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To the Graduate Council:

I am submitting herewith a thesis written by Jay Wolbert Johnson entitled "The Persistence, Degradation, Movement, and Adsorption of Phorate and Demeton in Clay and Soil Systems." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agronomy.

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THE PERSISTENCE, DEGRADATION, MOVEMENT, AND ADSORPTION
OF PHORATE AND DEMETON IN CLAY AND SOIL SYSTEMS

A Thesis
Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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Jay Wolbert Johnson
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ABSTRACT

The purpose of this investigation was to study several factors which influence the fate of phorate and demeton when applied to soil.

Radioactive P^{32} -labeled phorate and P^{32} -labeled thiol isomer of demeton were used in leaching and adsorption studies. In the investigation on persistence, thin-layer chromatography was employed for phorate; and paper chromatography was used for demeton. The degradation was determined by infrared analysis of phorate and phosphorus analysis of demeton.

The organic matter content of soils was found to be related to the number of metabolites found over a six-week period and the relative concentration of the metabolites.

The half-life of phorate was 62.4 hours at pH 4.5 and 70.0 hours at pH 7.0. The half-life of demeton was determined to be 1,525 hours at both pH 4.5 and 7.0 if calculated for the rate of decomposition for the period of three to seven days.

Either a change in order of kinetic decomposition or a catalytic effect resulting from a drop in the pH caused the decomposition rate to increase several fold in seven to fourteen days' treatment time.

In movement studies the quantity of phorate remaining in the leaching column was influenced by the moisture condition of the column at the time of application of the insecticide and thereafter before leaching. The dry columns retained more insecticide than did the moist

ones. The moisture status of the clay columns had little or no effect on the amount of demeton remaining after leaching.

The charge on the phorate molecule was predominantly positive, and the charge on the demeton molecule was predominantly negative. Both insecticides were adsorbed by Southern Bentonite from aqueous suspensions. Tako Kaolin adsorbed both phorate and demeton when calcium saturated. Phorate was adsorbed by Tako Kaolin when aluminum saturated, but demeton was repelled.

Phosphorus decreased the amount of phorate adsorbed by calcium-saturated Southern Bentonite. Nitrogen and potassium reduced the amount of demeton adsorbed by the same clay.

Phorate and demeton were found to expand Southern Bentonite in all cases. The insecticide which caused an expansion above 15.1 and 14.5 angstroms for calcium- and aluminum-saturated clay was very weakly adsorbed and could be removed by dialysis.

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CHAPTER I

INTRODUCTION

Pesticide pollution has become a problem of increasing magnitude in today's society. Several different types of pesticides, both organic and inorganic, are now in existence. The problems of fish kill, wildlife harm, and fowl annihilation have brought society to demand to know the effects of the herbicides and insecticides used.

Some of the factors dealing with the fate of phorate [O,O-diethyl-S-(ethylthiomethyl) phosphorodithioate] and demeton [O,O-diethyl-O-2 (ethylthio) ethyl phosphorothioate (I)] and [O,O-diethyl-S-2 (ethylthio) ethyl phosphorothioate (II)], in approximately a two-to-one ratio of I and II, two widely used organic phosphate insecticides, when applied to soil were studied.

One area of study dealt with the persistence of the insecticides in a water solution. Another area of study dealt with the degradation of each insecticide in soil and clay suspensions and in a water solution. What products were formed as influenced by soil acidity, microorganisms, or organic matter?

The movement of the insecticides through clay columns under various moisture conditions was also investigated. Another area of investigation was the determination of the amounts of insecticides adsorbed by clays and soils. The effect that the three major fertilizer elements have on the adsorption of insecticides was also investigated.

CHAPTER II

LITERATURE REVIEW

Much has been written in recent years on the subject of soil contamination by pesticides. According to Lambert et al. (19) the fate of a chemical in the soil is affected by several factors: (1) type of soil, (2) type of chemical, (3) climatic conditions, (4) biological population, and (5) method of application. Some of the factors which influence the length of time a pesticide remains in the soil are the adsorption of the pesticide to the clay or organic fraction of the soil, the amount of biodegradation, and the amount of water that moves through the soil.

The relationship between leachability and adsorption is not fully understood. Upchurch and Pearce (29) stated that at least two processes--entrance of the compound into solution and adsorption--determine the leachability of a herbicide. A report by Bailey and White (5) on leaching studies revealed that pesticides are leached less in heavier textured soils and organic soils than in the lighter textured soils.

Two general types of adsorption have been suggested by Bailey and White (5). Physical adsorption is one type, and chemical adsorption is another type. Physical adsorption, or Van der Waal's adsorption as it is often called, is caused by: (1) orientation or dipole-dipole interactions, (2) polarization or induced dipole interactions, (3) dispersion interactions, and (4) ion-dipole interactions in addition to Born repulsion interactions. Chemical adsorption is caused by coulombic forces and results from bond formation between the adsorbent and adsorbate. Bailey

and White (5) also disclosed that physical adsorption may have several monolayers present while in chemical adsorption only the first monolayer is chemically bonded to the surface although several layers may be present. The other layers are physically adsorbed. Infrared studies of clay organic complexes conducted by Bradley (7) revealed that a CH...O bond was being formed with the hydrogen of the methylene group and bonded directly to the clay surface.

Holstum and Loomis (17) indicated that dalapon (2,2-dichloropropionic acid) exhibited a high degree of mobility over a range of soil types when leached with one and one-half inches of water. Dalapon's resistance to leaching was increased by the addition of organic matter (manure) and decreased by the addition of sand. The amount of rainfall required to leach parathion (0,0-diethyl-0-p-nitrophenyl phosphorothioate) to a depth of 60 inches was estimated by Swoboda and Thomas (28) to range from 230 inches for a Nacogdoches clay subsoil to 1,725 inches for a Houston black clay surface soil.

Of the four soil properties, organic matter, total clay, cation exchange capacity, and pH, Sheets et al. (27) showed that organic matter was the best single predictor of bioactivity of simazine [2-chloro-4, 6-bis(ethylamino)-s-triazine] in the soil. Soils having a high cation exchange capacity and a high surface area have large capacities to adsorb pesticides. Hill (16) learned that more monuron [3-(p-chlorophenyl)-1, 1-dimethylurea] was adsorbed by bentonite than was adsorbed by kaolinite. Frissel (10) reported that montmorillonite adsorbed considerably more of various herbicides than did illite or kaolinite. According to Weed¹ malathion [S-(1, 2-bis(ethoxycarbonyl) ethyl) 0,0-dimethyl

¹S. B. Weed, Adsorption of Malathion by Montmorillonite, Unpublished paper, North Carolina State University.

phosphorodithioate] was adsorbed by montmorillonite in the interlayer space and was limited to a monolayer.

Research conducted by Frissel and Bolt (11) showed that the adsorption of organic ions by clays in aqueous environments was strongly dependent upon pH and electrolyte concentrations. Frissel (10) also proved that the adsorption of herbicides with widely different molecular structures increased as the pH decreased. The maximum and near minimum adsorption pH's were a function of the particular compound and the adsorbent with which it was associated.

Wolf et al. (31) discovered the degree of adsorption of four substituted ureas to be inversely related to the order of their solubilities. The order of lateral movement of certain substituted ureas and the order of their water solubilities were the same according to Ashton (3).

When radioactive phorate was applied to Lufkin fine sandy loam and cotton was grown for one to seven weeks, Hacskeylo et al. (14) found that 70 percent of the radioactivity could be accounted for in the top one and one-half inches of the soil.

The effect of soil moisture content upon the adsorption of EPTC (ethyl N,N-di-n-propylthiolcarbamate) was investigated by Ashton and Sheets (4). They concluded that more EPTC was adsorbed by a soil in the air-dry state than was adsorbed at field capacity regardless of soil texture or organic matter.

Research conducted by Getzin and Chapman (13) showed that phorate uptake by peas from three soils and quartz sand indicated that the largest amounts of toxicants were taken from quartz sand with lesser amounts being taken from sandy soils, clay loam, and muck, respectively.

If degradation of organic materials is complete, the constitutive elements of the parent substance will be recovered in an inorganic state Alexander (1) concluded. When oxygen is available, the final products of degradation are carbon dioxide, water, sulfate, nitrate, phosphate, chloride, etc.

Parker and Dewey (26) discovered that phorate breakdown is greatest during the first week in soils and almost complete at the end of one month. Approximately 10 percent of the phorate added remained after 30 days. The soils used were Chenango gravelly silt loam, Lordstone stony silt loam, and Dunkirk fine sandy loam.

O'Brien (25) has calculated the half-life of thiol and thiono isomers of demeton at pH 8.0 and 25°C to be 14,200 and 1,250,000 hours, respectively. Muller and Goldenson (24) discovered that demeton changes from its thiono isomer to the thiol isomer somewhere between zero and a first order rate. They suggested that the change resulted from a catalytic effect. According to Cook's (9) findings the parent material of demeton changed to a metabolite at a very fast rate upon exposure to light and air. In a study of plant metabolites Metcalf (22) determined that the thiono isomer of demeton was metabolized nearly as rapidly as it entered the plant and that after 24 hours only a single toxic metabolite, the thiol isomer, was present. Wilson and Van Middeltem (30) noted that very little or no demeton remained in cabbage 21 days after application of 15 pounds per acre.

