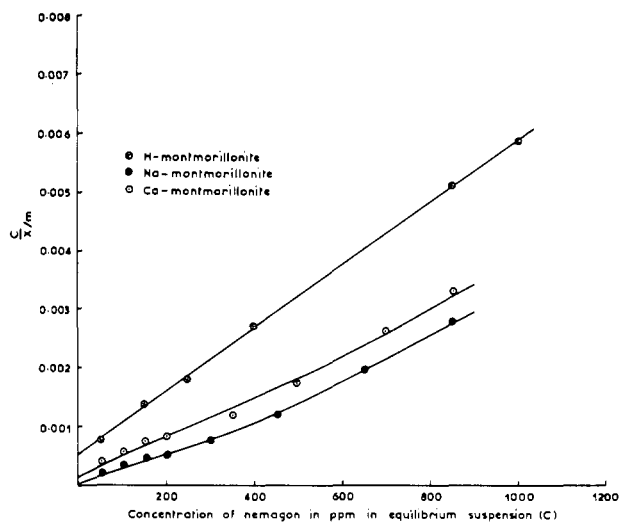
Nature of montmorillonite	Basal spacings at 001 reflections, Å <sup>a</sup>	Inter-lamellar separation, Å
H-treated, oven dry	9.9 (m)	
H-clay-Nemagon complex (I) at 61.9 mmol per 100 g of clay	16.4 (w)	6.5
H-clay-Nemagon complex (II) at 51.5 mmol per 100 g of clay	15.2 (w)	5.3
H-clay-Nemagon complex (I) at 550 °C	10.0 (m)	0.1
Na-treated, oven dry	9.6 (w)	
Na-clay-Nemagon complex (I) at 167.0 mmol per 100 g of clay	16.4 (w)	6.8
Na-clay-Nemagon complex (II) at 127.7 mmol per 100 g of clay	15.2 (w)	5.6
Na-clay-glycerine treated	17.7 (s)	8.1
Na-clay-Nemagon complex (I) treated with glycerine	19.6 (s)	10.0
Na-clay-Nemagon complex (I) at 550 °C	10.0 (w)	0.4
Ca-treated, oven dry	9.8 (w)	
Ca-clay-Nemagon complex (I) at 129.8 mmol per 100 g of clay	16.1 (m)	6.3
Ca-clay-Nemagon complex (II) at 104.8 mmol per 100 g of clay	15.2 (w)	5.4
Ca-clay-Nemagon complex (I) at 550 °C	10.0 (w)	0.2

<sup>a</sup> Letters in parentheses in column II indicate intensities: s = strong, m = medium; w = weak.

region occurred in the adsorption isotherms in the concentration range studied, indicating a decline, with negative adsorption of nemagon. The negative adsorption seemed to be due to a change in the hydrophilic nature of the systems resulting in preferential adsorption of the solvent or H<sub>3</sub>O<sup>+</sup> ions and release of nemagon. Such effects during clay organic interactions have been observed by other workers also (Singhal and Singh, 1972; Singhal and Kumar, 1976; Kalb and Curry, 1969).

A greater amount of nemagon was adsorbed by the base-saturated clays than the acid-saturated one. The adsorption followed the order Na-clay > Ca-clay > H-clay. The order of adsorption was in accordance with the partial molar free-energy changes that occurred during the interaction. The changes in partial molar free energy were calculated from the thermodynamic relationship,  $-\bar{F} = RT \ln(C_e/C_0)$ , where  $C_e$  and  $C_0$  are the equilibrium and initial concentrations of the suspension, respectively. An average of four values of  $\bar{F}$  in the case of H-, Na-, and Ca-saturated montmorillonite yielded 335.30, 811.98, and 664.99 cal/mol, respectively, thus confirming the order of adsorption of nemagon on the montmorillonites. The greater adsorption on Na-montmorillonite as compared to the Ca or H forms appeared to be due to the higher deflocculation of the montmorillonite caused by the Na<sup>+</sup> ions exposing a larger surface area for adsorption. Such effects have been observed by Alymore and Quirk (1959) as well as by Bowman (1973) during the adsorption of organics by clays. Thus, a greater amount of the pesticide will be needed for application as the optimum dose in base-saturated systems than in the acidic ones.

The adsorption data were in general agreement with the



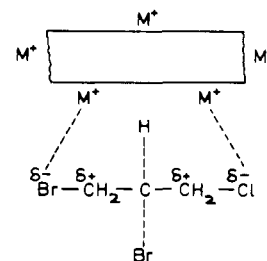
**Figure 2.** Langmuir plot of  $C/(x/m)$  against  $C$  during adsorption of nemagon.

Langmuir equation. A plot of  $C/(x/m)$  against  $C$ , where  $C$  was the equilibrium concentration of nemagon and  $x/m$  the amount adsorbed, yielded Langmuir isotherms; see Figure 2. The behavior corresponded with chemisorption of nemagon (Moore, 1962) in monolayers on the planar and lateral surfaces of montmorillonites.

Attempts to desorb the chemical from the montmorillonite surfaces by repeated treatments with KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub> solutions followed by washings with deionized water did not prove successful suggesting that a substantial part of the nematocide was strongly bound to the montmorillonites by electrostatic forces.

As compared to the blank no change occurred in the pH value (3.25) of the montmorillonite suspension during adsorption of the pesticide. Similar was the case during adsorption of nemagon on Na-montmorillonite (pH 7.2) and Ca-montmorillonite (pH 7.0). A slight fall in electrical conductivity was observed during the above interactions (EC order, 4 to  $3 \times 10^{-5}$  mho cm<sup>-1</sup>). These results were highly significant, ruled out any kind of protonation or exchange reaction, and provided a powerful clue as to the mechanism of adsorption.

