

AN ABSTRACT OF THE THESIS OF

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Title: THE MOVEMENT AND ADSORPTION OF 2, 4-DICHLORO-
PHENOXYACETIC ACID IN SELECTED OREGON SOILS
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The objectives of this study were to evaluate the effects of soil acidity on the movement and adsorption of 2, 4-dichlorophenoxyacetic acid (2, 4-D) and to investigate the bonding mechanisms involved in the adsorption phenomenon.

The movement of 2, 4-D acid through Lookout silt loam soil was studied by allowing radioactive ^{14}C -labeled 2, 4-D acid to leach through soil uniformly packed in plexiglass columns. The surface 0 to 0.4 cm layer of the soil was treated with 10 ml of 5 ppm of radioactive 2, 4-D acid and the soil was leached two days with water at a rate of 0.5 in/day. Additional soils were treated similarly with 2, 4-D but a zone of Fe^{3+} , Al^{3+} , or Cu^{2+} -saturated soil was included in the column after which the leaching was conducted.

Adsorption-desorption isotherms at 25°C were obtained by equilibration of the natural and the Fe^{3+} , Al^{3+} , or Cu^{2+} -saturated soil systems with 50 ppm of 2, 4-D for 24 hours. Upon attainment of

the maximum adsorption, the equilibrium solution was removed and two water wash treatments applied to these systems. Subsequent equilibration with 100 ml of distilled water for 285 hours was conducted at 25°C to study desorption phenomenon.

The presence of Fe^{3+} , Al^{3+} , or Cu^{2+} -saturated homoionic soil decreased the rate of 2,4-D movement and increased the quantity of 2,4-D adsorbed. The 25°C adsorption isotherm showed an inverse relationship between 2,4-D acid adsorption and the pH of the Fe^{3+} , Al^{3+} , or Cu^{2+} -saturated soil. The desorption studies showed that 40%, 60%, 81%, and 57% of the total adsorbed 2,4-D were desorbed from the natural soil, Cu^{2+} , Al^{3+} , and Fe^{3+} -saturated soil respectively. The Cu^{2+} , Al^{3+} , and Fe^{3+} salts of the 2,4-D were prepared and the solubility found to decrease in the order $\text{Cu}^{2+} > \text{Al}^{3+} > \text{Fe}^{3+}$. The solubility data correlated with the degree of 2,4-D adsorption although the concentration of 2,4-D in the soil solution did not exceed the solubility limit. Infrared spectrophotometry showed the carbonyl stretch frequency decreased to a lower frequency upon the complexation of 2,4-D acid with Fe^{3+} , Al^{3+} , or Cu^{2+} -saturated montmorillonite indicative of a hydrogen bond formation through the carbonyl group of 2,4-D.

The differences in 2,4-D movement through and adsorption on selected Oregon soils were mainly attributed to the acidity of the natural soil, a result of the presence of Fe^{3+} , Al^{3+} , and Cu^{2+} ions.

The hydrated Fe^{3+} , Al^{3+} , and Cu^{2+} cations possibly served as an adsorption site for the 2,4-D molecules. The water solubilities of the Fe^{3+} , Al^{3+} , and Cu^{2+} salts of 2,4-D accounted in part for the differences in the movement and adsorption of 2,4-D.

The Movement and Adsorption of 2, 4-Dichlorophenoxyacetic
Acid in Selected Oregon Soils

by

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THE MOVEMENT AND ADSORPTION OF 2, 4-DICHLOROPHENOXYACETIC ACID IN SELECTED OREGON SOILS

INTRODUCTION

As the population of the world increases day by day, the human need for a more abundant food supply becomes more urgent. A look at the environment of a food crop immediately reveals that crop production is related to soils, plant populations, and climatic conditions. Numerous weeds compete with crops for sunlight, nutrients, air, and water. Therefore, with this competition, crop production often suffers in quality and in total yield. It is in part with plant competition and increased labor cost that the development of selective herbicides was initiated to increase crop yields and profit margins.

The fate of herbicides, once they have been introduced into soils is a question asked with increased frequency. The herbicide, 2, 4 - dichlorophenoxyacetic acid (2, 4-D), is used quite extensively in agriculture. However, the research on the movement of 2, 4-D acid in soils as affected by soil properties is somewhat limited. It is with this philosophy that the study of 2, 4-D acid movement through and adsorption on the soil phase of the environment was initiated.

OBJECTIVES

The objectives of this study were to evaluate the effects of the soil properties of pH, organic matter, and cation saturation on the 2,4-D acid movement through and adsorption on selected Oregon soils. Consideration of possible bonding mechanisms of 2,4-D acid with soils was studied through infrared spectrophotometry.

LITERATURE REVIEW

Development and Formulation of 2, 4-D

Research on 2, 4-D compounds started during World War II, under wartime secrecy, with the first 2, 4-D acid chemical synthesis reported by Porkorny (1941). Initial use of 2, 4-D as a plant-growth regulator was conducted by the research group at Boyce Thompson Institute (Klingman, 1966). Two years later, Marth and Mitchell (1944) of the USDA, Beltsville, Maryland reported that 2, 4-D showed specificity to kill dandelion and plantain in a bluegrass lawn at rates of from 250 to 1, 000 ppm.

Suggested as a translocated spray in the United States and as a selective soil sterilant in Britain (Slade et al., 1945), 2, 4-D was soon found to be an ideal selective herbicide. The use of 2, 4-D as a pre-emergence herbicide (Anderson and Ahlgren, 1947; Anderson and Wolf, 1947), as a soil sterilant (Bohmont, 1952), and as a selective spray for use in corn, sugarcane, flax, coffee, pastures, turf, cereals, orchards, and non-crop land soon became widespread.

Different chemical formulations of 2, 4-D were investigated thoroughly in greenhouse and field tests to increase the efficiency and dependability and to broaden the spectrum of 2, 4-D applications (Crafts, 1961a). 2, 4-D was first marketed as a carbowax mixture and has since been formulated as the sodium salt, the alkyl ester,

the ammonium and amine salts, the low volatile esters, the emulsifiable acid, the dry powdered amine salt, the acid paste, and in several pelleted forms. Presently the commercial products are generally formulated as the salt or ester form (Crafts, 1961a).

Some growers now combine applications of fertilizers and pesticides. Growers in Georgia, Kansas and Missouri have used 2, 4-D and nitrogen solution combinations on pasture (Berg, 1967). Urea-herbicide combinations, including 2, 4-D, atrazine, lorox, and treflan are used preemergence and postemergence on grass crops (Berg, 1967). Problems of proper placement, compatibility, and labeling do occur, but combined application is being actively promoted by both fertilizer and 2, 4-D producers. In addition, combinations of 2, 4-D and other herbicides such as dicamba, EPTC, and 2, 4, 5-T, increase the spectrum of 2, 4-D effectiveness markedly (Mason, 1966).

Mode of Action of 2, 4-D in Plants

The 2, 4-D compounds penetrate the cuticle as the undissociated parent acid molecule and are assimilated by the living parenchyma cells of the mesophyll (Crafts, 1961a). By movement along the symplast, the 2, 4-D molecules reach the phloem. Upon entry into sieve tubes, 2, 4-D moves with the assimilation stream from the foliage to the regions of growth and reproduction. Having

reached the actively growing region of the plant, 2,4-D can affect respiration, carbohydrate utilization, nutrient uptake, mitosis, cell elongation, and cell differentiation (Crafts, 1961b; Crafts and Robbins, 1962; King, 1966).

Fate of 2,4-D in Soils

The increased use of pesticides in agricultural practices warrants the investigation of the reactions of these additives with the soil. The possibility of a gradual accumulation in the soil must be considered with a view to long-range effects on quantity and quality of crop yield and soil pollution. Higher degrees of selectivity and a longer period of weed control may be achieved with chemicals applied to the soil in contrast to those applied to foliage (Crafts and Robbins, 1962; Klingman, 1966). However, chemicals applied to the soil are also more subject to changes in the environment than are chemicals applied to foliage (Freed, 1958; Crafts and Robbins, 1962; Klingman, 1966). Five major factors often determine the ultimate biological effectiveness of any chemical: (1) adsorption; (2) leaching; (3) volatilization; (4) microbial breakdown; and (5) chemical breakdown (Audus, 1951; Blouch and Fults, 1953; Ogle and Warren, 1954; Sherburne and Freed, 1954; Hill et al., 1955; Bollen, 1961).

Microbial Degradation of 2, 4-D

One of the important properties of soils which determines the detoxification rate of 2, 4-D is the microorganism activity, principally the activity of certain groups of soil bacteria. The microbial degradation of 2, 4-D is enhanced by high soil moisture content, temperature, and organic content (Klingman, 1966). Low rates (0.25-1 lb/A) of 2, 4-D will normally be decomposed in one to four weeks in a warm, moist loam soil (Weed Society of America, 1967); therefore, the accumulation of 2, 4-D acid does not produce a problem in agricultural practice.

Adsorption and Movement of 2, 4-D

The adsorption of chemicals by soils has long been recognized as a major factor in the extent of biological activity of soil applied herbicides. Sorption of a compound by a solid phase is a complex phenomenon and is governed by chemical and physical forces. In chemical adsorption, a chemical bond forms between the monolayer of the adsorbate and adsorbent surface as a result of Coulombic forces (Kunze, 1966; Daniels and Alberty, 1967). Chemical adsorption generally gives high heats of adsorption (greater than 20 kcal/mole) or a high binding strength, while physical adsorption exhibits heats of adsorption less than 20 kcal/mole (Bailey and

White, 1964). A comprehensive review of the literature of the adsorption and desorption of organic pesticides has been excellently conducted by Bailey and White (1964).

The movement of herbicides in soil in association with water is a phenomenon of considerable importance in the determination of effectiveness of organic chemicals. The downward movement or leaching of a chemical generally is given the first consideration; however, lateral movement and even upward movement in the soil may be of great importance (Freed et al., 1962).

Downward Movement. The movement of water downward in soils occurs in the form of a thin film or by drainage through macropores, a result of the combined effects of capillary and gravitational forces. The most rapid and probably most predominant movement of dissolved solutes in the soil is with the mass water movement; therefore, both the direction and path of the movement of chemicals in the soil will be those followed by the water. It would be expected that the bulk chemical travel would be in the water flow lines found in the soil (Freed et al., 1962).

Lateral Movement. In addition to downward movement, isodiametric diffusion of a chemical in solution may occur. As the water percolation rate decreases, diffusion becomes a greater factor in the distribution of the chemical in the soil profile. Hartley (1960) proposed that the reduced leaching of pesticides through soil system was

primarily caused by diffusion of chemicals into pores inaccessible to the downward movement of water.

Upward Movement. The upward movement of 2,4-D results from a mass upward transfer of water under the influence of evaporation from the surface. Consequently, a chemical may concentrate at the soil surface, thus effectively removing it from the root zone.

Factors Affecting Adsorption and Movement of 2,4-D

The principal variables which affect the movement of organic chemicals include: (1) soil chemical and physical characteristics, such as clay, organic matter content, and pH, (2) properties of the pesticide molecule, such as water solubility, molecular weight, polarity and biodegradability, and (3) environmental factors, such as rainfall, temperature, and wind. Among those variables mentioned above, the effects of water solubility, soil acidity, clay and organic matter content, and cation saturation will be discussed.

Soil Acidity (pH)

Many investigators have observed the effect of pH on the adsorption and movement of pesticides in soils. Since the degree of dissociation of 2,4-D is determined by the pH, the extent of adsorption should logically depend upon the pH. The adsorption of 2,4-D by a hydrogen cation exchanger was nearly twice as great at pH of 2.5 or

below as at a pH of 3.3 (Weaver, 1947). On the other hand, adsorption of 2,4-D on charcoal was pH independent in the range pH 2.2 to 8.0 (Leopold et al., 1960). Therefore, pH dependence of adsorption did not universally apply to all adsorbents. Frissel and Bolt (1962) reported that both positive and negative adsorption of 2,4-D on montmorillonite and illite occurred as a function of pH. Montmorillonite negatively adsorbed 2,4-D at pH values above 3 while illite exhibited negative adsorption only above pH 7. The adsorption isotherms of 2,4-D on montmorillonite and illite showed a marked slope change at a pH of about 4, caused by the transition of 2,4-D anions to 2,4-D molecules. Above pH 4 the adsorption was attributed to an adsorption of 2,4-D anions on positive edges of the illite.

In studying the role of pH on the adsorption of 2,4-D by montmorillonite, Bailey et al. (1968) concluded that the pH of the bulk solution rather than the surface acidity determined the positive adsorption of 2,4-D. Theoretically, positive adsorption of the 2,4-D molecule should start to occur when the pH of the bulk solution was approximately 1-1.5 pH units above the dissociation constant. Takijima and Hayashi (1953b and 1954a) observed increased 2,4-D movement and decreased 2,4-D adsorption upon addition of Ca(OH)_2 to a soil system. Dregne (1967) has reported the order of leachability of 2,4-D passing through a cation exchange resin column to increase in the order $\text{H} < \text{Ca} < \text{Mg} < \text{K} < \text{Na}$. The solubility of the acid and the

various 2,4-D salts increased in a similar order. However, Hanks (1946) reported the same leachability in six soils, limed or unlimed, for 2,4-D acid and its Ca-salt form.

Organic Matter and Clay Content

Soil organic matter correlates positively with the phytotoxicity and adsorption of 2,4-D by soils (Ogle and Warren, 1954; Upchurch and Mason, 1962). Upchurch and Mason (1962) further demonstrated that the GR_{50} (dosage required to cause a 50% reduction in dry shoot weight) of a soil which contained 16.8% organic matter was about 70 times greater than a soil which contained 0.4% organic matter. Activated carbon has long been known as an effective adsorbent for slightly soluble ring-type compounds. Some of the groups which are present on charcoal are similar to those found in soil organic matter (i.e., $-COOH$, $-OH$, $-CH_3$, etc.) and hence adsorption by charcoal might be similar for some organic compounds (Hassler, 1963). The rate constants for adsorption of 12 organic pesticides on the 273-micron carbon were reported to be remarkably similar (Weber and Gould, 1966). Thus, it was concluded that the effectiveness of active carbon as it related to rate of removal of organic pesticides from solution should be relatively independent of the type of organic pesticides. However, a study of the relationship between molecular structure of phenoxyacetic acids and herbicide adsorption (Leopold

et al., 1960) indicated large differences of adsorption onto charcoal. Molecular changes which reduced the water solubility of the compounds also enhanced the adsorption properties. Thus, the percent adsorption of 2, 3, 4, 5, 6-pentachlorophenoxyacetic acid onto charcoal was eight times as great as that of phenoxyacetic acid.

Leaching studies have shown that organic chemicals leach deeper in lighter textured soils than in heavier textured and organic soils. 2, 4-D was leached more readily in soils of low organic matter content (Hernandez and Warren, 1950; Ogle and Warren, 1954). Harris and Warren (1964) have reported more desorption of 2, 4-D from bentonite than from muck soils in agreement with observed leaching measurements. Only about half of the initially adsorbed 2, 4-D could be recovered from the muck soil by four extractions with distilled water.