Metcalf et al. (23) established that dithio-demeton (0,0-diethyl S-ethyl-2-mercaptoethyl phosphorodithioate) and phorate were adsorbed by cotton and lemon plants at approximately equal rates but only about 0.5 to 0.75 times as fast as thiol isomers of demeton were adsorbed. The accumulation of phorate in leaves of cotton plants grown in treated sand

cultures was calculated by Hacskeylo et al. (15) to be linear with time and directly associated with environmental conditions which favor transpiration.

Measurable residues of disulfoton [O,O-diethyl S-2-(ethylthio) ethyl phosphorodithioate] and phorate remained in pea vines but not in the shelled peas 76 days after furrow treatments as reported by Chisholm and Speicht (8). According to Anderson, Schulz, and Hibbs (2) residues of phorate applied to Webster clay loam, three parts sand and two parts peat, remained in standard disbudded chrysanthemums 141 days after treatment if plants remained in treated soils. If plants were removed from treated soil after a 24-hour exposure time, detectable amounts of phorate existed 47 days later. The rate of application of phorate was 200 milliliters of 0.5 ounce per 100 gallons water per six-inch pot. Menn and Hoskins (21) determined that the chief metabolites of phorate applied to German cockroach and large milkweed bug were the sulfoxide and/or sulfone of phorate.

CHAPTER III

METHODS AND PROCEDURES

Two clays and six Tennessee soils (Table I) were selected for study. The American Colloidal Chemical Company provided the Southern Bentonite clay, and the Thomas Alabama Kaolin Company provided the Tako Kaolin clay. One set of both clays was aluminum saturated, and another set was calcium saturated. These were left in suspension until use. All soils were air dried and passed through a two-millimeter mesh sieve.

TABLE I

SELECTED SOIL CHARACTERISTICS

Soil Type	Lab. No.	Horizon	pH	Percent Organic Matter
Decatur silt loam	32	Ap 1- 8"	6.3	2.37
	35	B ₂ 20-40"	6.3	0.42
Halewood loam	59	A ₂ 0- 6"	4.5	5.33
	61	B ₂₁ 11-20"	5.0	1.04
Maury silt loam	73	Ap 0- 9"	6.1	2.57
	76	B ₂ 24-36"	6.3	0.42
Dewey silt loam	93	Ap 0- 8"	5.4	1.39
	95	B ₂₁ 14-22"	5.4	0.47
Hartsells loam	106	Ap 0- 9"	5.4	2.89
	107	B ₂ 9-19"	4.9	0.66
	109	C ₁ 30-38"	4.7	0.24
Cookeville silt loam	122	A ₁ 0- 2"	--	4.40
	123	A ₂ 2- 5"	4.9	1.75
	126	B ₂ 20-30"	4.9	0.74
Memphis silt loam	--	Ap 0- 8"	7.0	1.20

Source: Department of Agronomy, University of Tennessee, Knoxville

The insecticides used were 83 percent phorate, supplied by the American Cyanamid Company, and 95.5 percent demeton, supplied by the Farbenfabriken Bayer Company. In adsorption studies pure P^{32} -labeled material was used, and it was purchased from Amersham/Searle. Only the thiol isomer of demeton was used in radioactive studies.

The four areas of study dealt with the persistence, degradation, movement, and adsorption of phorate and demeton in clay and soil systems.

I. PERSISTENCE

Two thousand micrograms of the insecticide were added to one gram calcium-saturated Southern Bentonite in suspension, and the volume was adjusted to 60 milliliters. In one-half of the samples the pH was adjusted to 7.0, and in the other half the pH was 4.5. The pH of phorate was adjusted to 7.0 with phosphate buffer in the water solution and with 0.1N sodium hydroxide in the clay suspension. The pH of demeton was adjusted to 7.0 by using 0.1N sodium hydroxide. The pH of the solution of both phorate and demeton was 4.5; therefore, no adjustment was necessary. A set of samples was also prepared without the clay. Each set contained 18 replicates.

Each of the samples was shaken for five minutes at 25-minute intervals. Three replicates were analyzed immediately after application of the insecticide. Three replicates of each set were removed from the shaker after four hours, one day, three days, seven days, and fourteen days and analyzed. The samples were centrifuged until the supernatant became clear.

The amount of phorate remaining in the supernatant was determined by extracting with chloroform and evaporating on to KBr and analyzing on an infrared spectrophotometer (Perkin Elmer 337).

The amount of demeton remaining in solution was determined by extracting 40 milliliters of the supernatant of each sample with 10 milliliters chloroform. The chloroform was evaporated at 60-70°C until approximately one-half milliliter remained. The amount of phosphorus in each sample was determined by wet digestion and analyzed by a Technicon auto analyzer.

The digestion procedure consisted of the following steps: (1) adding three milliliters nitric acid and letting it stand for approximately three hours; (2) heating in 50-milliliter tubes with a reflux funnel on each for one hour at 150°C; (3) adding two milliliters perchloric acid; (4) heating the tubes to 220°C for one and one-half hours; (5) cooling to room temperature, adding one milliliter hydrochloric acid, and removing the funnels; and (6) heating the samples to 150°C for 15 to 20 minutes.

Each sample was diluted to 25 milliliters with distilled water and analyzed on the auto analyzer using Jackson's (18) vanadomolybdophosphorus yellow-color method.

The concentration of demeton in solution was determined by the following formula:
$$\frac{\text{micrograms phosphorus}}{\text{milliliter}} \times 8.32 \frac{\text{micrograms demeton}}{\text{micrograms phosphorus}} \times \frac{25 \text{ milliliters}}{40 \text{ milliliters}} = \text{micrograms demeton per milliliter.}$$

II. DEGRADATION

Two thousand micrograms of phorate or 1,250 micrograms of demeton were added to one gram calcium- or aluminum-saturated Tako Kaolin and Southern Bentonite suspension, soil numbers 32, 35, 59, 61, 106, 107, 109, and soil number 59 after it had been sterilized. The volumes were 60 and

35 milliliters, respectively. A blank with only phorate or demeton was also used. Only one replicate was conducted. Each of the samples was placed in a closed tube and shaken five minutes at 25-minute intervals for periods of one, two, three, four, and six weeks. At the end of these periods, one sample of each clay, soil, and water treatment was removed; and after centrifuging, the insecticide was removed from the supernatant with chloroform.

The procedure described by Blinn (6) for thin-layer chromatography was employed in establishing which metabolites of phorate were present. The paper chromatography procedure outlined by March et al. (20) was used in determining which metabolites of demeton were present. The size and intensity of the spots were used to estimate the quantity of each metabolite.

III. MOVEMENT

In order to check the movement of phorate and demeton in clays, one gram of aluminum-saturated Southern Bentonite was mixed with five grams cellulose and moistened to form a paste. The clay-cellulose mixture was dried in an analytical oven at 70°C. The dry clay-cellulose mixture was packed into a leaching column 1.5 centimeters in diameter and approximately 25 centimeters in length. Before packing the column, a glass wool plug was inserted and followed by approximately one-half gram of cellulose. The clay-cellulose mixture was added to the column and another glass wool plug added.

The volume pore space in the columns was calculated using the following formula: (weight of water-saturated column - weight of dry column) x $\frac{\text{one cubic centimeter water}}{\text{one gram water}}$ = cubic centimeter pore space. One

set of the columns was air dried, and two sets were kept moist until the insecticide was applied. Each set consisted of three columns.

Two hundred micrograms of P^{32} -labeled phorate were added in five-milliliter solution to the surface of each leaching column. One set of the moist columns was attached to a fraction collector and leached with distilled water until 30 samples of approximately 5.56 milliliters were collected. After adding 200 micrograms phorate, the other sets were air dried by drawing air down through the column before leaching. After leaching, the clay core was removed and sectioned in one-centimeter sections; and the radioactive phorate was extracted by shaking with five milliliters of chloroform.

One milliliter of the leachate and one milliliter of the clay extract were evaporated on to aluminum planchets, and the amount of phorate present was determined by counting the activity with a Nuclear Chicago scaler Model 186A.

The movement of demeton was determined in a similar manner. Eighty micrograms thiol isomer of demeton were added in two milliliters to two grams aluminum-saturated Southern Bentonite, and 100 milliliters of leachate were collected. A Nuclear Chicago 8712 scaler was used for analysis. The column was two centimeters in diameter and 17 centimeters in depth. The depth of the clay-cellulose column was approximately 10 centimeters.

For both phorate and demeton a column of only cellulose was leached after an application of the respective insecticide. It was then analyzed in the same manner as its clay-cellulose counterpart.

IV. ADSORPTION

Several studies were conducted on the adsorption of phorate and demeton by clays, soils, and other charged surfaces.