Our pesticide was a nonionic molecule. Its halides carried a negative potential and might behave as nucleophiles. The montmorillonite surface also may be supposed to carry electrophiles in the form of H<sup>+</sup>, Na<sup>+</sup>, and Ca<sup>2+</sup>. The strong possibility of adsorption occurring through a charge-transfer interaction (Clementz and Mortland, 1972) was, however, ruled out due to the tightly bonded structure of the molecule and incapability in its resonance. The dipolar character of the nematocide would, however, result in a strong electrostatic attraction between the organic molecule and the clay surfaces leading to formation of ion-dipole bonds (Ferguson, 1966) giving a complex of the form:



(M<sup>+</sup> = exchangeable cation H<sup>+</sup>, Na<sup>+</sup> or Ca<sup>2+</sup> at the planar and edge sites)

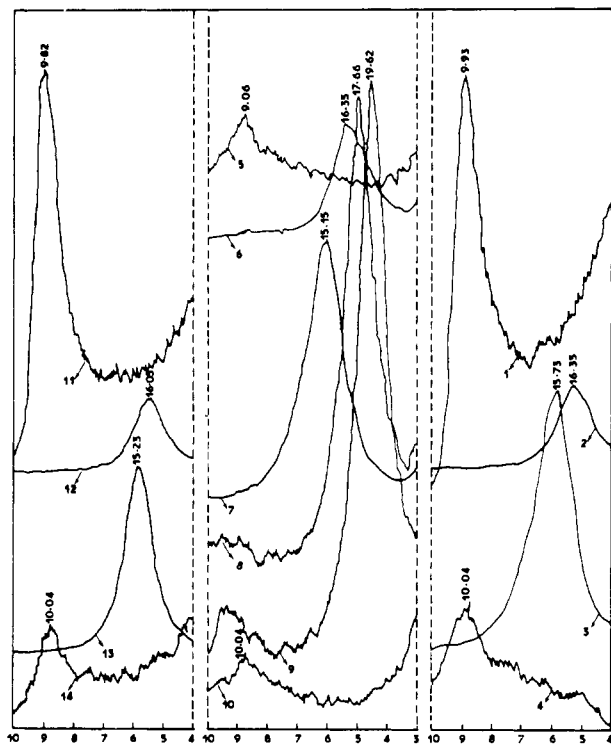


Figure 3. X-ray diffractograms of (1) H-montmorillonite oven dry, (2) H-montmorillonite-nemagon complex (I), (3) H-montmorillonite-nemagon complex (II), (4) H-montmorillonite-nemagon complex (I) at 550 °C, (5) Na-montmorillonite oven dry, (6) Na-montmorillonite-nemagon complex (I), (7) Na-montmorillonite-nemagon complex (II), (8) glycerine-treated Na-montmorillonite, (9) glycerine-treated nemagon complex (I), (10) Na-montmorillonite-nemagon complex (I) at 550 °C, (11) Ca-montmorillonite oven dry, (12) Ca-montmorillonite-nemagon complex (I), (13) Ca-montmorillonite-nemagon complex (II), (14) Ca-montmorillonite-nemagon complex at 550 °C.

This interaction was in accordance with the pH changes. The binding of the exchangeable cations resulted in a fall of the electrical conductivity ( $4$  to  $3 \times 10^{-5}$  mho  $\text{cm}^{-1}$ ). There is evidence for formation of such bonds between metallic cations and organic compounds as well as between clay, water, and nonionic polar pesticides (Mortland, 1970).

Some of the propositions made above found support from x-ray analysis. Table I and Figure 3 give the results of x-ray analysis of H, Na, Ca, nemagon, glycerine, and heat-treated samples of montmorillonite. The basal thicknesses of cation-saturated montmorillonites in the oven dry state were of the order of 9.6 to 9.9 Å. There resulted an expansion of 6.5, 6.8, and 6.3 Å, respectively, in the basal thickness of nemagon-treated hydrogen, sodium, and calcium montmorillonites at the maximum point of adsorption. The stereomodel structure of the pesticide yielded a van der Waals thickness of 4.62 Å in the upright

state of the molecule. This thickness along with the slow penetration of the solute in the micropores of the substrate and its consequent swelling strongly suggested an upright monomolecular adsorption of the pesticide with formation of ion-dipole complexes in the interlamellar spaces of H-, Na-, and Ca-montmorillonites, as envisaged earlier. Glycerine treatment further expanded the basal spacing (10.0 Å) suggesting creation of a second layer of glycerine (thickness 4 Å) above the complexed nemagon without its expulsion. Thus, nemagon adsorption was sufficiently strong and could not be expelled by glycerine treatment. Heat treatment of the clay-nemagon complex to 550 °C resulted in the oxidation of the organic molecule leaving some interlamellar residue (0.4 to 0.1 Å) as a by-product of oxidation reaction on the planar surface, suggesting that nemagon was chemisorbed firmly on the montmorillonites. A reduction in the basal spacings (5.3, 5.6, and 5.4 Å, respectively), observed during negative adsorption, suggested either some expulsion of the pesticide by  $\text{H}_3\text{O}^+$  ions or a reorientation of the molecules on the montmorillonite surface due to solvent effects. Such a reorientation may result in the discontinuity in the adsorption isotherms.

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