Studies of 2, 4-D diffusion in saturated Oregon soils have shown that the diffusion coefficient decreased with an increase in organic matter and clay content (Lindstrom et al., 1968). The diffusion coefficient values ranged from $1.24 \times 10^{-6} \text{ cm}^2/\text{sec}$ for a Kenutchen clay (63.7% clay) to $7.05 \times 10^{-6} \text{ cm}^2/\text{sec}$ for quartz sand. Since the diffusion coefficient measures the ease with which the 2, 4-D diffuses through the pores of the medium, a high value of diffusion coefficient should be expected for the coarse textured materials and a low value of diffusion coefficient for the fine

textured materials.

2, 4-D Water Solubility

Since the movement of non-adsorbed 2, 4-D in the soil is subject to mass water flow, it is reasonable to expect differences in the movement and in the chemical dissolved in the solution phase as a function of the moisture content. The solubility of 2, 4-D increases with an increase in the polarity of the solvent phase. Accordingly, the solubility is increased in the following order: 2, 4-D acid < NH_4^+ -salt < K^+ -salt < Na^+ -salt < alkanolamine-salt (Crafts and Robbins, 1962). Aldrich and Willard (1952) compared the availability and movement of the butyl ester and triethanolamine form of 2, 4-D in a mixture of sand and montmorillonite, using cucumber as a bio-assay, and reported the ester form was fixed more strongly than the salt form. The mobility of the ester form was accordingly found to be much less than that of the salt form. The ester form was less soluble in water than the salt form.

Cation Saturation

Differences exist between inorganic cations in their ability to exchange for other cations present on the exchange sites of the clay minerals. Evidence to date indicates that there also may be a difference in the replacement of an organic cation or adsorption of an

organic molecule as a function of the nature of the inorganic cation present on the exchange complex (Bailey and White, 1964). In a series of studies of the behavior of 2,4-D in soils, Takijima and Hayashi (1953a, b; 1954a, b) found that 2,4-D adsorbed by the homoionic soils were in the following order: Al^{3+} -soil $>$ H^{+} -soil $>$ Natural soil $>$ Ca^{2+} -soil. They suggested that the adsorption of 2,4-D by soils was caused by Al in the soils.

Mechanism of 2,4-D Acid Bonding to Soils

Hydrogen Bonding

In a study of the reaction of clay minerals with organic acids, ketones and carboxylate polymers, Kohl and Taylor (1961) attributed changes in the infrared frequency of the carboxyl group to hydrogen bonding between the carboxyl and the mineral surface. Larson and Sherman (1964) also interpreted the decrease of the carbonyl ($\text{C}=\text{O}$) stretch frequency to be indicative of hydrogen bonding with the clay lattice hydroxyl groups.

Coordinated Water Bridge

Urea (Mortland, 1966), amides (Tahoun and Mortland, 1966) and ketone (Parfitt and Mortland, 1968) compounds form either a direct bridge or have a water intermediate between the carboxyl

group and exchangeable metal cations on the clay surface. An infrared study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite showed direct coordination of Ca^{2+} and Mg^{2+} to the water molecules. A strong hydrogen bond was formed between the hydrated cations and pyridine which readily displaced water from the coordination spheres around the cations (Farmer and Mortland, 1966).

Direct Coordination

Infrared studies of EPTC sorbed to montmorillonite showed a decrease in the CO stretch and an increase in the CN stretch frequency. The decrease in CO and increase in CN stretch indicated coordination of EPTC to the exchangeable metal ion through the oxygen of the carbonyl group (Mortland and Meggitt, 1966). Upon EPTC complexation with Cu^{2+} -montmorillonite, the carbonyl stretch frequency shifted from $1,655 \text{ cm}^{-1}$ to $1,566 \text{ cm}^{-1}$. However, the band shift was found to a lesser extent in the complex formation between EPTC and Al^{3+} -montmorillonite (from $1,655 \text{ cm}^{-1}$ to $1,570 \text{ cm}^{-1}$). Therefore, the extent of band shift which reflected the stability of the different complexes was determined by the metal ions present on the exchange complex.

Protonation

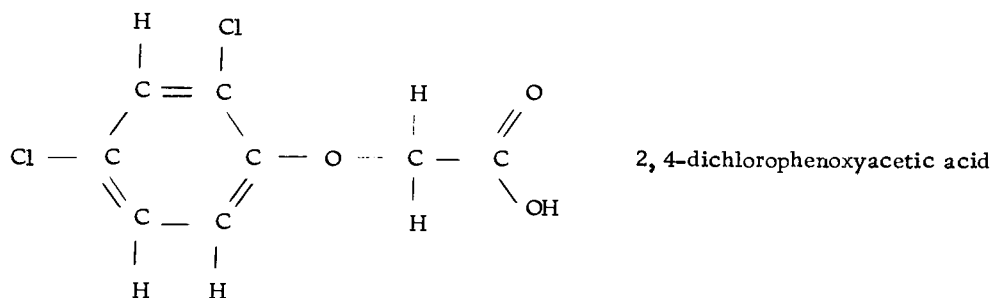
Montmorillonite which is saturated with Ca^{2+} , Cu^{2+} , Ni^{2+} , and Al^{3+} has been shown to protonate adsorbed 3-amino-triazole to form the 3-amino-triazolium cation. The protonation appeared to result from the highly polarized water molecules in direct coordination to the saturating cations. The protonated molecule followed normal exchange reactions with Ca^{2+} , Cu^{2+} , Ni^{2+} , and Al^{3+} cations.

To sum up, the movement and adsorption of 2,4-D acid in the soil system is a gross effect of the physicochemical properties of the 2,4-D compound and the environmental factors. An attempt has been made in this review to elucidate some of the factors which appear to affect the movement and adsorption of 2,4-D in the soil phase. Many investigators have shown that the degree of dissociation and the resultant adsorption of 2,4-D acid is dependent upon the pH of the environment. Other investigators have reported the formation of complexes between organic chemicals and cations in the soil which contribute to soil acidity, namely, those of aluminum, iron, and copper. A question which appears quite relevant in a study of 2,4-D movement and adsorption is whether the 2,4-D acid is adsorbed through an acidic cation or whether the extent of adsorption is merely dependent upon the pH of the system, irregardless of adsorptive sites.

MATERIALS AND METHODS

Chemical and Physical Properties of 2, 4-Dichlorophenoxyacetic Acid

The structural formula and various physical and chemical properties of 2, 4-D acid are given below:



Molecular formula: $C_8H_6Cl_2O_3$

Molecular weight: 221.0

Melting point: $135-138^{\circ}C$

Boiling point: $160^{\circ}C$ at 0.4 mm Hg.

Decomposition temperature: stable at its melting point.

The 2, 4-D acid was supplied in crystalline form by AmChem Products, Inc., Ambler, Pennsylvania. The radioactive 2, 4-D acid labeled at the carbonyl carbon was supplied by New England Nuclear Corporation, Boston, Massachusetts.

Chemical Characterization of Soils

Lookout silt loam soil was analyzed for free iron oxide, extractable Al, exchangeable bases, cation exchange capacity, organic matter, and pH. The soil pH, percent clay, and percent organic

matter of Dayton silt loam and Hembre loam were used as determined from soil survey laboratory reports.

Iron Oxide Content

The free iron oxide content was determined subsequent to the removal of calcium carbonate and organic matter. Three 30 ml aliquots of pH 5 1N sodium acetate were added to 15 gm of soil. The sodium saturated sample was heated with increments of 30% H_2O_2 to oxidize organic matter. The sample was then washed twice with pH 7 1N NaOAc and transferred to a centrifuge tube.

The iron oxide was extracted with 40 ml of a composite solution containing 0.125M sodium bicarbonate and 0.3M sodium citrate. One gm of $\text{Na}_2\text{S}_2\text{O}_4$ was added to each sample and after each sample was heated at 70°C for five minutes, a second one gm portion of $\text{Na}_2\text{S}_2\text{O}_4$ was added. The sample was then heated for an additional five minutes. After addition of 50 ml of 1N NaCl, the sample was centrifuged and the decantate diluted to volume in a 250 ml volumetric flask.

The iron content of the extractant was determined colorimetrically on a Bausch and Lomb Spectronic 20 spectrophotometer at 510 m μ (Jackson, 1958; Murti et al., 1966; Jackson, 1967).

Extractable Aluminum

Ten gm of air dry soil was extracted four times with 20 ml portions of pH 4.8 1N NH_4OAc . After each addition of NH_4OAc , the sample was thoroughly mixed, shaken for 15 minutes, centrifuged and the clear supernatant saved. Upon final extraction, the supernatant was diluted to 100 ml with 1N NH_4OAc . The extractant was colorimetrically analyzed for aluminum with aluminon as the color-complex-forming reagent. The colorimetric analysis was conducted on a Bausch and Lomb Spectronic 20 spectrophotometer at a wavelength of 530 $\text{m}\mu$ (Smith et al., 1949; Robertson, 1950; Jackson, 1958; Sandell, 1959; Page and Bingham, 1962; Hsu, 1963; Jackson, 1967).

Exchangeable Bases (Ca, Mg, K)

Exchangeable bases were determined in a 1N pH 7 NH_4OAc extract of ten grams of air dry soil. The extraction procedure was identical to that used for extractable aluminum. The calcium and magnesium content was determined with a Perkin Elmer 303 atomic absorption unit at 212 and 285.1 $\text{m}\mu$ respectively (Kahn, 1966). The potassium content in the extract was measured by a Beckman flame photometer at a wavelength of 767 $\text{m}\mu$.

Cation Exchange Capacity

Ten grams of air dry soil was saturated with calcium ion by four 30 ml washings of 0.5N CaCl_2 . Excess CaCl_2 was removed by two washes with 30 ml portions of H_2O . The soil was washed finally with a 0.01 N CaCl_2 solution to eliminate the salt effect. The adsorbed calcium was displaced by three 30 ml extractions of 0.5 N MgCl_2 . Each time the sample was shaken for 15 minutes, centrifuged, and the clear supernatant diluted to 100 ml in a volumetric flask. The calcium in the extract was determined with a Perkin Elmer 303 atomic absorption unit at 212 m μ .

Organic Matter Content

Ten ml of 1N $\text{K}_2\text{Cr}_2\text{O}_7$ was added to one gram of air dry soil and the suspension gently swirled while a 20 ml increment of concentrated H_2SO_4 was added. The mixture was cooled for 10 to 15 minutes and then 5 gm of NH_4F and 100 ml of distilled water were added to the system. The system was vigorously stirred and shaken after which 10-20 drops of diphenylamine indicator was added. The final solution was titrated with 0.34N $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ until the color changed from purple to green. Then, at least 0.5 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ solution was added to turn the solution to a purple color and again the solution was titrated with $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution to the green

endpoint. The percentage of organic carbon and organic matter in the soil was calculated as follows:

$$\%C = \frac{\text{millieq of ox.} - \text{millieq of red.}}{\text{wt. of sample} \times 0.76} \times 0.003 \times 100$$

where millieq of ox. = ml $K_2Cr_2O_7$ \times N $K_2Cr_2O_7$

millieq of red. = ml $Fe(NH_4)_2(SO_4)_2$ \times N $Fe(NH_4)_2(SO_4)_2$

0.003 = millieq wt. of carbon

0.76 = fraction of organic carbon which was oxidized
to CO_2

$$\%O.M. = \%C \times 1.724$$

where

1.724 = conversion of carbon to organic matter

$$= \frac{1}{0.58}$$

pH

Ten grams of air dry soil was weighed into each of three small beakers. Sufficient distilled water was added to one beaker to prepare a soil paste. The soil paste was frequently stirred for 30 minutes and the soil pH measured. Distilled water and 1N KCl was added to the second and third beaker (1:10 soil solution ratio) respectively. The system was mixed frequently for 30 minutes and the soil pH measured.

Movement of 2, 4-D Acid

Saturation of Soils with Fe^{3+} , Al^{3+} , and Cu^{2+} Ions

A quantity of 21.385 gm of Lookout silt loam soils were treated three times with 100 ml aliquots of 1N AlCl_3 , FeCl_3 , and CuCl_2 solutions to produce Al^{3+} , Fe^{3+} and Cu^{2+} homoionic saturated soil. The excess chlorides were removed by water treatments until a dilute AgNO_3 solution showed a negative chloride test. After the last wash treatment, the homoionic soils were air-dried, and ground to a uniform size with a mortar and pestle.

Preparation of Soil Columns

Untreated air dry Lookout silt loam soil (433.075 gm) was packed uniformly below the 2.0 cm line of a plexiglass column (7.45 cm x 10.15 cm, Figure 1). The homoionic soil (21.385 gm) was packed above the untreated soil into the 1.6-2.0 cm layer of the column. Untreated soil (64.155 gm) equivalent to three 0.4 cm thick layers was subsequently packed on the top of the homoionic soil layer. The top 0-0.4 cm layer was filled with the soil which had been mixed with 10 ml of 5 ppm 2, 4-D-1- ^{14}C acid solution (^{14}C activity = 0.0555 $\mu\text{C}/\text{ml}$), air-dried and ground to a uniform size with a mortar and pestle.

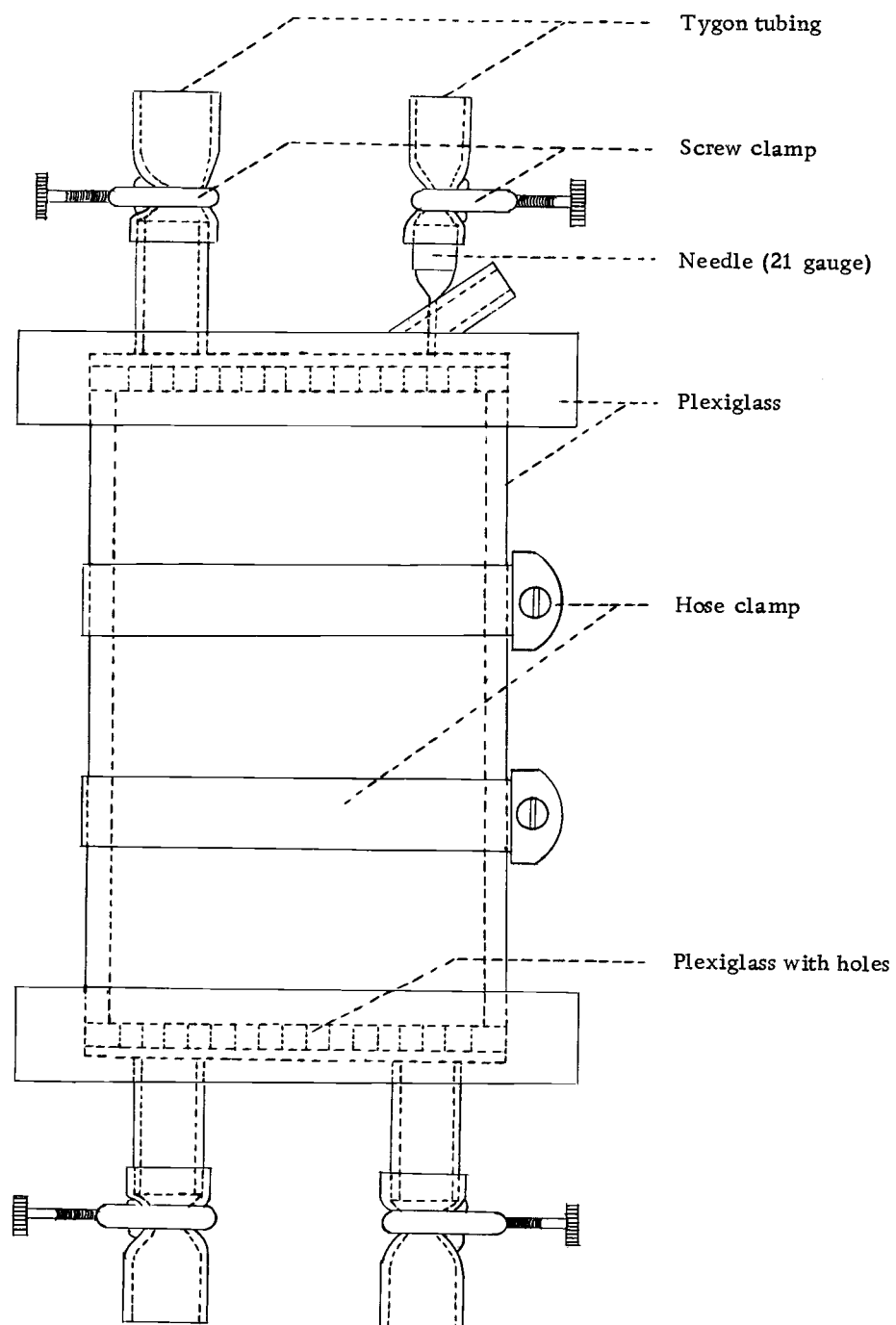


Figure 1. Plexiglass column for studying the movement of 2, 4-D.