Exchange Resins

Four hundred micrograms radioactive pesticide were added to one gram cation exchange resin Amberlite IR-120 (H+) and to one gram anion exchange resin Amberlite IRA-400 (Cl-). The volume was adjusted to 16 milliliters with distilled water. After shaking for 30 minutes, one milliliter of solution was counted; and the amount of insecticide in solution was determined from a standard curve. The amount of insecticide retained by the resins was determined by subtracting the amount left in solution from the concentration added.

Glass Adsorption

Forty-five borosilicate glass beads approximately two millimeters in diameter were placed in 50 milliliters of 40 micrograms per milliliter radioactive insecticide and shaken for 30 minutes. The beads were removed, washed with distilled water, and air dried. After drying, a known quantity was placed on a planchet and counted.

Clay Adsorption

Three replicates of calcium- or aluminum-saturated Southern Bentonite, Tako Kaolin, and a water standard were used. Forty micrograms radioactive insecticide were added to one gram of each clay, and the volume was adjusted to 25 milliliters. After shaking for two hours, the sample was centrifuged; and one milliliter of supernatant was removed. The amount of insecticide remaining in solution was determined by

radiometric assay. The formula used in calculating the amount of insecticide adsorbed was: micrograms per milliliter (water standard) - micrograms per milliliter (clay) $\times \frac{25 \text{ milliliters}}{\text{one gram clay}}$ = micrograms adsorbed per gram clay.

Soil Adsorption

Two hundred micrograms of the insecticide were added to five grams of soil numbers 32, 35, 59, 61, 106, 107, and 109. A standard solution with no soil was also used for each time period. The volume was adjusted to 25 milliliters, and the samples were shaken five minutes at 25-minute intervals for one, two, and three days. The samples were centrifuged, and the amount of radioactive insecticide was determined by counting one milliliter of the supernatant. Three replicates of each standard and soil were used. The amount adsorbed was calculated by the following formula: micrograms per milliliter (water standard) - micrograms per milliliter (soil) $\times \frac{25 \text{ milliliters}}{\text{five grams soil}}$ = micrograms adsorbed per gram soil.

Moisture Tension

Two hundred micrograms of the radioactive insecticide were added to five grams of air-dry Tako Kaolin, Southern Bentonite, and Memphis soil. Two hundred micrograms of the insecticide were also added to another set of these samples at field capacity. Each of the samples was leached with 100 milliliters distilled water. A portion of the sample was placed on a planchet and counted. After counting, the sample was dried at 60°C; and the quantity of insecticide retained per gram dry soil or clay was calculated from a standard curve.

Fertilizer Effects

Two hundred micrograms of nitrogen as ammonium nitrate were added to one gram calcium-saturated Southern Bentonite which was in suspension with 40 micrograms labeled insecticide, and the volume was adjusted to 40 milliliters. One standard without nitrogen added was also used. After shaking for two hours, the amount of insecticide remaining in solution was determined by counting and plotting on a standard curve. Three replicates of each set were conducted. Phosphorus as monobasic calcium phosphate and potassium as potassium chloride were added to one gram calcium-saturated Southern Bentonite which was in suspension with 40 micrograms labeled insecticide in a similar manner.

The effect on the amount of adsorption was determined by adding 100 micrograms nitrogen, phosphorus, and potassium to one gram of calcium- or aluminum-saturated Southern Bentonite and Tako Kaolin which contained 40 micrograms insecticide per 25 milliliters solution. After shaking for two hours, the amount of adsorption by the clays was determined by comparing the amount of insecticide in solution with that of a standard which had 100 micrograms nitrogen, phosphorus, and potassium per microgram insecticide.

Interlayer Spacings

The adsorption of insecticides by clays was determined by adding 0, 26, 52, 78, 156, 234, and 468 milligrams insecticide per gram in N-pentane to an aqueous suspension of clays and evaporating the N-pentane. The clays used were calcium- or aluminum-saturated Southern Bentonite and Tako Kaolin. After shaking overnight, X-ray slides were made of the clay suspension. After air drying, the slides were placed in a desiccator

over magnesium nitrate with six water molecules for 24 hours. The slides were X-rayed with a Norelco vertical goniometer X-ray. The kilowatt and milliamp settings were 35 and 18, respectively. The basal spacings for the first order peaks were calculated according to Bragg's equation.

After saturating with the insecticide, the 234 milligrams per gram samples of Bentonite were dialyzed for periods of 46 and 108 hours. At the end of these times, slides were prepared in the manner mentioned above and X-rayed.

CHAPTER IV

RESULTS AND DISCUSSION

I. PERSISTENCE

The graphs of the log initial concentration divided by the concentration remaining in solution versus decomposition time in days are shown in Figures 1 and 2. The velocity constants and half-lives were calculated for both phorate and demeton in water solutions with the initial pH of one set adjusted to 7.0 and another to 4.5. By plotting the log concentration remaining versus time, the order of the reaction was determined to be first order.

The velocity constants for phorate were 8.75×10^{-3} per hour at pH 4.5 and 1.15×10^{-2} per hour at pH 7.0. For demeton the velocity constants were 4.55×10^{-4} per hour at pH 4.5 and 7.0. The half-lives were 79.0 and 62.4 hours for phorate at pH 4.5 and 7.0, respectively. The half-life of demeton was 1.525×10^3 hours in both cases.

By calculating the half-lives of phorate and demeton from the amount of decomposition from three to seven days, the persistence of demeton appears to be approximately 22.5 times longer than that of phorate. For demeton in the period of from seven to fourteen days, either a change in decomposition order or a catalytic effect caused the rate of decomposition to increase several fold. It is suspected that on decomposition the inorganic sulfate and phosphate products lowered the pH sufficiently to cause this acceleration in decomposition rate.

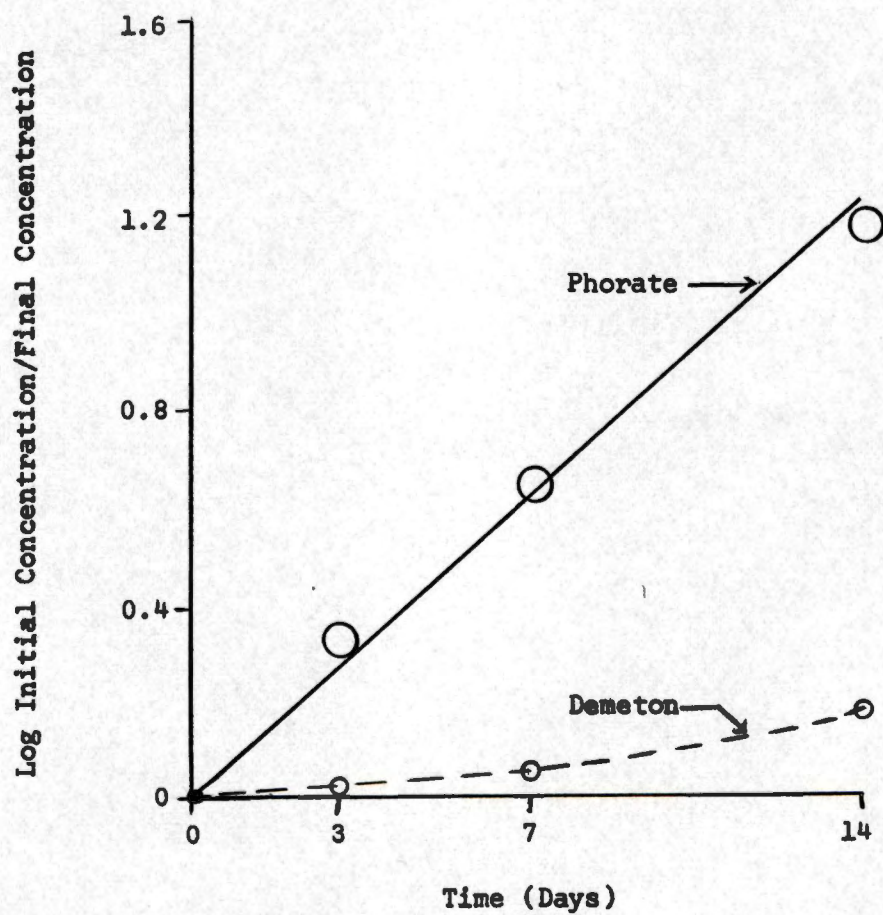


Figure 1. Log Initial Concentration/Final Concentration versus Time in Days for Phorate and Demeton at an Initial pH of 4.5

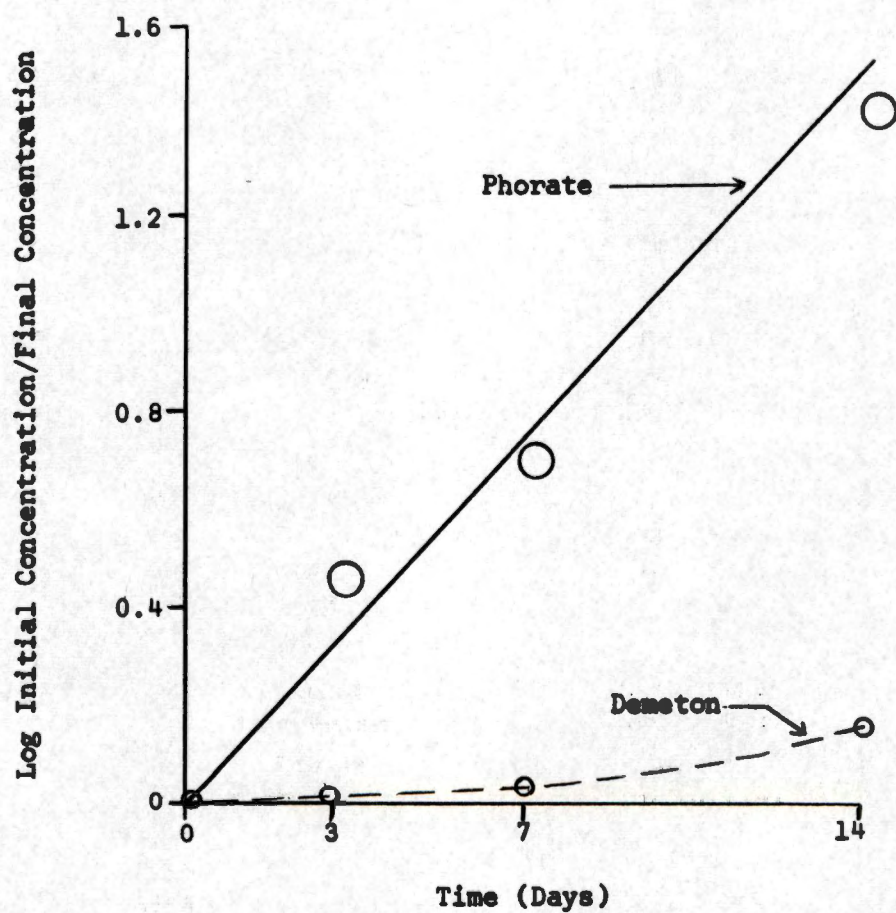


Figure 2. Log Initial Concentration/ Final Concentration versus Time in Days for Phorate and Demeton at an Initial pH of 7.0

The rates of decomposition for demeton are much higher than those reported by O'Brien (25), which were calculated at pH 8.0.

A buffer was used to control the change in pH for phorate. A phosphate buffer caused an initial lowering of concentration but did not seem to affect the order of decomposition.

The persistence in clay systems was not determined because the adsorption by the clay confounded the amount of insecticide remaining in solution; therefore, no results were obtained. The decomposition curves for phorate in which clay was added were very similar to ones in which no clay was added. For demeton the initial adsorption lowered the concentration of insecticide remaining in solution greatly. After 14 days the amount in solution was about the same in both cases where clay was added in comparison with those where no clay was added.

II. DEGRADATION

For phorate the major metabolite present in soils having appreciable amounts of organic matter was I Sulfoxide, which appeared after one week's treatment time and persisted for the next five weeks. In systems having little or no organic matter, the major metabolite was I Sulfoxide for the first two weeks. After this time Metabolite II was the predominant metabolite, and it persisted for the duration of the testing time.

The degradation studies of demeton revealed that only a very small amount of the thiono isomer was present at the end of one week, and what March et al. (20) described as the major plant metabolites appeared and persisted for the duration of the treatment. The thiono isomer was completely lacking after two weeks, but the thiol isomer remained for the entire six-week testing period.

III. MOVEMENT

The elution patterns of both phorate and demeton in aluminum-saturated Southern Bentonite columns were graphed.

The maximum concentration for phorate in instances where the insecticide was applied to a moist column and leached immediately occurred after 1.0 volume displacement (Figure 3). Greater than 90 percent of the insecticide had leached out by 1.6 volume displacements. After leaching with approximately 166 milliliters of water or 12.6 volume displacements, the amount of insecticide remaining in the column ranged from 0 to 1.5 micrograms.

For demeton the maximum concentration occurred from 1.73 to 2.08 volume displacements; and by 3.0 volume displacements, greater than 90 percent had leached through (Figure 4). The amount of insecticide remaining in the column after 100 milliliters of water had leached through ranged from 0.65 to 6.8 micrograms.

The maximum concentration of phorate where the insecticide was applied to a moist column and then air dried before leaching occurred from 1.0 to 1.5 volume displacements (Figure 5). Greater than 90 percent was collected by the time 2.0 volume displacements were leached. After leaching with 166 milliliters of water, the amount of phorate remaining in the column ranged from 6.5 to 26.5 micrograms.

For demeton the maximum concentration occurred from 0.9 to 1.0 volume displacements; and by 2.0 volume displacements, greater than 90 percent had leached through the column (Figure 6). The amount remaining in the column after leaching with 100 milliliters water ranged from 1.9 to 2.8 micrograms.

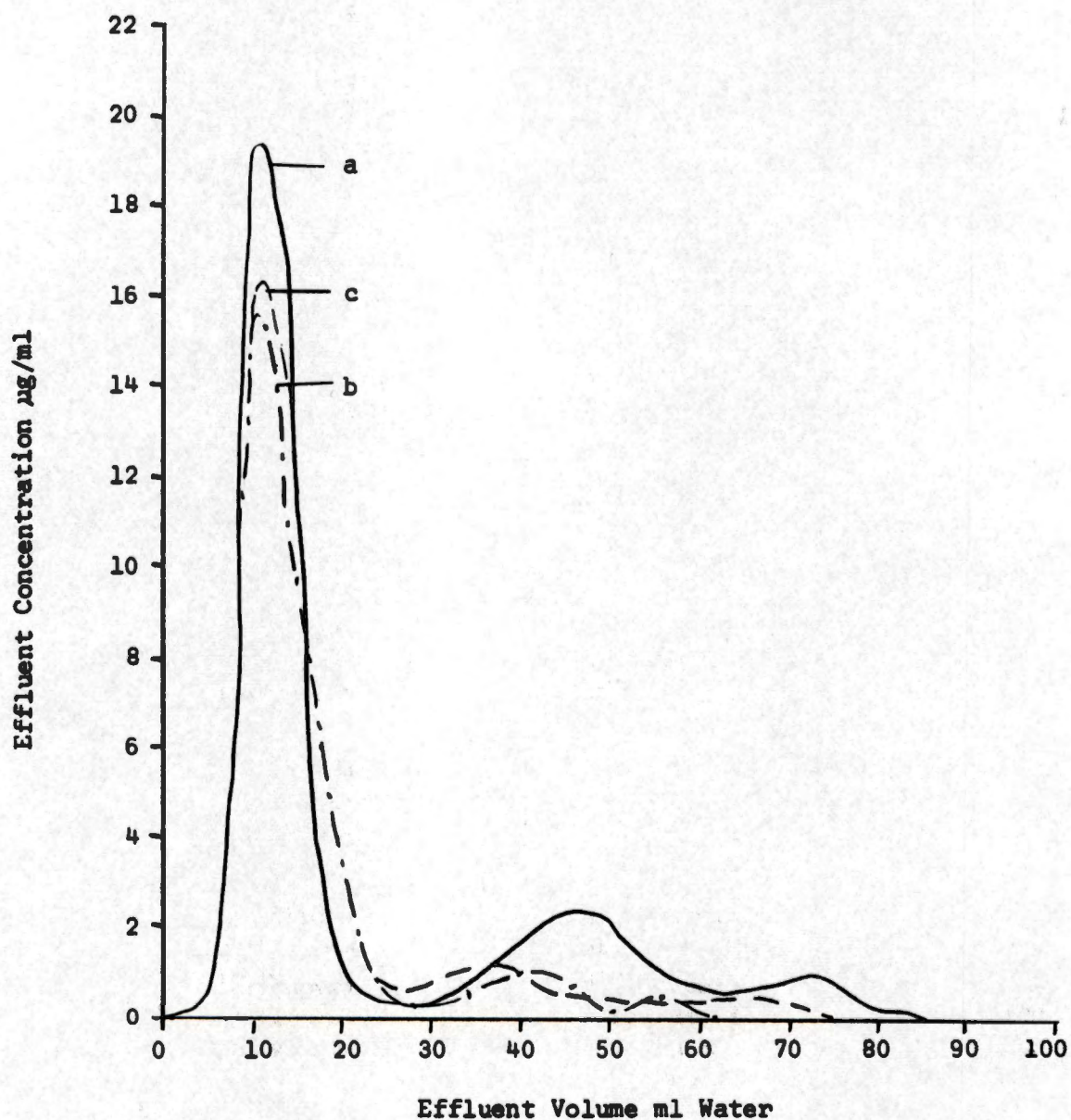


Figure 3. Phorate Effluence from an Aluminum-Saturated Southern Bentonite Clay-Cellulose Column when Applied at Field Capacity and Leached Immediately. Volume Displacements: a - 13.4 ml; b - 13.1 ml; c - 13.1 ml