Saturation and Leaching of Soil Columns

The plexiglass column which contained the soil was sealed with silicon rubber adhesive, and saturated with distilled water from the bottom inlet for 24 hours. Upon saturation with about 200 ml of distilled water, the soil was leached with distilled water for two days with the flow rate adjusted to be equivalent to 0.5 inch precipitation per day (Figure 2).

^{14}C Activity Determination

After leaching, the soil column was immediately frozen and the plexiglass disassembled longitudinally. With a hand-knife, the frozen soil was cut into half-slices 0.4 cm long. After the frozen soil slices thawed, the soil solution was removed by centrifugation at 11,000 RPM for five minutes. The ^{14}C activity in a 0.1 ml aliquot of the supernatant liquid was measured by liquid scintillation (Packard Tricarb). The scintillation fluor consisted of toluene and methanol as solvents, PPO (6 gm/liter) as the primary fluor, and POPOP (0.3 gm/liter) as the secondary fluor. Ten ml of this solution was mixed with 5 ml of ethanolamine and ethanol (1:4) solution. The counting efficiency was determined by a spiking technique with an internal toluene standard. The other half-slices of column were cut with the technique identical to that mentioned above and the con-

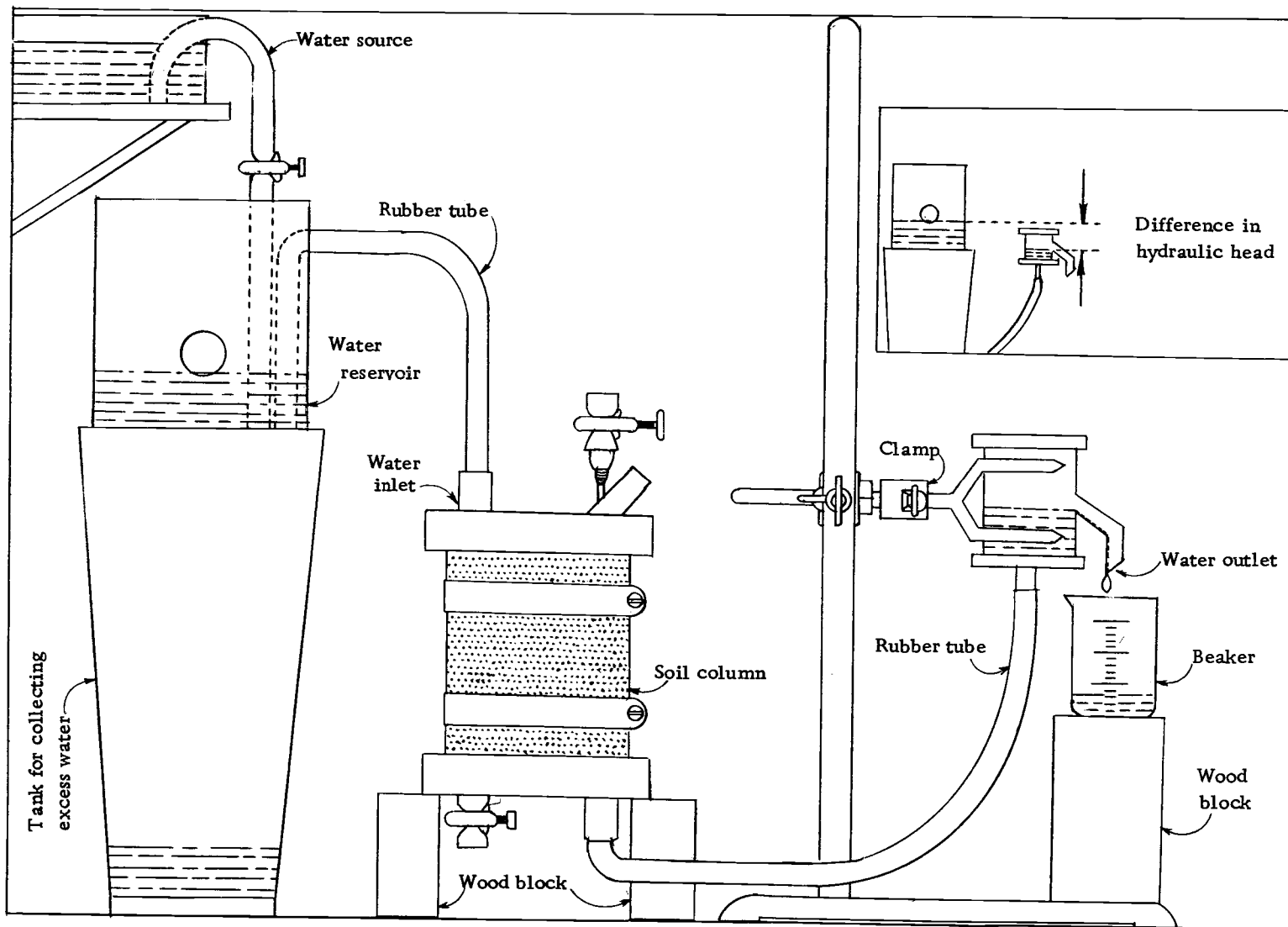


Figure 2. Experimental design to study 2, 4-D leaching.

concentrations of Al^{3+} , Fe^{3+} and Cu^{2+} measured by spectrophotometry (Al^{3+} and Fe^{3+}) and atomic absorption (Cu^{2+}) after extraction with 1N NH_4OAc (pH 4.8).

Statistical Analysis of Column Cutting

To assess the reliability of the technique of slicing a frozen soil column with a hand-knife, experimental data (Table 1) obtained from preliminary and normal studies were tested by student's "t" test. The null hypothesis that the sample mean weight of soil solution extracted from the soil slices was not different from the expected means was tested at both 0.05 and 0.01 probability levels.

Adsorption-Desorption Isotherms

A quantity of 20 gm of the natural or Al^{3+} , Fe^{3+} and Cu^{2+} -saturated Lookout silt loam soil was introduced into each of four centrifuge bottles which contained 200 ml of 50 ppm 2,4-D acid solution respectively. The systems were kept in a constant temperature room and immediately dispersed by a wrist-action shaker. Five ml of the soil suspension were pipetted from each of the bottles at the 0.5, 1, 2, 3, 4, 5, 6, 7, 8, and 24 hour time periods.

The soil suspension which had been removed was immediately centrifuged and the supernatant saved for determination of ^{14}C activity by a liquid scintillation counter. After the adsorption

Table 1. Sample data for statistical inference of sample means.

No. soil slice	No. soil column						
	1	2	3	4	5	6	7
	Wt. soil solutions, gm						
	y_i	y_i	y_i	y_i	y_i	y_i	y_i
1	4.71	4.49	4.57	4.14	4.63	3.69	4.07
2	3.73	3.93	3.90	3.91	4.32	3.83	3.24
3	3.90	4.35	4.05	3.64	3.99	3.87	3.85
4	4.03	4.00	4.04	3.68	4.20	3.68	3.81
5	4.06	3.39	3.99	3.96	3.69	3.50	3.54
6	4.16	3.99	3.29	3.84	4.58	3.92	3.84
7	4.03	4.00	4.40	3.64	3.69	3.68	3.39
8	4.11	4.33	4.93	3.60	3.63	4.05	3.75
9	4.05	4.21	4.10	3.77	3.80	4.04	3.58
10	3.94	3.61	3.81	3.87	3.69	3.63	3.37
11	4.00	4.16	4.06	3.92	4.41	3.95	3.64
12	3.73	4.45	3.84	4.17	3.54	3.30	3.95
13	4.33	3.70	4.39	4.08	4.52	3.49	3.98
14	3.71	3.37	3.86	3.47	4.35	3.58	3.67
15	3.70	--	3.38	4.30	4.09	3.96	3.44
16	4.16	--	3.31	4.03	3.94	4.01	4.38
17	3.97	--	--	4.29	3.79	3.73	4.21
18	4.10	--	--	4.30	4.09	--	--
19	4.27	--	--	--	--	--	--
20	4.29	--	--	--	--	--	--
Total, Σ	80.98	55.98	63.92	70.63	72.95	63.91	63.71
Mean, μ	4.05	4.00	4.00	3.92	4.05	3.76	3.75

-- not determined

maximum was attained (from the plot of the adsorption isotherm), the soil suspension was centrifuged and the supernatant solution saved. After centrifugation, 50 ml of distilled water was added to the centrifuge bottle which contained the soil sample that already had adsorbed the maximum amount of 2, 4-D. The system was shaken for one minute after which the suspension was centrifuged again. The water wash treatment was repeated one time. Finally, 100 ml of distilled water was added to the bottle and the suspension was shaken intermittently. At 1, 4, 6, 93, 97, 261, and 285 hours, 5 ml aliquots of the suspension were sampled and the concentration of the adsorbate was measured by a liquid scintillation counter.

Effect of pH, Organic Matter, and Exchange
Cations on 2, 4-D Adsorption

A quantity of 100 ml (10 ml for the montmorillonite system) of 50 ppm 2, 4-D-1-¹⁴C acid solution was placed in a centrifuge bottle. The 2, 4-D solutions, the Lookout silt loam, Dayton silt loam, and Hembre loam soil samples and the montmorillonite clay suspensions were equilibrated at 25°C for 24 hours to attain a constant temperature. The initial 2, 4-D acid concentration was determined prior to the addition of soil or clay samples to the bottle which contained 2, 4-D acid solution. The soil (10 gm) was introduced into each centrifuge bottle and immediately dispersed by a wrist action shaker. Into the other centrifuge bottles, 0.5 gm of

montmorillonite was added and the system was equilibrated in the constant temperature water bath (25°C) with continuous shaking. After equilibration for 24 hours, the equilibrium concentration of 2,4-D acid was determined by liquid scintillation counting. The 2,4-D adsorbed was calculated by difference between the initial and final 2,4-D concentration in solution.

Effect of Aging of Acid-Treated Soils on 2,4-D Adsorption

To a series of air-dry Lookout silt loam soil samples (5 gm), 5 ml of 0.09851 N HCl solution was added. To the first two duplicate samples was added 25 ml of 60 ppm 2,4-D- $1-^{14}\text{C}$ acid solution and the pH of the suspension was measured immediately. After pH measurement, the systems were equilibrated in a water bath at 25°C for one hour. The suspensions were centrifuged and the 2,4-D activity of the supernatant solutions assayed by a liquid scintillation counter. The extractable aluminum was also measured by spectrophotometry prior to the incorporation of 2,4-D acid into the soil after three 1N NH_4OAc (pH 4.8) extractions had been performed. The same procedures for pH measurement, extractable aluminum determination and 2,4-D acid concentration before and after adsorption were followed upon aging for 1, 5, 10, 26, 36, and 120 hours.

Microbial Degradation of 2, 4-D

To duplicate 21.384 gm samples of Lookout silt loam soil, 10 ml of 5.8 ppm of radioactive 2, 4-D acid was applied. The $^{14}\text{CO}_2$ evolved from the microbial degradation of the 2, 4-D acid was trapped by a monoethanolamine solution. Upon aging for 4, 5, 6, 7, 7.5, 8.5, 9.5, 10.5, 16, 17, and 18 days, the activity of $^{14}\text{CO}_2$ was determined by liquid scintillation and the percent degradation calculated (Figure 3).

Infrared Studies on 2, 4-D-Clay Bonding Mechanisms

Spectral Analysis of Fe^{3+} , Al^{3+} , and Cu^{2+} Salts of 2, 4-D

Crystalline 2, 4-D acid (1.1 g) was dissolved in 4 ml of 100% ethanol after which 15 ml of water was added. The AlCl_3 , FeCl_3 , and CuCl_2 solutions were prepared by dissolution of 1.0635 gm of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 0.6579 gm $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.8520 gm $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ respectively into 20 ml of water. The 2, 4-D acid solution was mixed with the AlCl_3 , FeCl_3 or CuCl_2 solution until a precipitate occurred. The pH was measured on the final solutions.