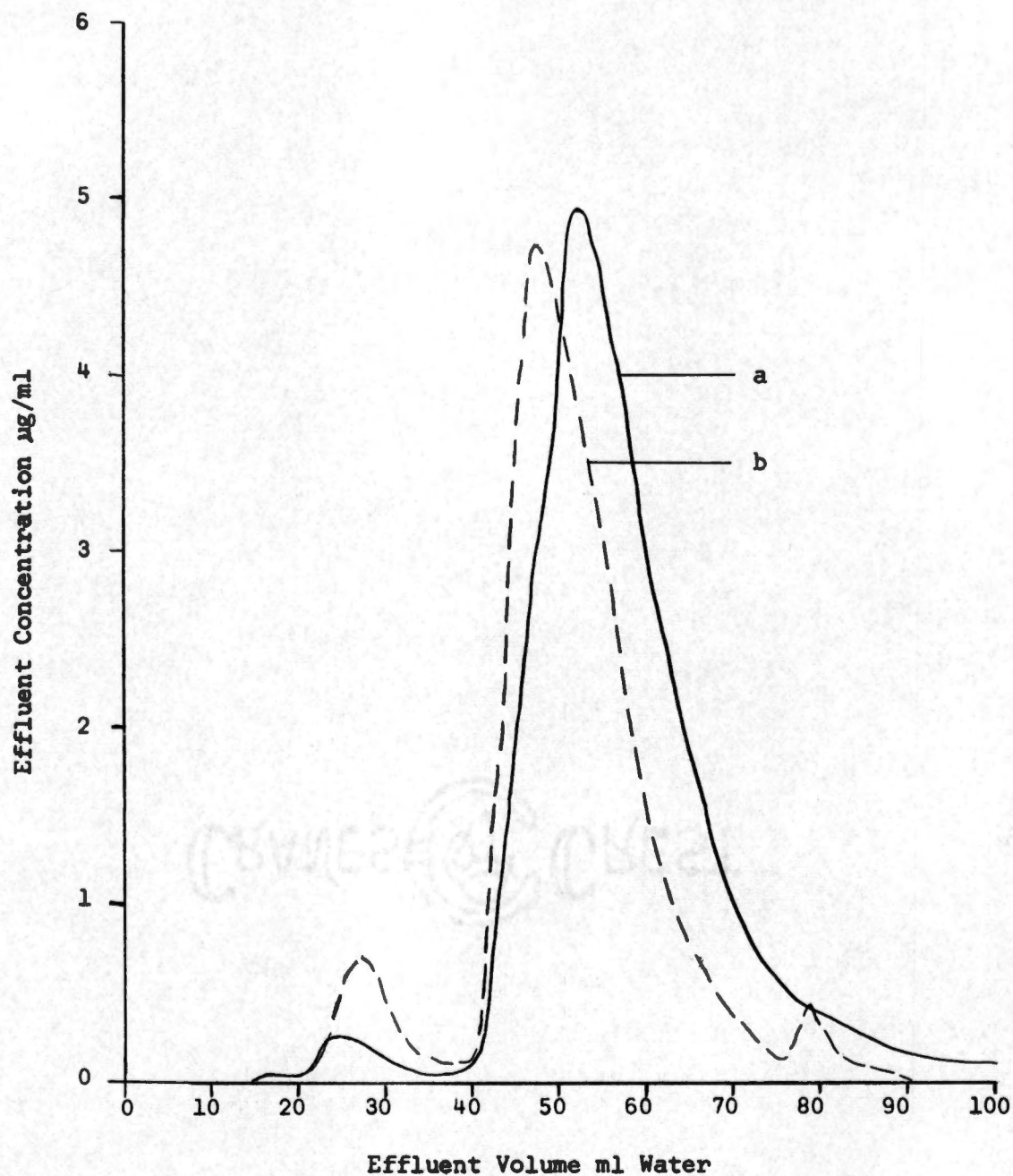


Figure 4. Demeton Effluence from an Aluminum-Saturated Southern Bentonite Clay-Cellulose Column when Applied at Field Capacity and Leached Immediately. Volume Displacements: a - 25.0 ml; b - 27.5 ml

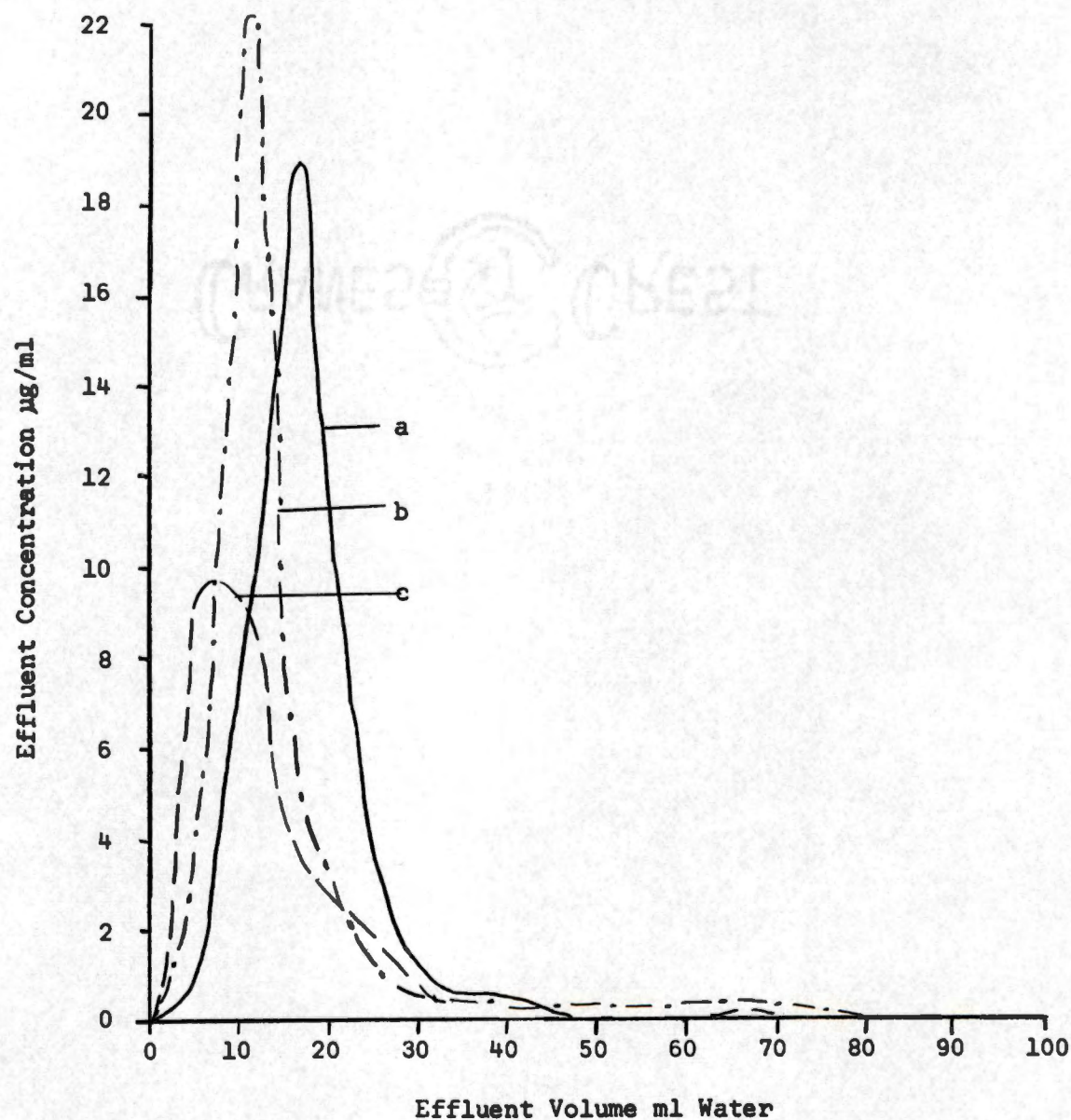


Figure 5. Phorate Effluence when Applied to Aluminum-Saturated Southern Bentonite Cellulose Column at Field Capacity and Air Dried before Leaching. Volume Displacements: a - 11.2 ml; b - 12.0 ml; c - 8.1 ml

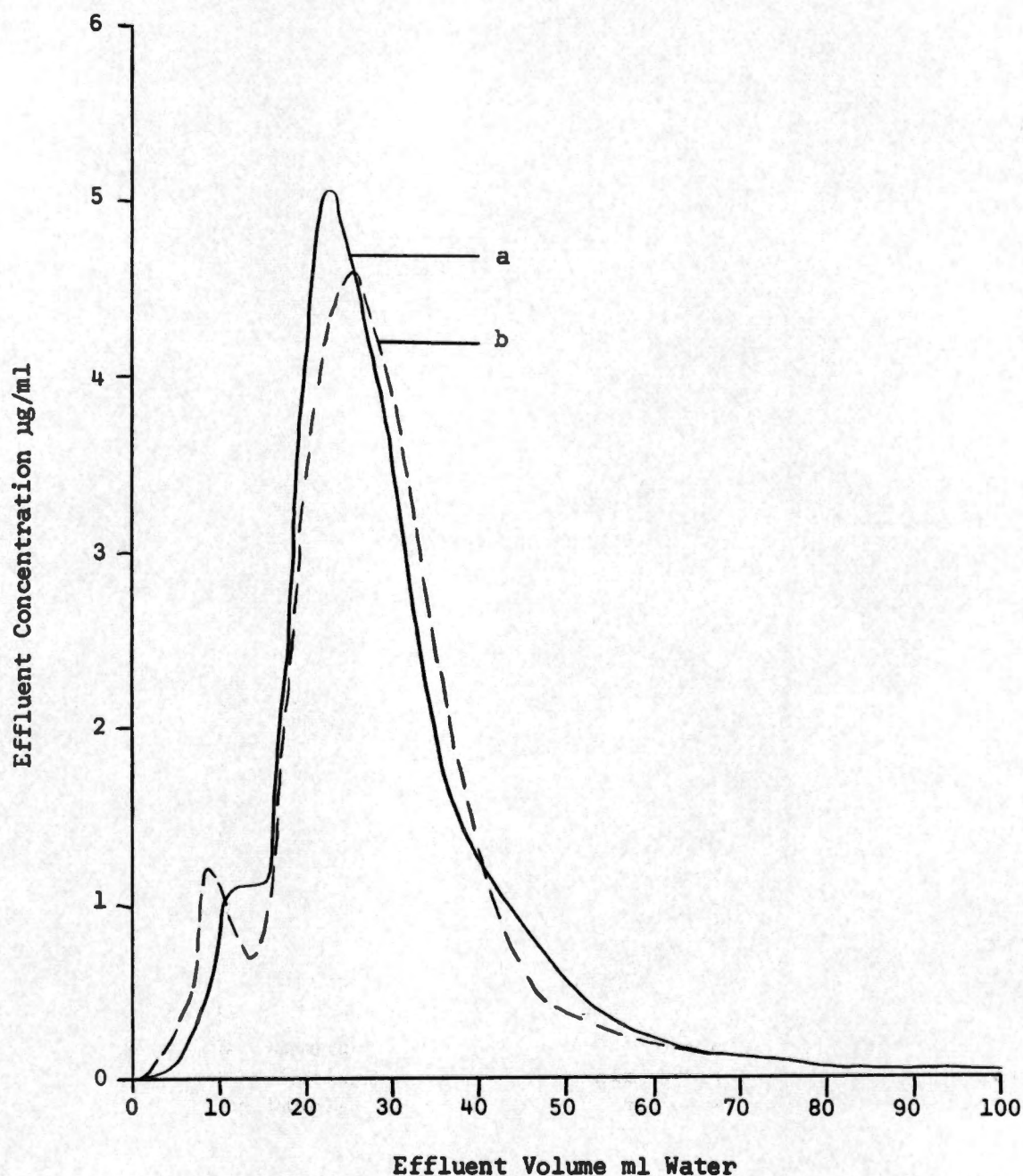


Figure 6. Demeton Effluence when Applied to Aluminum-Saturated Southern Bentonite Cellulose Column at Field Capacity and Air Dried before Leaching. Volume Displacements: a - 25.8 ml; b - 25.0 ml

The maximum concentration for phorate in instances where the insecticide was applied to an air-dry column and then air dried before leaching occurred between 1.0 and 1.4 volume displacements (Figure 7). Greater than 90 percent was collected by 2.0 volume displacements. After leaching with approximately 166 milliliters water, the amount of phorate remaining in the column ranged from 17 to 46 micrograms.

When demeton was applied to an air-dry column and air dried before leaching, the maximum concentration occurred from 1.72 to 1.75 volume displacements (Figure 8). After 3.0 volume displacements, more than 90 percent had moved through the column. After leaching with 100 milliliters water, the amount retained in the column ranged from 0.5 to 0.75 microgram.

In columns which were packed with only cellulose, the elution of each insecticide occurred after 1.0 volume displacement. This indicates that there was no adsorption of the insecticide by cellulose.

Peaks other than the ones indicating the maximum concentration of insecticide occurred in phorate columns. They were most prominent in columns which were never air dried after the insecticide application. These peaks occurred after the main peak, indicating that they moved slower or were more strongly adsorbed. The metabolites which move at a slower rate are probably adsorbed on drying of the column.

For demeton a secondary peak occurred before the major peaks in all instances. This metabolite moves faster than the major one; therefore, it appears that this was caused by negative adsorption of this metabolite to the clay since it occurred in some instances in less than 1.0 volume displacement.

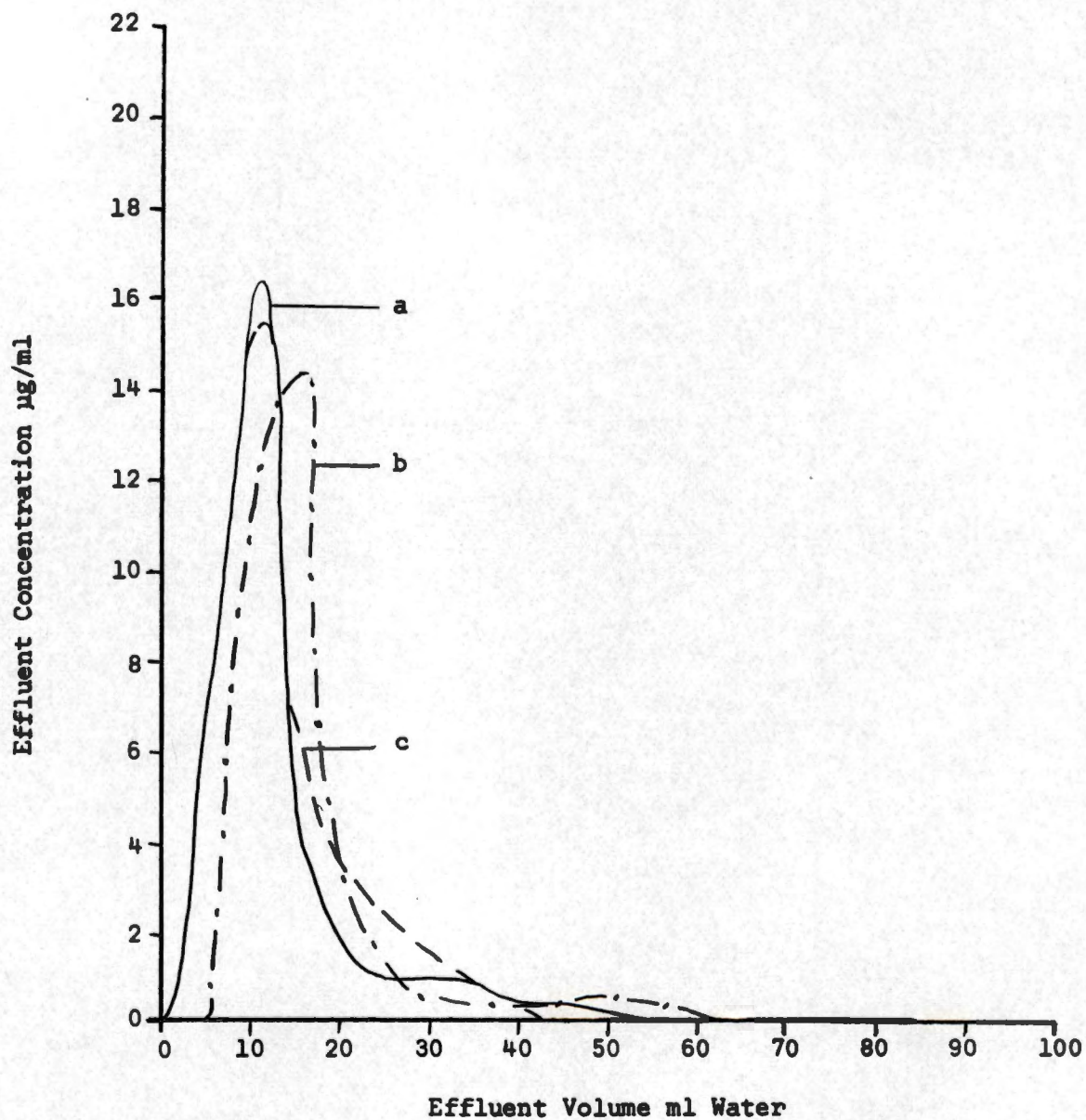


Figure 7. Phorate Effluence when Applied to Aluminum-Saturated Southern Bentonite Cellulose Column when Dry and Air Dried before Leaching. Volume Displacements: a - 12.5 ml; b - 11.0 ml; c - 11.3 ml