One mg of each prepared inorganic salt of 2, 4-D was added to 400 mg of KBr, after which the mixture was ground and mixed in a mortar. The mixture was placed in a metal die with a thickness of 0.046 cm. Then the system was exposed to a pressure of 10,000

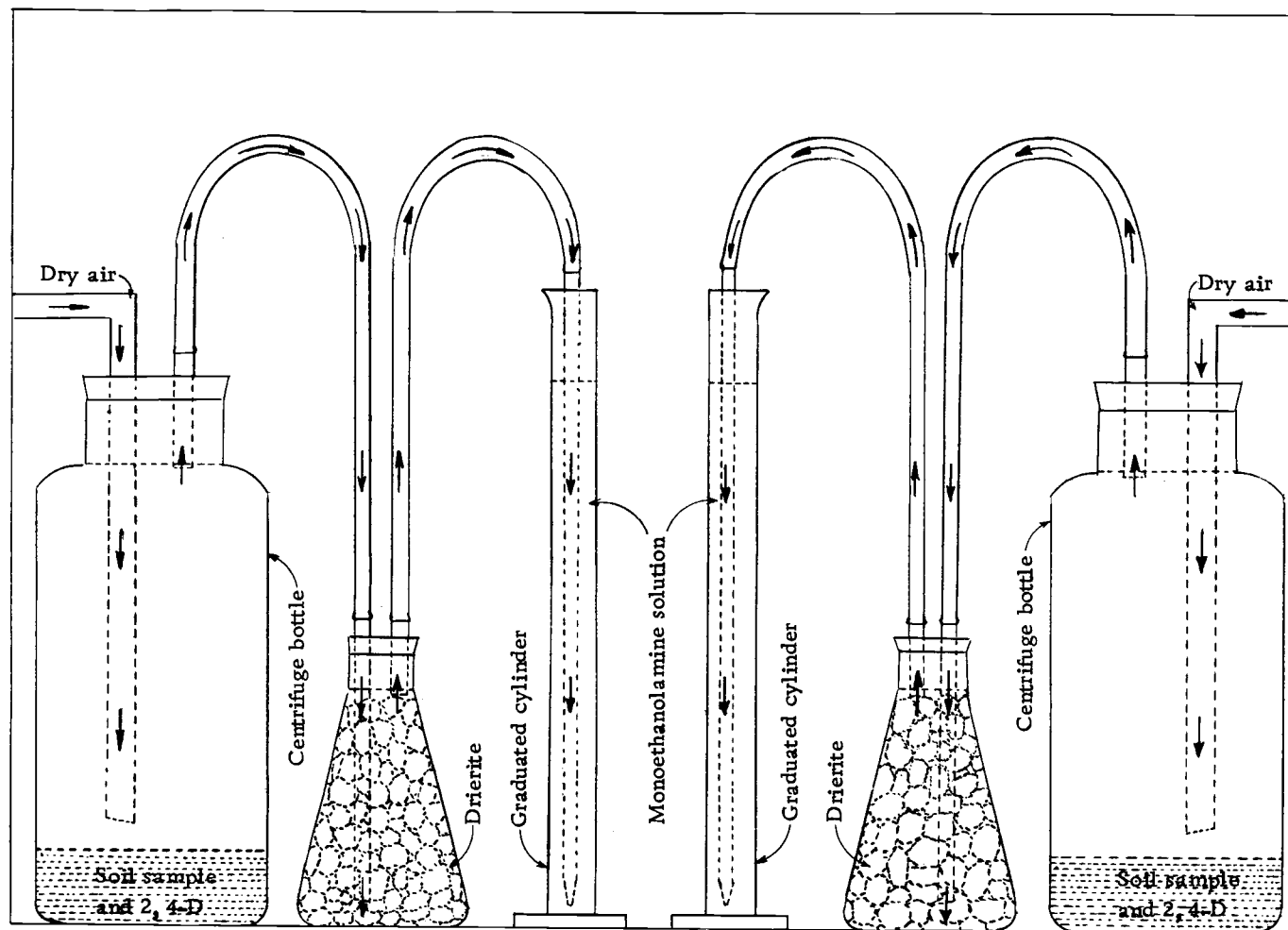


Figure 3. Experimental apparatus to entrap CO₂ evolved from 2, 4-D by microbial degradation.

psi for 30 minutes until the pellet became transparent. The KBr pellets were analyzed by infrared spectrophotometry.

Spectral Analysis of 2,4-D sorbed to Fe^{3+} , Al^{3+} , or Cu^{2+} -Saturated Montmorillonite

To clay suspensions which contained 0.1 gm of Fe^{3+} , Al^{3+} or Cu^{2+} -saturated montmorillonite, 15 ml of 600 ppm 2,4-D acid was added. The systems were equilibrated at 25°C for 24 hours after which 10 ml of each suspension was pipetted into aluminum foil dishes and air-dried for two days. The clay films were peeled from the dishes and placed in a desiccator until analyzed by infrared spectrophotometry.

Water Solubility of Fe^{3+} , Al^{3+} , and Cu^{2+} -2,4-D Salts

Salts of Fe^{3+} , Al^{3+} , and Cu^{2+} -2,4-D were prepared by reaction of radioactive 2,4-D acid with FeCl_3 , AlCl_3 , or CuCl_2 solutions as outlined in the previous section. Each salt which was prepared was water-washed until free of excess chlorides and 2,4-D acids. The specific activities of Cu^{2+} and Fe^{3+} salts were determined by dissolution of 0.05 gm of Cu^{2+} salt and 0.05 gm of Fe^{3+} salt in 100 ml of 100% ethanol respectively. The ^{14}C activity of one ml of each solution was measured by a liquid scintillation counter. The specific activity of the Al^{3+} salt was determined by dissolution of 0.005

gm of Al^{3+} salt in a concentrated HCl and HNO_3 solution due to the insolubilities of Al^{3+} salt in several organic solvents such as methanol, ethanol, acetone, dioxane, and chloroform. The solution was diluted with distilled water to 100 ml. One ml of this solution was assayed to determine the specific activity of Al^{3+} salt of 2, 4-D.

The water solubility of each salt was determined by weighing 0.05 gm of the Fe^{3+} and Al^{3+} salt and 0.025 gm of the Cu^{2+} salt into 50 ml centrifuge tubes which contained 20 ml of distilled water respectively. The systems were shaken by a wrist-action shaker for 24 hours. After centrifugation, the supernatant solutions were discarded, and another 20 ml of distilled water added. Equilibration and centrifugation was followed in the same manner as mentioned above after which duplicate 1 ml of solution was counted by liquid scintillation. The determination of water solubility was repeated until the concentration of 2, 4-D in the supernatant solution remained constant.

RESULTS AND DISCUSSION

Movement of 2, 4-D

Effect of Cation Saturation

The 2, 4-D present in the soil solution of the check column (contains natural Lookout silt loam soil in the whole column) was distributed fairly symmetrically and showed a peak in the 3.6-4.0 cm layer (Tables 2, 3 and Figures 4, 5 and 6) after leaching. The maximum concentration of 2, 4-D in this layer was $0.509 \mu\text{g/ml}$. The pH of this layer was 6.9 (Table 4).

Analysis of the soil column which contained a layer of Fe^{3+} -saturated soil showed that the maximum 2, 4-D concentration in the soil solution ($0.436 \mu\text{g/ml}$) occurred in the 3.2-3.6 cm layer (Table 2 and Figure 4). The pH of the Fe^{3+} -saturated layer of soil was 3.34 (Table 4). In addition to the lower concentration of 2, 4-D present in the soil solution, the column which contained Fe^{3+} -saturated soil showed a definite skewness, perhaps indicative of an adsorption and desorption kinetic phenomenon. The Fe^{3+} initially added to the 1.6-2.0 cm layer moved very little after two days of leaching (Table 5 and Figure 4).

The maximum concentration of 2, 4-D in the soil solution ($0.424 \mu\text{g/ml}$) of the column which contained Al^{3+} -saturated soil

Table 2. Concentration of radioactive 2,4-D in the soil solution of the natural and treated Lookout silt loam soil after leaching.

Soil depth, cm	Concentration of radioactive 2,4-D acid, $\mu\text{g/ml}$			
	Natural soil	1.6-2.0 cm layer saturated with		
		Fe^{3+}	Al^{3+}	Cu^{2+}
0.0-0.4	0.024	0.019	0.027	0.019
0.4-0.8	0.027	0.019	0.035	0.027
0.8-1.2	0.042	0.032	0.056	0.041
1.2-1.6	0.081	0.064	0.113	0.063
1.6-2.0	0.117	0.218	0.277	0.155
2.0-2.4	0.178	0.331	0.360	0.297
2.4-2.8	0.298	0.370	0.424	0.352
2.8-3.2	0.372	0.400	0.387	0.395
3.2-3.6	0.491	0.436	0.321	0.493
3.6-4.0	0.509	0.331	0.224	0.378
4.0-4.4	0.437	0.215	0.111	0.257
4.4-4.8	0.274	0.098	0.063	0.160
4.8-5.2	0.181	0.056	0.027	0.058
5.2-5.6	0.103	0.021	0.010	0.021
5.6-6.0	0.041	0.001	0.004	0.008
6.0-6.4	0.010	0.000	0.005	0.004
6.4-6.8	0.005	0.000	0.000	0.003

Table 3. Total amount of radioactive 2,4-D in the natural and treated Lookout silt loam soil after leaching.

Soil depth, cm	Natural soil	Concentration of radioactive 2,4-D acid, $\mu\text{g}/7.88 \text{ ml}^*$		
		1.6-2.0 cm layer saturated with		
		Fe^{3+}	Al^{3+}	Cu^{2+}
0.0-0.4	0.191	0.146	0.215	0.152
0.4-0.8	0.210	0.146	0.276	0.209
0.8-1.2	0.331	0.251	0.445	0.322
1.2-1.6	0.636	0.508	0.890	0.497
1.6-2.0	0.921	1.719	2.184	1.223
2.0-2.4	1.404	2.606	2.838	2.340
2.4-2.8	2.348	2.917	3.339	2.776
2.8-3.2	2.930	3.150	3.046	3.115
3.2-3.6	3.873	3.436	2.526	3.881
3.6-4.0	4.009	2.610	1.768	2.978
4.0-4.4	3.441	1.696	0.875	2.027
4.4-4.8	2.160	0.770	0.495	1.262
4.8-5.2	1.430	0.441	0.214	0.456
5.2-5.6	0.812	0.165	0.080	0.166
5.6-6.0	0.326	0.006	0.035	0.061
6.0-6.4	0.080	0.000	0.038	0.029
6.4-6.8	0.043	0.000	0.000	0.021
Total 2,4-D acid recovered from column,** μg	25.145	20.567	19.264	21.515
2,4-D re- covery, %	50.34	41.18	38.57	43.07

*7.88 ml of H_2O extracted from each slice.

**2,4-D acid input in each column = 49.95 μg .

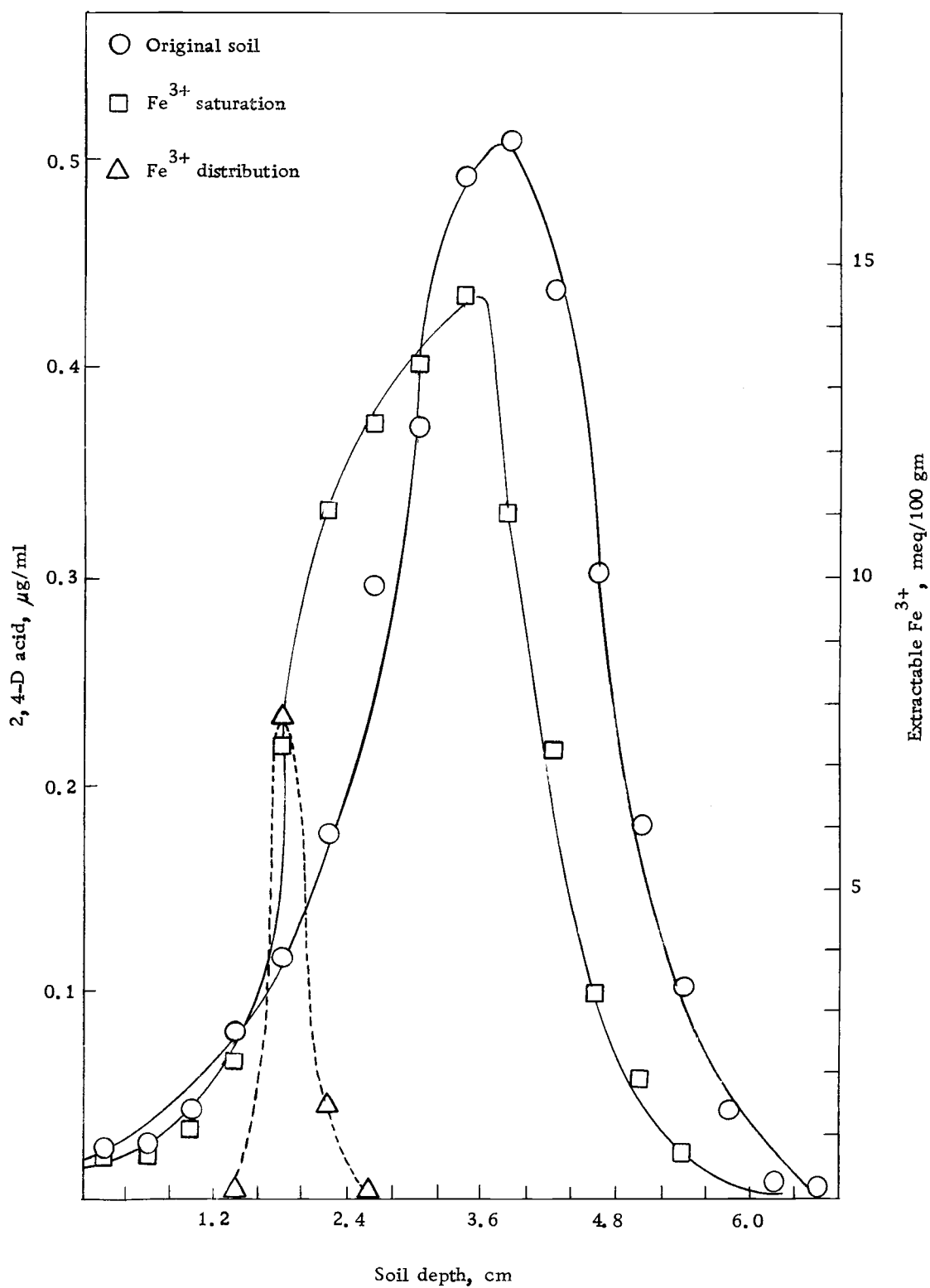


Figure 4. Effect of Fe^{3+} saturation on 2,4-D movement in Lookout silt loam soil.

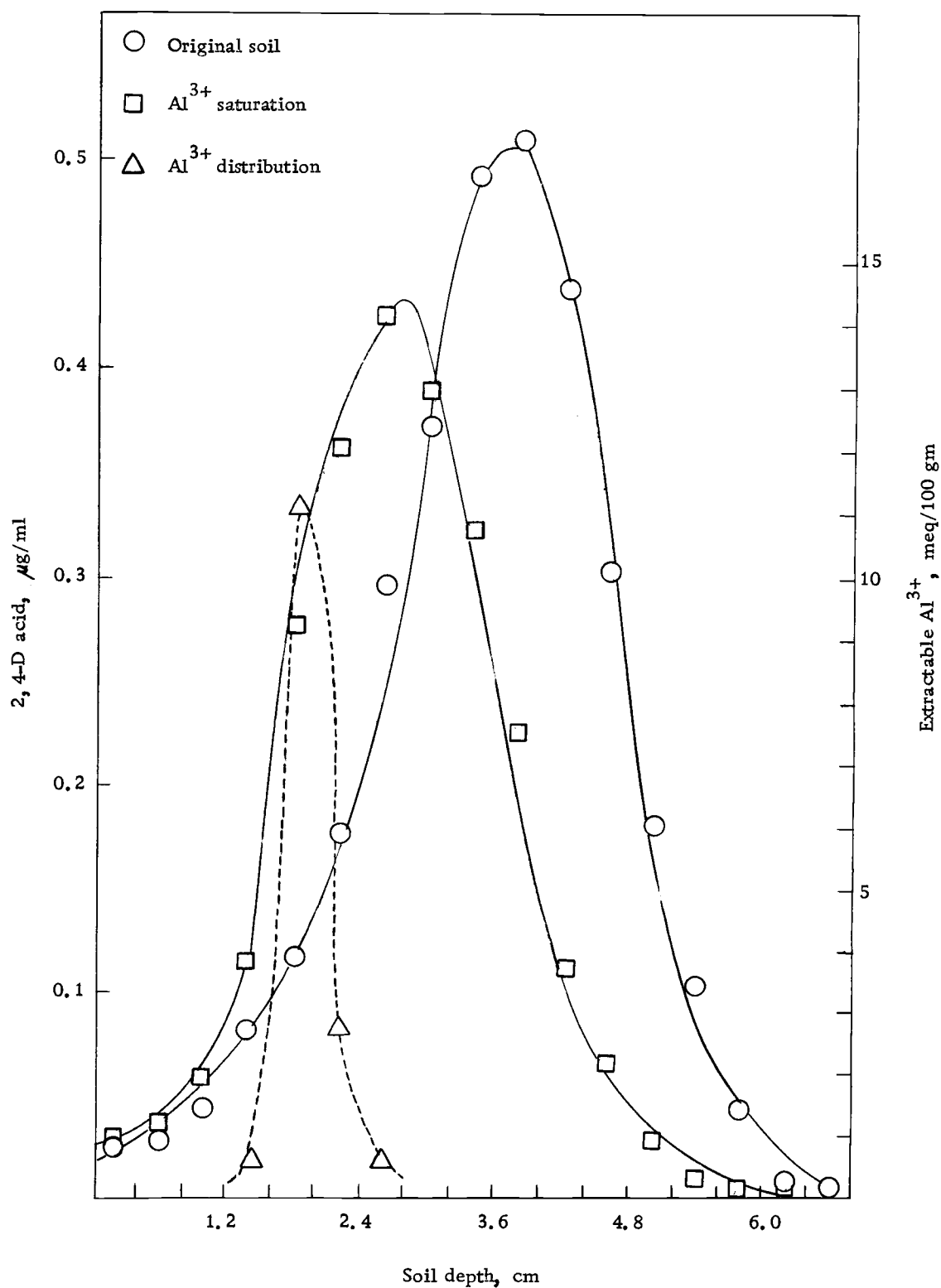


Figure 5. Effect of Al^{3+} saturation on 2,4-D movement in Lookout silt loam soil.