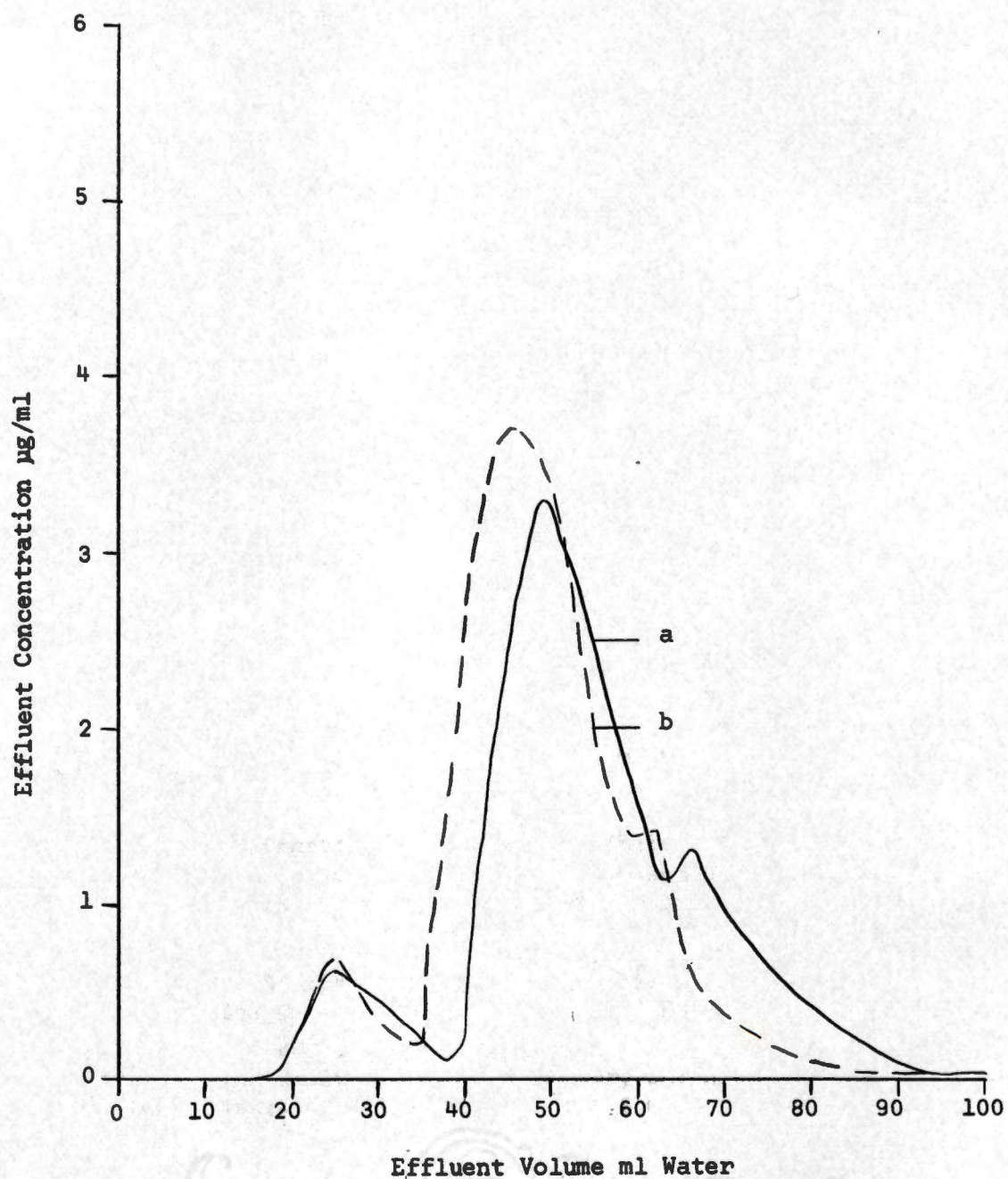


Figure 8. Demeton Effluence when Applied to Aluminum-Saturated Southern Bentonite Cellulose Column when Dry and Air Dried before Leaching. Volume Displacements: a - 28.0 ml; b - 26.5 ml

Because of the low activity of phorate, 200 micrograms per gram clay were added in order to make analysis possible. Demeton specific activity was much higher; therefore, only 40 micrograms insecticide per gram clay were necessary for analysis.

In cases where the insecticides were applied to a moist column and kept moist until leaching, demeton moved through the column at a slower rate than did phorate. This was probably due to a greater amount of very weak adsorption of demeton to the clay surface. Also, the quantity of insecticide applied could have influenced the maximum concentration peak position as a result of over saturation of clay with insecticide.

When the insecticides were applied to a moist column and air dried or applied to a dry column and air dried, the passage of air through the column caused some movement of the insecticide in the column. Such movement should be greater in the liquid phase of movement when the insecticide was applied to the moist column. The movement in the vapor or gas phase through the column should have also been greater in the moist columns upon air drying. This movement would lower the number of volume displacements necessary for the largest peak positions of insecticide flowing through the column.

IV. ADSORPTION

Exchange Resins

Upon the addition of 400 micrograms phorate per gram cation exchange resin Amberlite IR-120 (H+), 328 micrograms were adsorbed. One hundred twenty-five micrograms were adsorbed per gram with the anion exchange resin Amberlite IRA 400 (Cl-). In a similar manner, 93 micrograms

demeton were adsorbed to the same cation exchange resin and 146 micrograms to the anion exchange resin.

Both phorate and demeton showed an affinity for both the cation and anion exchange resins. Either the insecticides have charged sites on their molecules or they possibly react with the resins by replacing an H^+ ion or $-CH_3^+$ group of the $N-CH_3$ on the anion exchange resins. The net charge for phorate was shown to be positive to a greater magnitude than the thiol isomer of demeton.

Less demeton was adsorbed by the cation exchange resin than was adsorbed by the anion exchange resin, thus suggesting a net negative charge on the insecticide.

Glass Adsorption

The amount of insecticide adsorbed by glass was very low, much less than 0.1 microgram per 12.7 square centimeter of glass exposed. Extreme care was taken to insure that all glassware used was thoroughly rinsed with the solution being sampled before the actual sample was taken in all adsorption studies.

Clay Adsorption

The amount of insecticide adsorbed per gram clay as influenced by the predominant ion saturation is shown in Table II. In each case calcium-saturated Southern Bentonite tended to adsorb more insecticide than did the other clays.

More phorate was adsorbed by the calcium-saturated clay than the thiol isomer of demeton. The fact that 12.75 micrograms thiol isomer of demeton were adsorbed to aluminum-saturated Tako Kaolin versus negative

TABLE II

EFFECT OF ION SATURATION AND NPK ON
 μ G INSECTICIDE ADSORBED PER G CLAY
 FROM 40 μ G INSECTICIDE PER 25 ML
 AQUEOUS SUSPENSION WITH 1 G CLAY*

Ion Saturation	Tako Kaolin		Southern Bentonite	
	Demeton	Phorate	Demeton	Phorate
Ca^{+2}	12.25	13.00	10.50	20.00
Al^{+3}	12.75	-3.75	8.50	8.50
Ca^{+2} + 100 μ g NPK	4.25	12.50	-2.00	10.00
Al^{+3} + 100 μ g NPK	3.25	-7.50	3.75	1.65

*Average of three replications

3.75 micrograms for phorate can be attributed to the demeton isomer being more negatively charged and reacting with the aluminum ion or reacting with broken edges of the kaolin mineral to positive sites.

Since the aluminum ion had little or no effect on the amount of phorate or thiol isomer of demeton adsorbed per gram, it indicates that the demeton was most probably adsorbed to the clay at positive sites on the clay. This does not imply that no adsorption occurred to negative sites or by clay-aluminum bonding.

Soil Adsorption

The results of the adsorption of the insecticide to soil over a three-day period are shown in Table III. For both phorate and demeton, soils 59 and 61 tended to adsorb more insecticide than did the other soils. The amount of insecticide adsorbed also tended to increase slightly with time.

As the amount of clay increased, the amount of insecticide adsorbed also increased. Also, the greater the amount of organic matter in the soil, the greater the amount of adsorption. Several other factors seemed to influence the amount and rate of adsorption. As pH or base saturation decreased, the amount of thiol isomer adsorption increased.

All the variables which influenced the uptake of phorate and the thiol isomer of demeton appeared to be similar except for clay content. As the clay content increased, the amount of thiol isomer adsorbed seemed to decrease; however, this was most probably due to the fact that as the clay content increased, the percent organic matter decreased. The variable having the greatest effect upon the amount of insecticide adsorbed appeared to be organic matter content.

TABLE III

EFFECT OF TIME ON μG INSECTICIDES ADSORBED
 PER G SOIL FROM 200 μG INSECTICIDE IN 25
 ML AQUEOUS SUSPENSION WITH 5 G SOIL*

Lab. No.	One Day		Two Days		Three Days	
	Demeton	Phorate	Demeton	Phorate	Demeton	Phorate
32	7.5	-5.4	5.0	-0.5	6.0	3.6
35	-6.0	-3.9	-4.5	-4.2	10.5	-2.7
59	7.0	21.3	8.5	15.0	10.0	23.1
61	4.0	0.3	0.0	13.2	10.0	12.9
106	0.5	-3.9	9.0	0.6	6.5	0.0
107	8.5	-3.9	8.5	0.0	4.0	2.7
109	10.5	1.8	16.0	-0.3	4.5	2.1

*Average of three replications

Moisture

The effect of the moisture condition at time of application on retention of insecticide by clays or soil at the time of application and leaching is shown in Table IV. In every case when the insecticide was applied under dry conditions, more of the insecticide was retained after leaching. This effect was most pronounced in the Tako Kaolin clays. For demeton the amounts retained per gram Tako Kaolin clay were 0.3 and 1.0 microgram when added at field capacity and air-dry conditions, respectively. For phorate the amounts retained by Tako Kaolin were 0.3 and 1.6 micrograms when applied to the clay at field capacity and air-dry conditions, respectively.

Clay or soil adsorbs more insecticide at the air-dry state than at field capacity. This statement is in agreement with findings reported by Ashton and Sheets (4) in work done with EPTC. The greatest magnitude of change was in the Tako Kaolin for both phorate and demeton. From three to five times more insecticide was adsorbed when added at the air-dry state as compared to field capacity.

Fertilizer Effects

The results of adding nitrogen, phosphorus, or potassium to a clay suspension on the amount of insecticide remaining in solution are shown in Table V. In phorate the addition of 200 micrograms phosphorus caused the concentration to drop from 1.05 to 0.57 micrograms insecticide remaining in solution. Nitrogen and potassium had little or no effect on the concentration of phorate in solution.

For demeton the addition of phosphorus had little or no effect, but the addition of nitrogen and potassium reduced the amount in solution from 1.25 to 1.00 and 1.13 micrograms, respectively.

TABLE IV

EFFECT OF MOISTURE AT TIME OF APPLICATION ON μG
INSECTICIDE RETAINED PER G IN CLAYS AND SOIL*

Sample	Field Capacity		Air Dry	
	Demeton	Phorate	Demeton	Phorate
Tako Kaolin	0.3	0.3	1.0	1.6
Southern Bentonite	0.5	3.0	0.7	3.8
Memphis soil Ap horizon	0.5	0.6	0.6	1.4

*200 μg insecticide per 5 g clay or soil and leached with 100 ml distilled water

TABLE V

EFFECT OF N, P, OR K ON CONCENTRATION OF INSECTICIDES
IN SOLUTION FROM 40 μ G INSECTICIDE IN 40 ML
AQUEOUS SUSPENSION WITH 1 G CALCIUM-
SATURATED SOUTHERN BENTONITE*

System	μ g Demeton per ml	μ g Phorate per ml
STD	1.25	1.05
STD + 200 μ g N	1.00	0.97
STD + 200 μ g P	1.30	0.57
STD + 200 μ g K	1.13	1.09

*Average of three replications

Where nitrogen, potassium, or phosphorus was added to calcium-saturated Southern Bentonite, the amount of phorate remaining in solution decreased by approximately 50 percent upon the addition of phosphorus. Nitrogen and potassium had no effect on the concentration of phorate in solution. The phosphate ion possibly caused the insecticide to salt out of solution.

The phosphorus did not cause any change in the amount of demeton in solution, but nitrogen and potassium did lower the concentration. Nitrogen and potassium compounds possibly caused salting out of the insecticide.

The amount of insecticides adsorbed by clays decreased upon the addition of nitrogen, potassium, and phosphorus. Part of this could be caused by a lower concentration of insecticide in solution, therefore, less in contact with the clay.

Interlayer Spacing

The effects of adsorbed phorate and demeton are shown in Table VI. Upon an increase of insecticide concentration, the basal spacings of both aluminum- and calcium-saturated Southern Bentonite expanded until a maximum was reached. The maximum basal spacing for phorate was when 234 milligrams insecticide per gram clay were added, at which time the basal spacing was 16.3 angstroms for calcium-saturated Southern Bentonite and 16.9 angstroms for aluminum-saturated Southern Bentonite. The clay was still expanding at 234 milligrams demeton per gram clay. At the rate of 468 milligrams per gram clay, the clay clumped together; and X-ray analysis was difficult to interpret.

All efforts to effect a change in the X-ray pattern for Tako Kaolin failed.

TABLE VI

EFFECT OF INSECTICIDES ADSORBED ON BASAL
SPACING (Å) OF SOUTHERN BENTONITE

mg Insecticide per Gram Clay	Calcium-Saturated Clay		Aluminum-Saturated Clay	
	Demeton	Phorate	Demeton	Phorate
0	13.7	13.7	13.5	13.5
26	15.3	15.4	14.7	14.0
52	15.2	15.4	15.5	14.9
78	16.0	15.4	15.7	15.3
156	17.1	16.0	17.0	16.4
234	17.7	16.3	17.3	16.9
468	--	16.3	--	16.9

Both phorate and demeton were removed from the clay lattice by dialysis in water as shown in Table VII. The rate of desorption seemed faster for demeton in both cases of aluminum- and calcium-saturated Southern Bentonite than for phorate. At a dialysis time of 108 hours, the basal spacings were approximately the same for calcium-saturated Southern Bentonite in the phorate and demeton treatments. The same relationship existed for the aluminum-saturated Southern Bentonite samples.

Because of the increased expansion of Southern Bentonite in every case of addition of either phorate or demeton, it was apparent that the adsorption was greater than one monolayer thick. This principle was confirmed by dialysis since by diffusion water removed most of the insecticide from the clay lattice. This suggests, as did Weed², that the chemical adsorption occurs only at the first molecular layer of the insecticide in the clay lattice. The other layers are weaker bonded, suggesting physical adsorption.

The radioactive thiol isomer of demeton was found to expand the lattice of Southern Bentonite. The basal spacings of calcium- and aluminum-saturated Southern Bentonite were 15.5 and 15.7 angstroms after a treatment of 7.8 milligrams insecticide per gram clay.

²Weed, loc. cit.

TABLE VII

EFFECT OF DIALYSIS AS INDICATED BY BASAL SPACING ($\text{\AA}$)
 ON DESORPTION OF INSECTICIDES FROM SOUTHERN
 BENTONITE AFTER TREATMENT WITH 234
 MG INSECTICIDE PER G CLAY

Dialysis Time	Calcium-Saturated Clay		Aluminum-Saturated Clay	
	Demeton	Phorate	Demeton	Phorate
Standard	13.7	13.7	13.5	13.5
0 hour	17.7	16.3	17.3	16.9
46 hours	14.9	15.5	14.8	16.4
108 hours	15.1	15.2	14.5	14.5

CHAPTER V

SUMMARY AND CONCLUSIONS

The objective of this course of study was to compare the persistence, degradation, movement, and adsorption of phorate and demeton, two organic phosphates similar in molecular makeup. The major results and conclusions are:

1. Both insecticides seem to follow the first order kinetics of degradation. After seven days, the decomposition rate of demeton increased several fold. This change in rate is suspected to be the result of a catalytic effect caused by a drop in pH. The half-life for phorate was calculated to be 62.4 hours at pH 7.0 and 70.0 hours at pH 4.5. The half-life of demeton was calculated for the rate of decomposition for the first seven days. No difference could be distinguished for pH 4.5 or 7.0. The half-life was calculated to be 1.525×10^3 hours.

The long half-life of demeton renders it more hazardous than phorate. Since it exists 20 to 25 times longer than phorate, more care should be exercised in its use. Its possibilities for causing extended pollution problems are greater than those of phorate because after only a few days' time the concentration of phorate remaining would be negligible.

2. The degradation rate of the insecticide appears to be related to the amount of organic matter in the soil. As the organic matter content increased, more metabolites appeared earlier in larger amounts; therefore, soils high in organic matter would tend to alleviate possibilities of pollution because of the rapid breakdown of the insecticide.

3. The peak concentration of the insecticides leached through the clay columns is fairly independent of the moisture condition at the time of the insecticide application or thereafter before leaching. The volume displacement for phorate ranged from 1.0 to 1.5 for maximum concentration of insecticide to occur. The volume displacement for demeton was from 0.9 to 2.08 for maximum peak height.

4. The amount of insecticide remaining in the column was affected by the moisture condition of the column. In cases where the column was dry at the time of application or dried thereafter before leaching, the amount of insecticide retained increased considerably for phorate. The moisture condition had little or no effect on the amount of demeton remaining in the clay column. The amount of demeton movement would be approximately the same no matter when applied to the soil. The amount of phorate retained by the soil would be greater when applied to a dry soil. The danger of stream pollution would be greatest when the insecticide is applied to a moist soil.

5. Both insecticides are adsorbed by aluminum- and calcium-saturated Southern Bentonite from aqueous solutions. Tako Kaolin adsorbed demeton readily when it was calcium saturated but repelled it when aluminum saturated.

6. The addition of phosphorus decreased the adsorption of phorate by clays. The addition of nitrogen and potassium decreased the adsorption of demeton slightly, but had no effect on phorate.

7. Southern Bentonite lattice spacing can be expanded by heavy applications of either insecticide. The amount of expansion is a function of the concentration of insecticide used. The multiple layers of

insecticide can be desorbed from the clay lattice by dialysis until lattice spacings of approximately 15.1 and 14.5 angstroms are reached for calcium- and aluminum-saturated clay, respectively. This desorption suggests that upon heavy application to a montmorillonite soil the clay can hold the insecticide until rain or other sources of water are present to remove it from the clay lattice down to one molecular layer.

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LITERATURE CITED

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