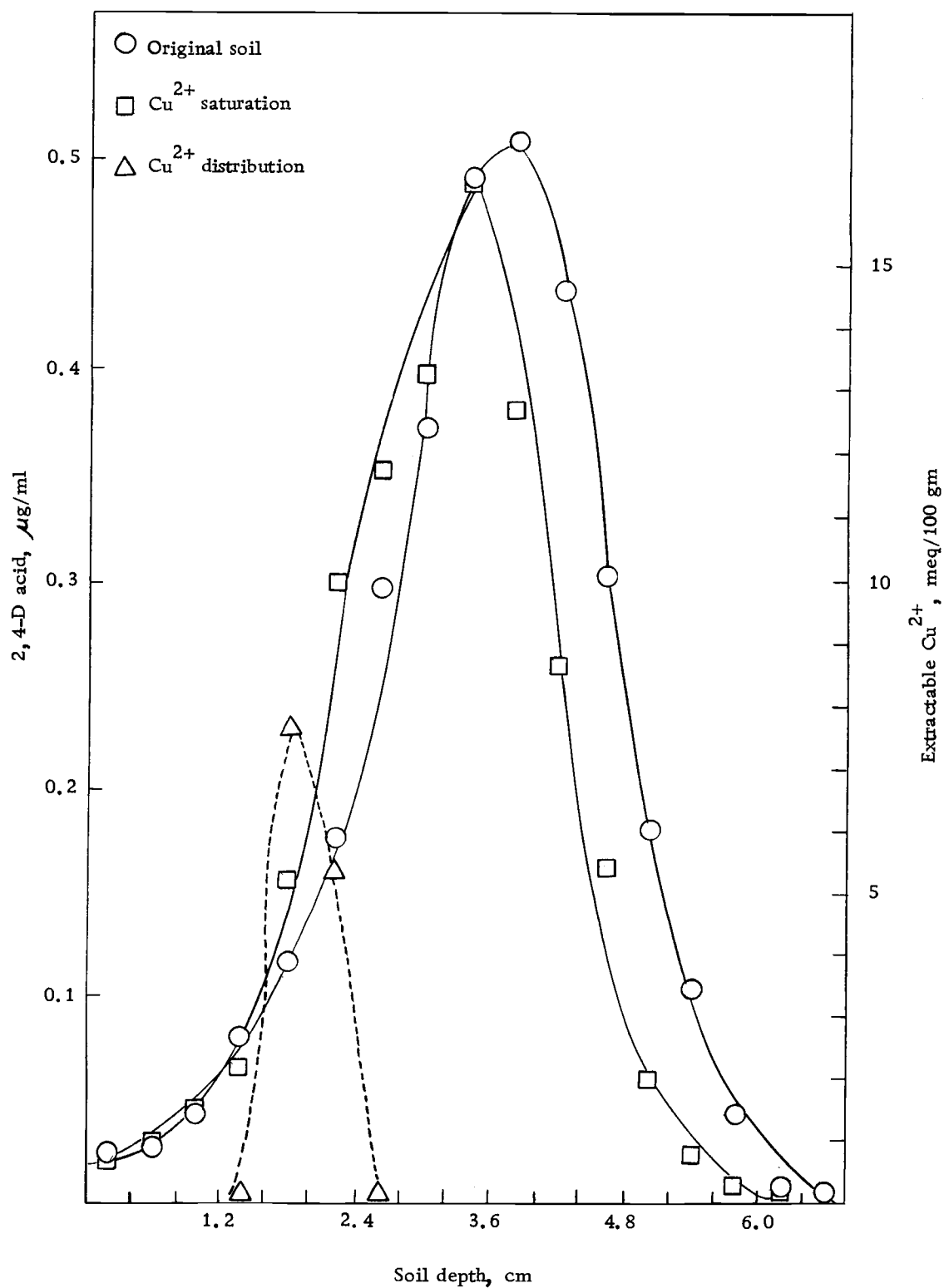


Figure 6. Effect of Cu^{2+} saturation on 2,4-D movement in Lookout silt loam soil.

Table 4. pH of the natural and the Fe^{3+} , Al^{3+} , and Cu^{2+} -saturated Lookout silt loam soils. (Soil: H_2O = 1:10)

Adsorbent	Fe^{3+} - saturated soil	Al^{3+} - saturated soil	Cu^{2+} - saturated soil	natural soil
pH before addition of 2,4-D solution*	3.34	3.85	5.10	6.90
pH after addition of 2,4-D solution	3.70	4.15	4.90	6.45

*pH of 2,4-D stock solution = 3.90.

Table 5. The distribution of Fe^{3+} , Al^{3+} , and Cu^{2+} in the soil solution of the 1.2 to 2.8 cm layers of the Lookout silt loam soil after leaching.

Soil depth, cm	Concentration of cation, meq/100 gm		
	Extractable Fe^{3+}	Extractable Al^{3+}	Extractable Cu^{2+}
1.2-1.6	0.06	0.51	0.10
1.6-2.0	7.78	11.09	7.71
2.0-2.4	1.47	2.71	5.28
2.4-2.8	0.08	0.51	0.01

occurred in the 2.4-2.8 cm layer (Table 2). A slight tailing effect also was observed in the distribution of 2,4-D in this column. Al^{3+} , as would be expected, moved very little during leaching process (Table 5). The pH of the Al^{3+} -saturated layer of soil was 3.85 (Table 4).

In contrast to the columns which contained the Fe^{3+} and Al^{3+} -saturated layers, the column which contained the Cu^{2+} -saturated layer showed the 2,4-D distribution in the soil solution very similar to that of the natural soil. The maximum 2,4-D concentration observed in the soil solution ($0.493 \mu\text{g/ml}$) occurred in the 3.2-3.6 cm layer (Table 2). The extractable Cu also showed a tendency to move from the initial saturated layer to the layer below during the leaching time (Table 5). The pH of the Cu^{2+} -saturated soil was 5.10, a value above the pK of 2,4-D acid (Table 4).

The lack of movement of the Fe^{3+} and Al^{3+} cations which were added to the soil would be expected both because of their trivalent cationic character and as a result of the initial drying treatment of the cation-saturated soil. Some of the added Fe^{3+} and Al^{3+} must have been hydrolyzed to form less soluble hydroxy compounds. On the other hand, the added Cu^{2+} possesses only divalent cationic character and hydrolyzes to a smaller extent. It would be expected that certain hydrolytic products of all the ions added would maintain a cationic character and be susceptible to a degree of leaching.

The rather large pH difference between the Fe^{3+} , Al^{3+} , or Cu^{2+} -saturated soil and the natural soil would be expected to cause a large difference in the relative proportions of the molecular and anionic forms of 2,4-D present in the soil solution. As the pH of the soil decreased and approached the pK of 2,4-D, the proportion of the non-charged molecular constituent would increase and lead to increased adsorption. As indicated earlier, the 2,4-D present in the soil solution generally decreased as the pH of each soil system decreased. The 2,4-D did show more mobility in the Fe^{3+} system than in the Al^{3+} system. This difference may be the result of a stronger bond formation between the Al and the 2,4-D. In addition to the simple effect of pH on the equilibrium of 2,4-D, the phenomenon of complexation between the added cations and 2,4-D must be considered. The solubility of the Fe^{3+} , Al^{3+} , and Cu^{2+} salts of 2,4-D is different and will be discussed later.

The highest recovery percentage (50%) of the added 2,4-D was obtained from the soil solution for the column without cation treatment. The columns which had been pretreated with the Fe^{3+} , Al^{3+} , and Cu^{2+} showed 2,4-D recovery percentages respectively of 41%, 38%, and 43% (Table 3). Microbial degradation probably accounted for some of the 2,4-D loss but adsorption was considered to be the most important factor to account for the remaining 50-60% of the 2,4-D initially added.

Statistical Analysis of Column Slicing Technique

To determine the reliability of the slices cut from the soil column, a "student's t" test was conducted on seven columns. The "student's t" values calculated from the standard deviations were smaller than the "tabulated t" values at both 0.05 and 0.01 probability levels (Table 6). Since the experimental data did not present sufficient evidence to indicate that the mean solution weight exceeds the expected mean in any of the columns studied, therefore, it is concluded that the technique of slicing a soil column uniformly with a knife falls within a 99% confidence level.

2, 4-D Adsorption-Desorption

pH, Water Solubility and Possible Complex Formation

Since the movement and adsorption of 2, 4-D acid on Lookout silt loam was influenced by Fe^{3+} , Al^{3+} , or Cu^{2+} saturation, a quantitative study of adsorption and desorption was conducted to help interpret both the difference in the percentage of 2, 4-D recovered and the distribution of 2, 4-D from the soil columns.

The pH of the natural soil and the soil saturated with Cu^{2+} , Al^{3+} , and Fe^{3+} after addition of the 2, 4-D solution was 6.45, 4.90, 4.15 and 3.70 respectively (Table 4). After equilibration for 24 hours with 50 ppm of 2, 4-D acid, the natural soil had adsorbed 29

Table 6. Statistical inference of sample means.

Column Number	1	2	3	4	5	6	7
Wt. of soil sample, gm	500	500	540	540	540	540	540
Wt. of soil solution, gm	202.18	202.18	200.15	200.15	200.15	185.34	185.34
Length of column, cm	10.15	10.15	10.15	10.15	10.15	10.10	10.10
No. of soil slices	25.40	25.40	25.40	25.40	25.40	25.25	25.25
Sample mean (\bar{y})*	4.05	4.00	4.00	3.92	4.05	3.76	3.75
Expected mean (μ_0)**	3.98	3.98	3.94	3.94	3.94	3.67	3.67
No. of sample (n)	20	14	16	18	18	17	17
Standard deviation(s) +	0.245	0.368	0.445	0.255	0.354	0.218	0.311
Student's "t" ++	1.279	0.20	0.539	0.332	1.319	1.699	1.061
$t_{0.05}$	1.729	1.771	1.753	1.740	1.740	1.746	1.746
$t_{0.01}$	2.539	2.650	2.602	2.567	2.567	2.583	2.583
99% confidence limit (upper) †	4.21	4.30	4.33	4.09	4.29	3.91	3.97
99% confidence limit (lower) †	3.89	3.70	3.67	3.75	3.81	3.61	3.53

*From Table 1.

**From total solution weight divided by no. of soil slices.

$$+\text{Standard deviation} = \sqrt{\frac{\sum (y_i - \bar{y})^2}{n - 1}} = \sqrt{\frac{\sum y_i^2 - \frac{(\sum y_i)^2}{n}}{n - 1}}$$

$$++\text{Student's "t"} = \frac{(\bar{y} - \mu_0) \sqrt{n}}{s}$$

† (1 - α) confidence limit is calculated as follows: $\bar{y} \pm t_{\alpha/2} S / \sqrt{n}$

μg of 2, 4-D acid per g of soil or 5.8% of the total available 2, 4-D acid (Tables 7 and 8).

As would be expected from the results of the 2, 4-D movement studies the 2, 4-D adsorbed on the Fe^{3+} -saturated soil increased to a maximum of 226 μg of 2, 4-D per g of soil (Table 7). This represented 45.2% of the total available 2, 4-D in the soil system. The Al^{3+} -saturated soil adsorbed approximately twice the amount of 2, 4-D (70 $\mu\text{g}/\text{gm}$) adsorbed by the Cu^{2+} -saturated soil (34 $\mu\text{g}/\text{gm}$). These 2, 4-D adsorption results showed some similarity with the results obtained by Takijima and Hayashi (1954a) which showed that the 2, 4-D adsorbed by the homoionic soils were in the following order: Al^{3+} -soil > H^{+} -soil > original soil > Ca^{2+} -soil. From the kinetic studies, it was observed that the maximum adsorption occurred after four hours of equilibration time (Figure 7).

Since the adsorption of 2, 4-D by soils also relates to the water solubility, the determination of the water solubility of Fe^{3+} , Al^{3+} , and Cu^{2+} salts of 2, 4-D was necessary. Synthetic preparation of these respective salts revealed the solubilities to be Fe^{3+} -2, 4-D (195 ppm), Al^{3+} -2, 4-D (354 ppm), and Cu^{2+} -2, 4-D (1069 ppm) (Table 9). The solubilities of the Ca^{2+} , Mg^{2+} and Na^{+} salts have been measured by Dregne (1967). All of these cations exhibit much greater solubilities than the 2, 4-D acid and salts used in this study. Because of the high water solubility of the 2, 4-D salts of Na and Ca,

Table 7. 2,4-D adsorption on the natural and the Fe^{3+} , Al^{3+} , and Cu^{2+} -saturated Lookout silt loam soil as a function of time.

Soil sample	Time, hours									
	0.5	1	2	3	4	5	6	7	8	24
	2,4-D acid adsorbed, $\mu\text{g/gm}^*$									
Natural Lookout silt loam soil	21	25	27	28	29	28	28	27	29	29
Cu^{2+} -saturated Lookout silt loam soil	17	24	26	26	27	29	30	32	31	34
Al^{3+} -saturated Lookout silt loam soil	43	52	60	63	68	69	71	68	70	70
Fe^{3+} -saturated Lookout silt loam soil	195	204	213	216	222	222	221	224	224	226

*Total 2,4-D acid input = 10 mg.

Table 8. 2,4-D adsorption on the natural and the Fe^{3+} , Al^{3+} , and Cu^{2+} -saturated Lookout silt loam soil as a percent of total 2,4-D acid added.

Soil sample	Time, hours									
	0.5	1	2	3	4	5	6	7	8	24
	2,4-D acid adsorbed, %									
Natural Lookout silt loam soil	4.2	5.0	5.4	5.6	5.8	5.6	5.6	5.4	5.8	5.8
Cu^{2+} -saturated Lookout silt loam soil	3.4	4.8	5.2	5.2	5.4	5.8	6.0	6.4	6.2	6.8
Al^{3+} -saturated Lookout silt loam soil	8.6	10.4	12.0	12.6	13.6	13.8	14.2	13.6	14.0	14.0
Fe^{3+} -saturated Lookout silt loam soil	39.0	40.8	42.6	43.2	44.4	44.4	44.2	44.8	44.8	45.2

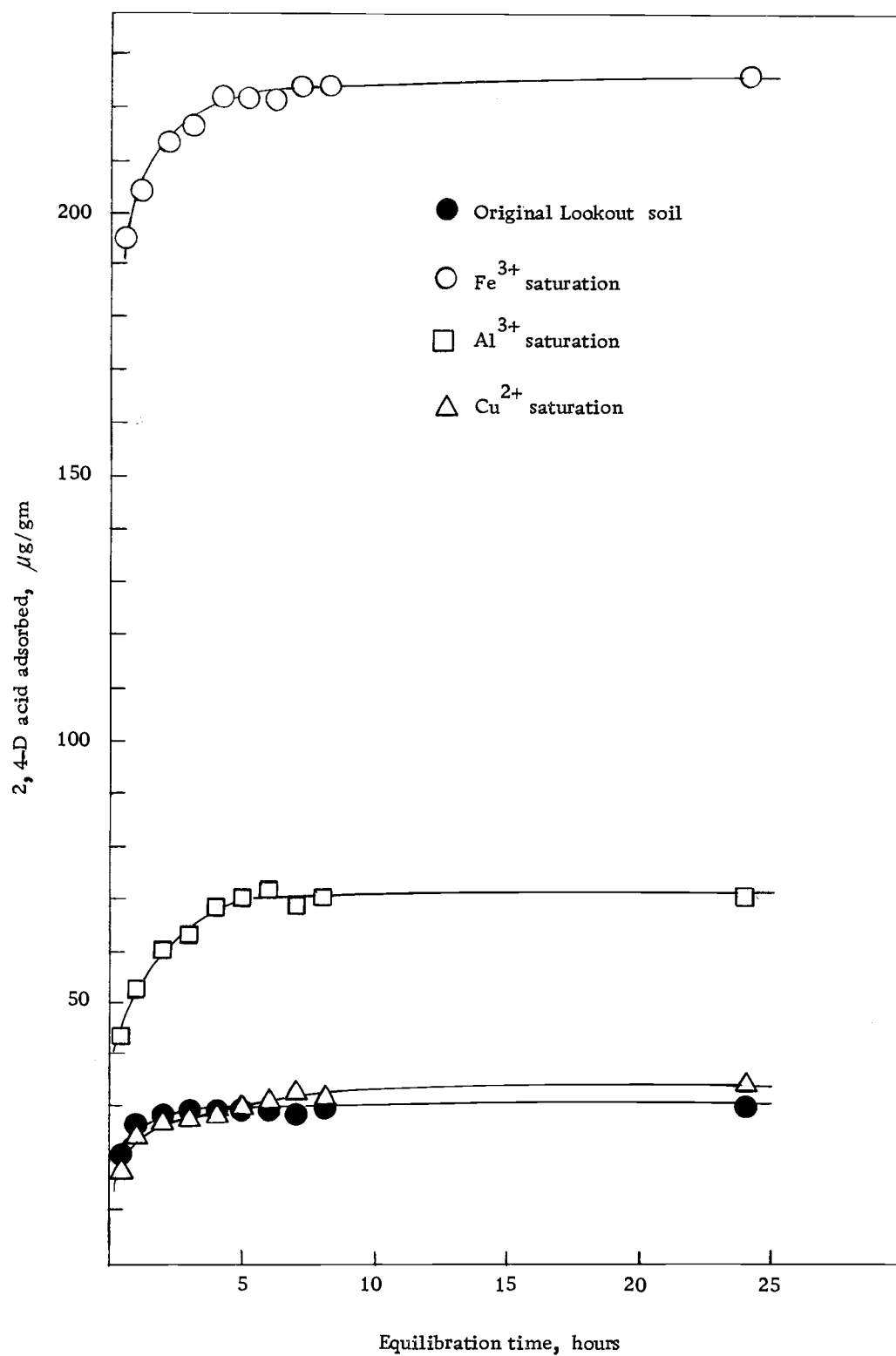


Figure 7. Adsorption isotherms of 2, 4-D on Lookout silt loam soil at 25°C.

Takijima and Hayashi (1954a) attributed the adsorption of 2, 4-D acid by soils to Al present in the soil. As can be seen from the adsorption isotherms (Figure 7), the adsorption of 2, 4-D on Lookout silt loam may partially be explained by the water solubility of the Fe^{3+} , Al^{3+} , and Cu^{2+} salts. It is interesting to note, however, that the initial 2, 4-D concentration in the adsorption isotherm studies did not exceed the solubilities of any of acid 2, 4-D salts.

Table 9. Water solubilities of the synthetic metal ion salts of 2, 4-D and 2, 4-D acid.

	Compound						
	Fe^{3+} - salt	Al^{3+} - salt	Free Acid*	Cu^{2+} - salt	Ca^{2+} - salt*	Mg^{2+} - salt*	Na^{+} salt*
Water solubility, ppm (25°C)	195	354	890	1069	2500- 4000	11100- 17400	35000

*Data from Dregne, H. E. (1966).

After the 2, 4-D adsorption maximum had been achieved by the natural soil and the soils saturated with Fe^{3+} , Al^{3+} , and Cu^{2+} , the equilibrium solution was removed and two water wash treatments applied to each system. The two water wash treatments removed 9.09 μg of 2, 4-D per g of the natural soil. In sharp contrast, the two water wash treatments desorbed 77.05 μg of 2, 4-D per g of Fe^{3+} -saturated soil. The water wash treatments of the Cu^{2+} and Al^{3+} -saturated soil removed 12.20 and 29.05 μg of 2, 4-D per g of soil respectively (Table 10). The 2, 4-D which was removed by the

Table 10. 2, 4-D desorption from the natural, and the Fe^{3+} , Al^{3+} , and Cu^{2+} -saturated Lookout silt loam soil as a function of time.

Soil sample	Time, hours								Total 2, 4-D desorbed, μ g/gm	
	1st water wash	2nd water wash	1	4	6	93	97	261		285
	2, 4-D desorbed (cumulative), μg/gm									
Natural Lookout silt loam soil	8.48	9.09	1.05	1.05	1.15	1.15	1.40	2.50	2.50	11.59
Cu ²⁺ -saturated Lookout silt loam soil	9.45	12.20	5.05	5.05	5.20	7.40	7.85	7.85	8.05	20.25
Al ³⁺ -saturated Lookout silt loam soil	17.60	29.05	6.35	9.00	10.05	16.90	25.75	25.75	27.30	56.35
Fe ³⁺ -saturated Lookout silt loam soil	42.20	77.05	33.25	35.00	35.00	46.80	46.80	46.80	51.95	129.00

water wash treatments from the natural and the Fe^{3+} , Al^{3+} , and Cu^{2+} -saturated soil was approximately 31%, 34%, 42%, and 36% of the total adsorbed 2,4-D acid (Table 11). The relatively large quantity of 2,4-D removed from the Fe^{3+} -saturated soil would account for the slightly more 2,4-D movement that occurred in the soil columns that contained Fe^{3+} in contrast to Al^{3+} .

Upon desorption with water for one hour, 1.05 μg of 2,4-D was desorbed from 1 gm of the natural soil. This represented 4% of the total adsorbed 2,4-D (Tables 10 and 11, and Figure 8). Within one hour, Cu^{2+} and Al^{3+} -saturated soil desorbed 5.05 and 6.35 μg of 2,4-D per g of soil respectively. On the other hand, 33.25 μg of 2,4-D was desorbed from the Fe^{3+} -saturated soil after one hour (Table 10). In each system studied, a very small quantity of 2,4-D was further desorbed with time. After 12 days, the total 2,4-D desorbed (not including the two wash treatments) from the natural soil and the soils saturated with Cu^{2+} , Al^{3+} , and Fe^{3+} was 2.50, 8.05, 27.30, and 51.95 μg per g of soil respectively (Table 10). This represented 9%, 24%, 39%, and 23% of the total adsorbed 2,4-D on the natural soil and the soils saturated with Cu^{2+} , Al^{3+} , and Fe^{3+} (Table 11). If one includes the two water wash treatments in the desorption totals the adsorbed 2,4-D which was removed increased to 40%, 60%, 81%, and 57% for the natural soil and the Cu^{2+} , Al^{3+} , and Fe^{3+} -saturated soil. The ease of desorption of 2,4-D from each soil

Table 11. 2, 4-D desorption from the natural and the Fe^{3+} , Al^{3+} , and Cu^{2+} -saturated Lookout silt loam soil as a percent of total 2, 4-D adsorbed.

Soil sample	Time, hours									Total 2, 4-D desorbed, %
	1st water wash	2nd water wash	1	4	6	93	97	261	285	
	2, 4-D desorbed, %									
Natural Lookout silt loam soil	29	31	4	4	4	4	5	9	9	40
Cu ²⁺ -saturated Lookout silt loam soil	28	36	15	15	15	22	23	23	24	60
Al ³⁺ -saturated Lookout silt loam soil	25	42	9	12	14	24	36	36	39	81
Fe ³⁺ -saturated Lookout silt loam soil	19	34	15	16	16	21	21	21	23	57

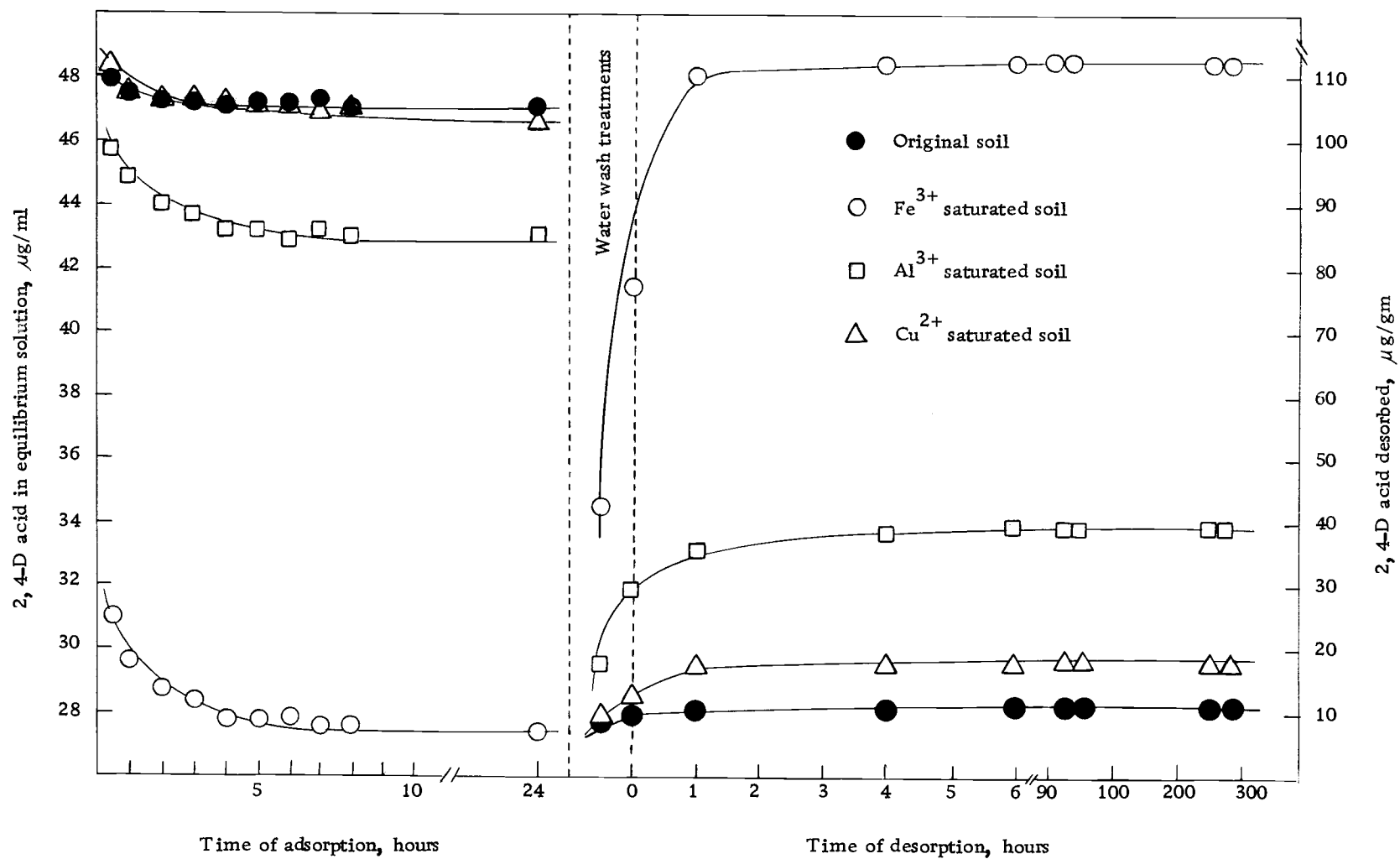


Figure 8. Adsorption and desorption of 2,4-D in Lookout silt loam soil.

system studied might indicate that a physical bonding mechanism was involved upon complexation of 2, 4-D with these systems.

The 2, 4-D still adsorbed by the several soil systems after the desorption treatment was obtained by subtraction of the 2, 4-D desorbed by the two water wash treatments and that desorbed after equilibration with distilled water for 12 days from the 2, 4-D initially adsorbed (Table 12). It is interesting to note that upon desorption the natural Lookout silt loam soil still held 348 μg of 2, 4-D. The Cu^{2+} and Al^{3+} -saturated soil contained 276 μg and 273 μg of 2, 4-D respectively (Table 12). In sharp contrast, the Fe^{3+} -saturated soil held up to 1930 μg of 2, 4-D after the desorption (Table 12). The amount of 2, 4-D desorbed followed the same order as that initially adsorbed by the four soil systems, i. e., natural soil < Cu^{2+} -soil < Al^{3+} -soil < Fe^{3+} -soil. Therefore, the 2, 4-D desorbed was shown to be directly proportional to the 2, 4-D initially adsorbed by the soil. However, the percentage of 2, 4-D desorption was shown to follow the order: natural soil (40%) < Fe^{3+} -soil (57%) < Cu^{2+} -soil (60%) < Al^{3+} -soil (81%) (Table 12).

Analysis of the curves which represent the relative movement of 2, 4-D in the soil columns (Figures 4, 5 and 6) showed that 2, 4-D leached least in the soil column which contained the Al^{3+} -saturated layer of soil. The area beneath the curve would represent the 2, 4-D which remains in the soil solution. To compare the relative

Table 12. 2, 4-D adsorption on Lookout silt loam soil after water wash and desorption treatments.

Treatment	Soil sample			
	Natural Lookout silt loam soil	Cu ²⁺ -saturated Lookout silt loam soil	Al ³⁺ -saturated Lookout silt loam soil	Fe ³⁺ -saturated Lookout silt loam soil
2, 4-D initially added, μg	9,900	9,949	9,900	9,949
2, 4-D adsorbed, μg	580	680	1,400	4,520
2, 4-D desorbed, μg	232	404	1,127	2,590
2, 4-D adsorbed by the soil system after desorption, μg	348	276	273	1,930
$\frac{2, 4\text{-D desorbed}}{2, 4\text{-D adsorbed}}, \%$	40	60	81	57

reduction in 2,4-D movement as a function of cation saturation, the area beneath each 2,4-D distribution curve which was not coincident with the 2,4-D distribution curve of the natural soil was calculated. The relative area thus calculated was shown to be: $\text{Cu}^{2+}\text{-soil}:\text{Fe}^{3+}\text{-soil}:\text{Al}^{3+}\text{-soil} = 100:133:198$. The relative area reflected, at least to a certain extent, the reduction in rate of 2,4-D movement. Data from the 2,4-D adsorption-desorption study would suggest that 2,4-D would be leached faster in the Al^{3+} -soil than in the Fe^{3+} -soil. This was not observed in the soil column study. The deviation between the 2,4-D movement in the soil columns and the expected movement from desorption studies reflects the complexity of the soil variables.

In summary, the 2,4-D movement through the soil was governed by the pH of the system, and the adsorption-desorption kinetics. Experimental data show that the 2,4-D acid was most readily adsorbed on the Fe^{3+} -saturated soil; however, the percentage of 2,4-D desorption was highest on the Al^{3+} -saturated soil. The 2,4-D movement through an acid soil must reflect both the pH and in turn the cation saturation of the soil.

Organic Matter and Exchange Cations

To investigate the effects of organic matter and exchange cations on 2,4-D adsorption, the Lookout silt loam, Dayton silt

loam, and Hembre loam soils were equilibrated with 50 ppm of 2, 4-D for 24 hours. Results showed that 21.29 μg of 2, 4-D was adsorbed by 1 gm of Lookout silt loam soil. However, one g of Dayton silt loam soil adsorbed more than twice the amount adsorbed by Lookout silt loam soil (Table 13). In sharp contrast, the Hembre loam soil which contained 29% organic matter and 16.8 meq/100 gm of extractable aluminum adsorbed 125.16 μg of 2, 4-D/g of soil, about six times greater than that adsorbed by Lookout silt loam soil. In viewing the chemical properties of these soils (Table 13), one would expect the 2, 4-D adsorbed to be a function of organic matter content. The Lookout silt loam and Dayton silt loam soils contained almost the same quantity of organic matter. The pH of the Dayton silt loam soil (5.1) was lower than Lookout silt loam soil (6.9) and the extractable aluminum content was higher in Dayton silt loam soil (2.1 meq/100 gm) than in Lookout silt loam soil (0.5 meq/100 gm). The combined effects of pH and extractable aluminum caused an increased 2, 4-D adsorption on Dayton silt loam soil.

To investigate the effect of exchange cations on the 2, 4-D adsorption, montmorillonite clays were either saturated with Al^{3+} or Cu^{2+} cations. Upon equilibration for 24 hours with 50 ppm of 2, 4-D, a striking difference was observed in the amount of 2, 4-D adsorbed by the clay systems (Table 13). One g of Al^{3+} -montmorillonite adsorbed 183.9 μg of 2, 4-D while Cu^{2+} -montmorillonite only adsorbed

Table 13. Adsorption of 2, 4-D on soils and clays as a function of organic matter and exchange cation status.

Sample	pH	O. M., %	Clay, %	Extractable Al, meq/100 gm	Fe ₂ O ₃ , %	2, 4-D acid added, mg	2, 4-D acid adsorbed, μ g/gm
Lookout silt loam	6.9	2.0	18.4	0.5	0.7	5	21.29
Dayton silt loam	5.1	2.6	14	2.1	1.1	5	44.39
Hembre loam	5.0	29.0	12.6	16.8	3.5	5	125.16
Cu ²⁺ -saturated montmorillonite	4.8	0	100	--	--	0.5	31.20
Al ³⁺ -saturated montmorillonite	3.1	0	100	--	--	0.5	183.90

-- not determined

31.2 μg of 2, 4-D/g of clay. The pH of Al-montmorillonite and Cu-montmorillonite was 3.1 and 4.8 respectively (Table 13).

pH and Al^{3+} Saturation

To determine the relative importance of pH and Al^{3+} or hydroxy aluminum in the adsorption of 2, 4-D acid, Lookout silt loam soil was treated with HCl and allowed to age for 1, 5, 10, 26, 36, and 120 hours. During the aging process, the extractable Al^{3+} increased from 1.67 to 2.39 meq per 100 g of soil (Table 14 and Figure 9). The increase in Al^{3+} and the pH increase from one hour to five hours was found to be more rapid than that between any other time interval. The increase in extractable Al^{3+} is easily explained by the release of aluminum during the hydronium ion attack on the clay lattice (Bradfield, 1923; Paver and Marshall, 1934; Slabaugh, 1952; Harward et al., 1954; Low, 1955; Barshad, 1960). During the initial hydronium ion saturation, the basic cations on the exchange complex are replaced. The presence of hydronium ion immediately initiates a reaction with Si-O^- groups and causes a release of aluminum from the clay lattice. The adsorption of 2, 4-D acid decreased with an increase in pH of the HCl-treated soil. At pH 3.19, 88 μg of 2, 4-D acid was adsorbed per g of soil while at pH 3.5, only 50 μg of 2, 4-D/g of soil was adsorbed. Since the extractable aluminum concentration increased while the adsorption of 2, 4-D decreased one must conclude

Table 14. Effect of aging on 2, 4-D adsorption on Lookout silt loam soil as a function of pH and concentration of extractable aluminum.

Time, hr.	Vol. of 0.09851N HCl added, ml	pH of total system	Concentration of extractable Al, meq/100 gm	2, 4-D acid added, μ g	Weight of soil sample, gm	2, 4-D acid adsorbed in one hour, μ g/gm
0	5	3.19	1.67	1,500	5	88
1	5	3.21	1.72	1,500	5	78
5	5	3.34	1.92	1,500	5	63
10	5	3.35	2.11	1,500	5	60
26	5	3.40	2.22	1,500	5	57
36	5	3.45	2.28	1,500	5	53
120	5	3.50	2.39	1,500	5	50

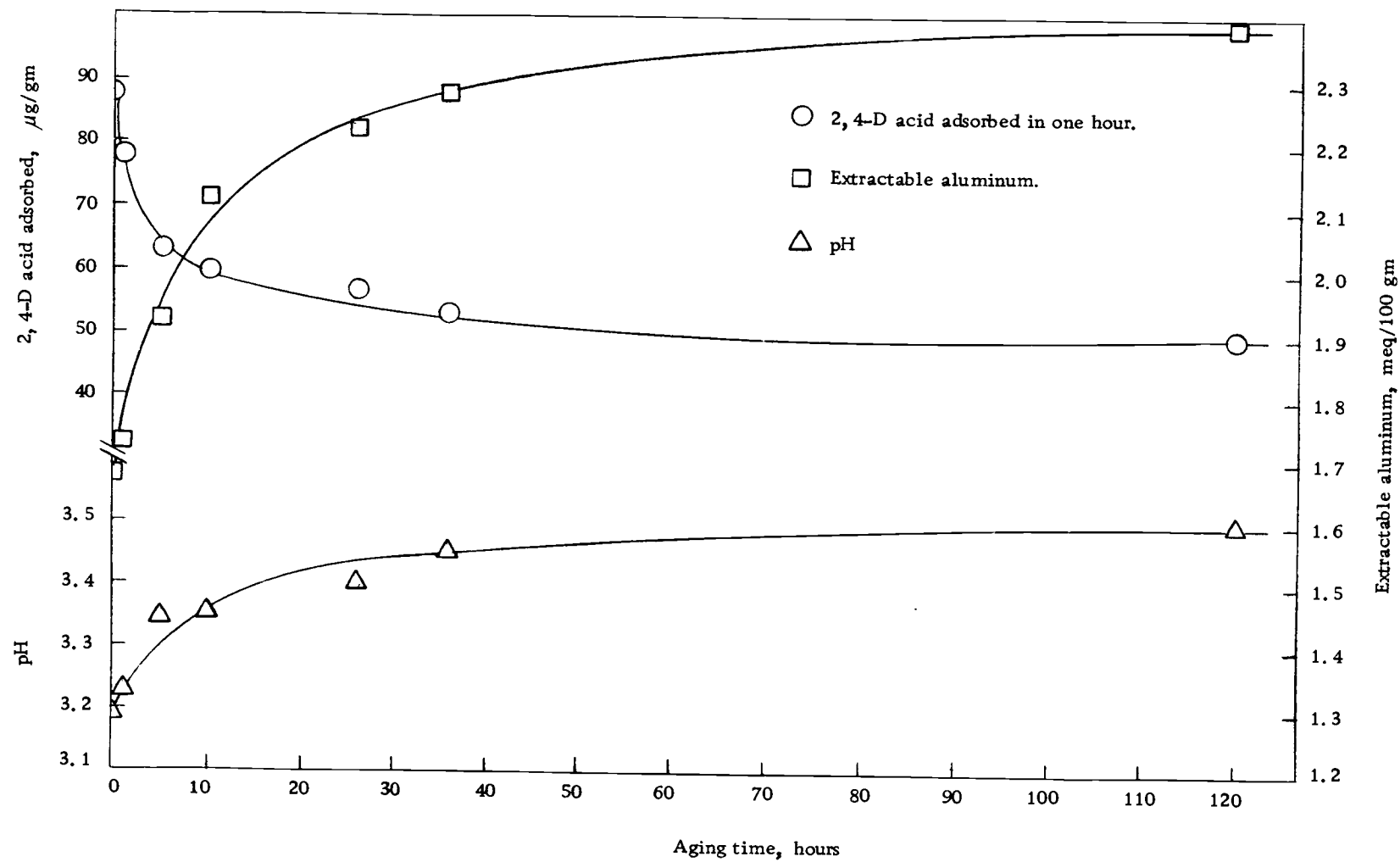
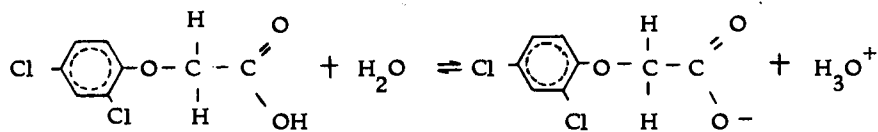


Figure 9. Effect of aging on 2, 4-D adsorption on Lookout silt loam soil.

pH and its effect on 2, 4-D dissociation to play the major role in determining the extent of 2, 4-D adsorption at pH values near the pK of 2, 4-D.

To further assess whether the pH or extractable Al plays the more important role in the adsorption of 2, 4-D acid, theoretical calculations of amounts of dissociated and undissociated 2, 4-D acid under present experimental conditions were made by the law of mass action as follows: The chemical reaction involved in the dissociation of 2, 4-D acid is as follows:



$$(1) \quad K = \frac{[2, 4\text{-D anion}][\text{H}_3\text{O}^+]}{[2, 4\text{-D acid}]} \quad (\text{Concentration is used to simulate activity at low 2, 4-D levels})$$

$$(2) \quad K_{2, 4\text{-D acid}} = \text{antilog}(-2.8) = 1.585 \times 10^{-3} \quad (\text{pK} = 2.8)$$

$$(3) \quad \frac{[2, 4\text{-D anion}]}{[2, 4\text{-D acid}]} = \frac{K}{[\text{H}_3\text{O}^+]} = \frac{1.585 \times 10^{-3}}{[\text{H}_3\text{O}^+]}$$

The proportion of dissociated 2, 4-D to the undissociated 2, 4-D is calculated by substitution of each $[\text{H}_3\text{O}^+]$ into equation (3) (Table 15).

Let

x = amount (μg) of dissociated 2, 4-D.

y = amount (μg) of undissociated 2, 4-D

then,

$$(4) \quad x + y = 1,500 \text{ } \mu\text{g (total 2,4-D acid added initially).}$$

By solving equations (4) and $\frac{x}{y} = Z$ as shown in Table 15 simultaneously, the amounts of dissociated and undissociated 2,4-D acid can be obtained as shown in Table 16. The calculated amount of undissociated 2,4-D was very close to the amount of 2,4-D adsorbed by the soil at each particular pH value (Table 16 and Figures 10 and 11). It should be noted that although the extractable Al^{3+} did increase with aging, the amount of 2,4-D adsorbed at each particular pH value was less than that should be adsorbed from the theoretical calculation. This again would support the idea that pH in the adsorption of 2,4-D is more important than the extractable Al. However, one must certainly consider that the organic matter content of a soil (perhaps the aluminum is the active fraction of the organic matter) may play even a more important role than pH when comparing 2,4-D adsorption between soils.

Table 15. The hydronium ion concentration and proportion of [2,4-D anion] to [2,4-D acid] at different pH values.

pH	$[\text{H}_3\text{O}^+], \text{ M} \times 10^4$	$\frac{x}{y} = \frac{[2,4\text{-D anion}]}{[2,4\text{-D acid}]}$
3.19	6.457	2.4547
3.21	6.166	2.5705
3.34	4.571	3.4675
3.35	4.467	3.5482
3.40	3.981	3.9814
3.45	3.548	4.4673
3.50	3.162	5.0127

Table 16. Effect of pH on the 2, 4-D adsorption on Lookout silt loam soil and dissociation of 2, 4-D.

pH	Theoretical calculation		Experimental determination	
	2, 4-D acid dissociated, μg	2, 4-D acid undissociated, μg	2, 4-D acid adsorbed, μg	2, 4-D acid in equilibrium solution, μg
3.19	1,066	434	440	1,060
3.21	1,080	420	390	1,110
3.34	1,164	336	315	1,185
3.35	1,170	330	300	1,200
3.40	1,200	300	285	1,215
3.45	1,226	274	265	1,235
3.50	1,250	250	250	1,250

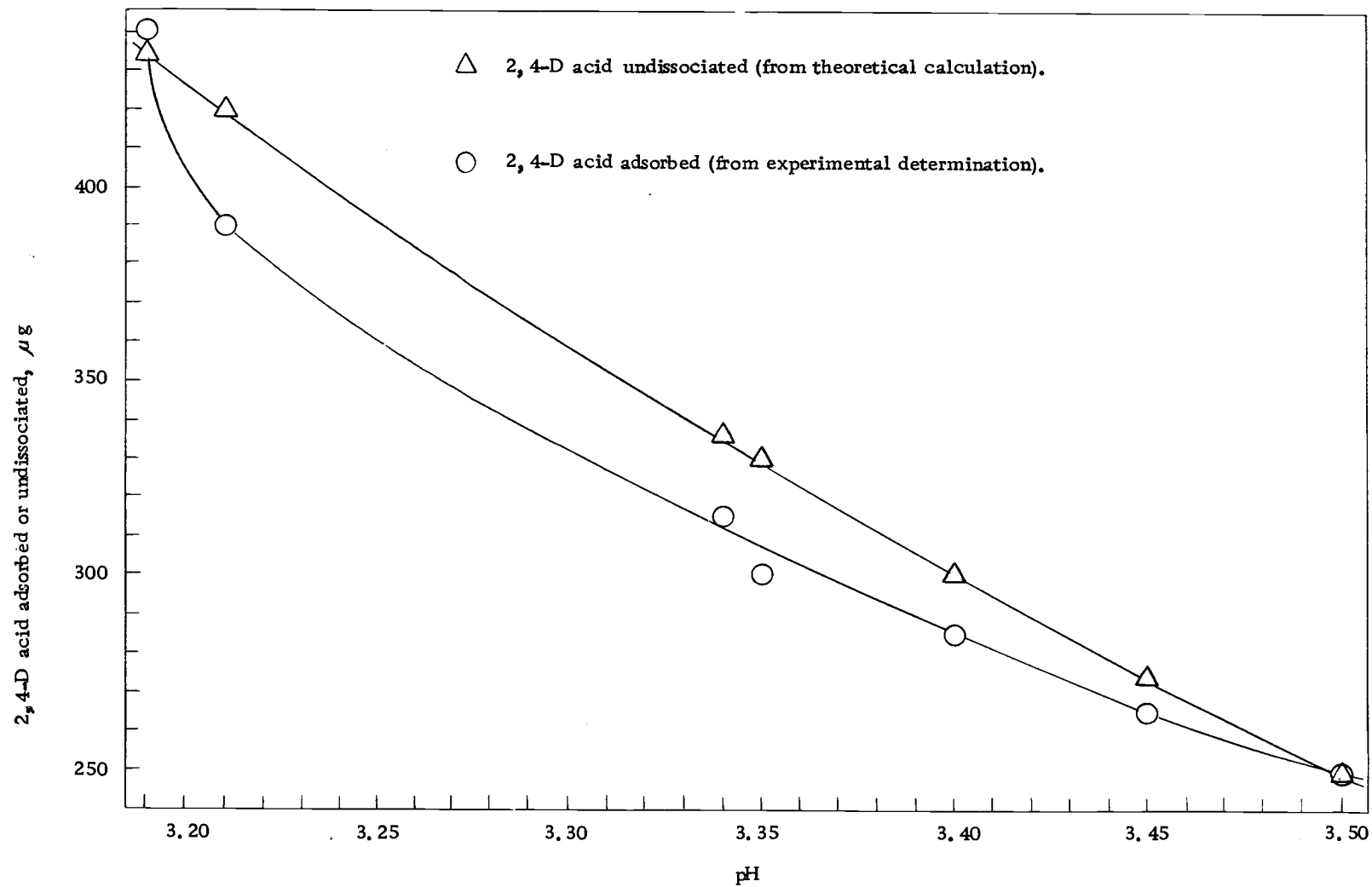


Figure 10. Effect of pH on the adsorption and association of 2, 4-D.

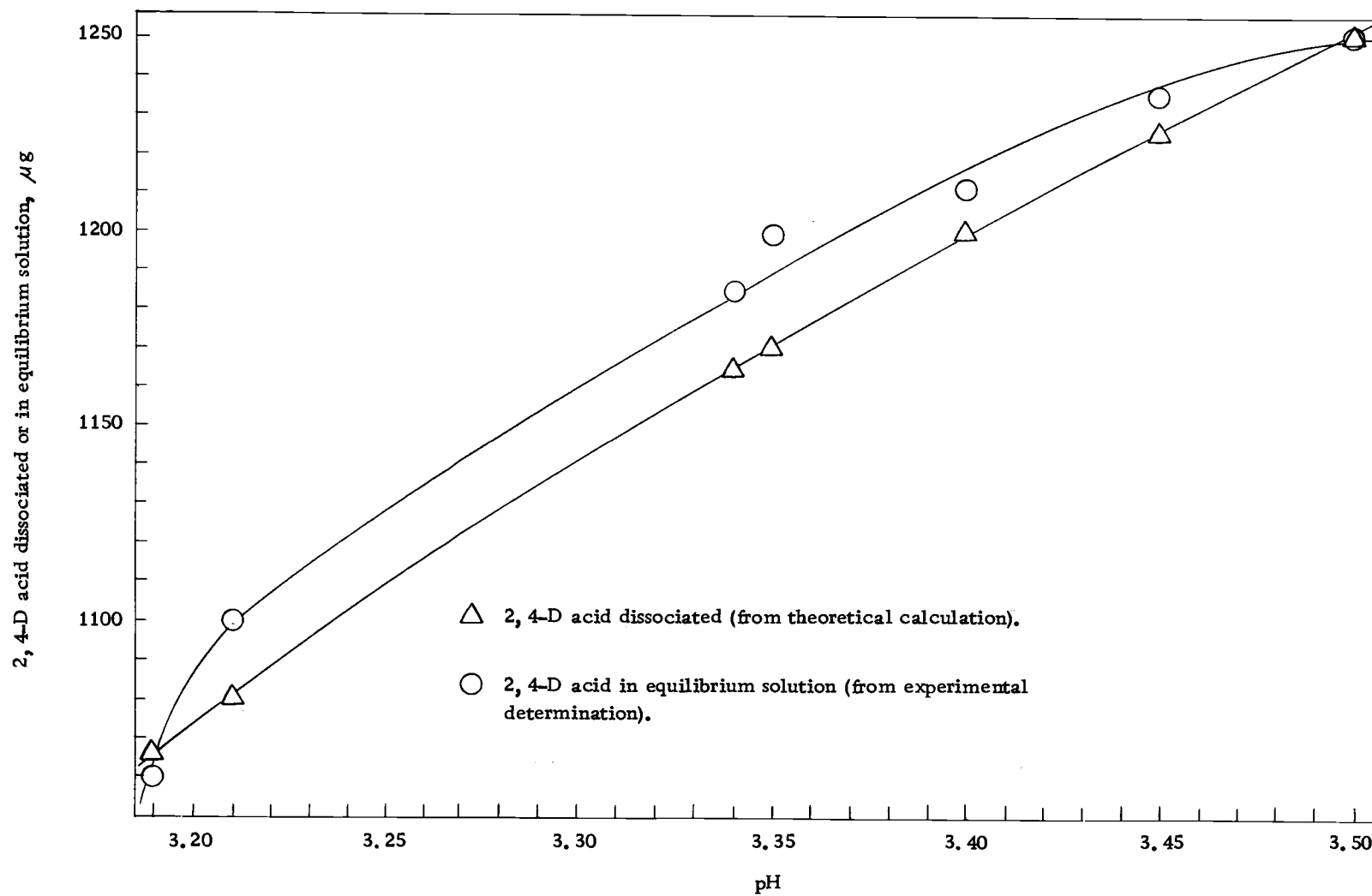


Figure 11. Effect of pH on the dissociation of 2,4-D.

Microbial Degradation of 2, 4-D

The microorganisms present in the Lookout silt loam soil respired approximately 3.5% of the input carbonyl side chain of 2,4-D-1- ^{14}C acid as $^{14}\text{CO}_2$ in the first week (Figure 12). Since the studies which involved the movement of 2,4-D in soil columns extended for no longer than one week, one would expect no more than two to three percent of 2,4-D which was added to be degraded. With increased time, the 2,4-D rapidly decomposed with 20% of the added 2,4-D degraded after two weeks (Figure 12). After 18 days, 30% of the added 2,4-D was degraded.

The lag period which was observed in the degradation of 2,4-D agreed nicely with the general reaction rate of microbial decomposed compounds. Time is required for the microbial population to develop in sufficient number to rapidly decompose a large quantity of the substrate.

Infrared Analysis of 2,4-D Adsorbed to Montmorillonite

2,4-D Acid and Its Fe^{3+} , Al^{3+} and Cu^{2+} Salts

The adsorption-desorption studies have shown a considerable quantity of 2,4-D to be easily desorbed from the soil systems. To investigate the functional group of the 2,4-D molecule which is involved in a possible complex formation with Fe^{3+} , Al^{3+} , or Cu^{2+} ,

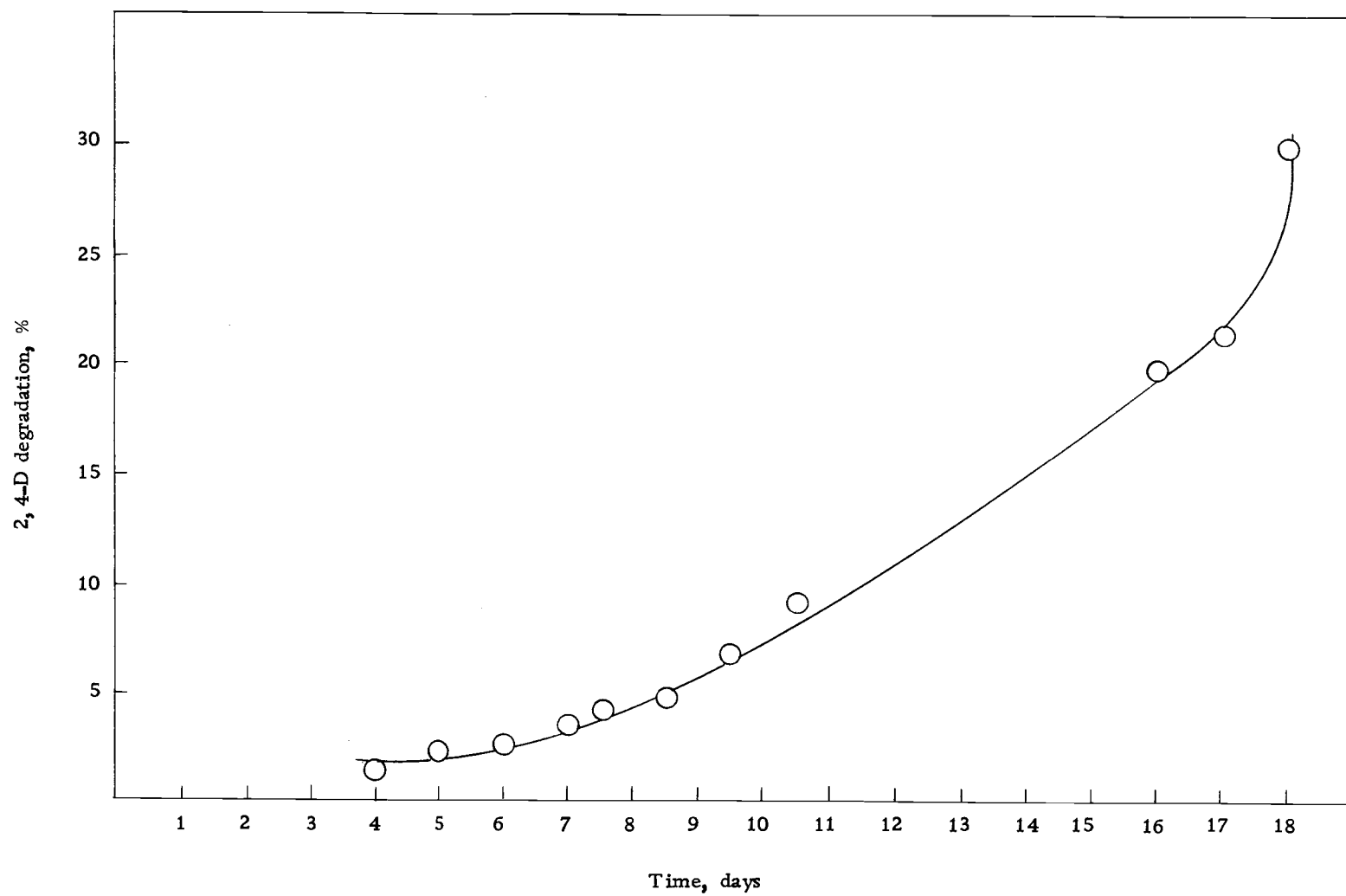


Figure 12. Microbial degradation of 2,4-D in Lookout silt loam soil.

the infrared spectra of 2,4-D acid and its Fe^{3+} , Al^{3+} and Cu^{2+} salts were obtained by a KBr pellet technique (Tables 17 and 18, and Figures 13 and 14). In viewing the IR spectrum for 2,4-D acid, a very strong carbonyl stretch frequency occurs at 1739 cm^{-1} with a weak shoulder at 1713 cm^{-1} . This band shifts to 1642 cm^{-1} for Fe^{3+} -2,4-D salt; to 1628 cm^{-1} for Al^{3+} -2,4-D salt; and to 1636 cm^{-1} for Cu^{2+} -2,4-D salt. The striking shift in the carbonyl stretch frequency indicated that carbonyl was the principal functional group affected by the salt formation. The 1739 cm^{-1} band in the IR spectra still could be observed in the Fe^{3+} , Al^{3+} , and Cu^{2+} salts because of the presence of 2,4-D acid.

Bonding Mechanisms of 2,4-D Acid with Fe^{3+} , Al^{3+} , and Cu^{2+} -Saturated Montmorillonite








The carbonyl adsorption band for 2,4-D adsorbed on montmorillonite clay saturated with each cation shifted to lower frequency (Figure 15). The extent to which the carbonyl band was shifted depended upon the cation saturation of the clay. Both the Fe^{3+} and Al^{3+} -saturated montmorillonite shifted the carbonyl stretch frequency of the 2,4-D molecule from 1739 cm^{-1} to 1620 cm^{-1} while the Cu^{2+} clay shifted less (from 1739 to 1630 cm^{-1}) (Figure 15). Mortland (1966) also observed this trend with EPTC clay systems in that a larger shift of the carbonyl frequency

Table 17. Infrared absorption frequencies of 2, 4-D acid, and the Fe^{3+} , Al^{3+} , and Cu^{2+} salts of 2, 4-D.

2, 4-D acid		Fe^{3+} salt of 2, 4-D		Al^{3+} salt of 2, 4-D		Cu^{2+} salt of 2, 4-D	
Wave number, cm^{-1}	Intensity*	Wave number, cm^{-1}	Intensity	Wave number, cm^{-1}	Intensity	Wave number, cm^{-1}	Intensity
1739	v. s.	1744	v. s.	1739	w	1739	v. s.
1713	sh	1715	sh	--	-	--	-
--	-	1642	v. s.	1628	v. s.	1636	v. s.
1584	m	1584	m	--	-	1581	w
1483	v. s.	1486	v. s.	1488	v. s.	1486	v. s.
1453	m	1458	m	--	-	1458	m
1433	m	1436	m	1442	s	1433	m
1396	S	1397	S	1397	m	1394	m
1364	w	1347	S	1347	S	1344	S
1311	S	1315	w	--	-	--	-
1300	sh	1294	S	1300	v. s.	1294	v. s.
1272	w	1267	w	1272	m	1267	w
1263	w	--	-	1263	sh	--	-
1253	w	--	-	--	-	1250	w
1236	S	1238	S	1244	m	1239	m
1158	w	1159	w	1156	w	1158	w
1118	w	--	-	--	-	--	-
1106	sh	1107	m	1110	m	1106	w
1094	S	1097	m	1084	S	1097	sh
--	-	1075	m	--	-	1081	m
1049	m	1047	w	1050	w	1047	m
--	-	--	-	1017	S	--	-
907	b	910	b	950	w	910	b
871	m	872	m	872	S	872	m
836	m	838	m	841	m	838	m
--	-	808	m	806	v. s.	--	-
794	v. s.	797	v. s.	775	w	798	v. s.
--	-	768	w	750	w	768	m
717	S	717	S	719	m	717	S
692	m	700	m	700	w	693	m
--	-	680	w	--	-	--	-
--	-	661	w	--	-	661	w
641	w	642	m	647	m	642	m

*Intensity: v. s. = very strong; S = strong; m = medium; w = weak; sh = shoulder; b = broad.

Table 18. Suggested infrared band assignments of 2,4-D.

Band Location, cm^{-1}	Band Assignment
1739	C = O stretching
1584	 vibration (in-plane)
1483	CH ₂ deformation
1453	 substitution
1433	CH bending
1396	OH bending
1236	CH ₂ wagging
1158	 vibration
1118	C-C stretching
1106	CH rocking
907	 vibration (out of plane)
871	 vibration (1 free H)
836	 vibration (2 free H)
794	 vibration (out of plane)

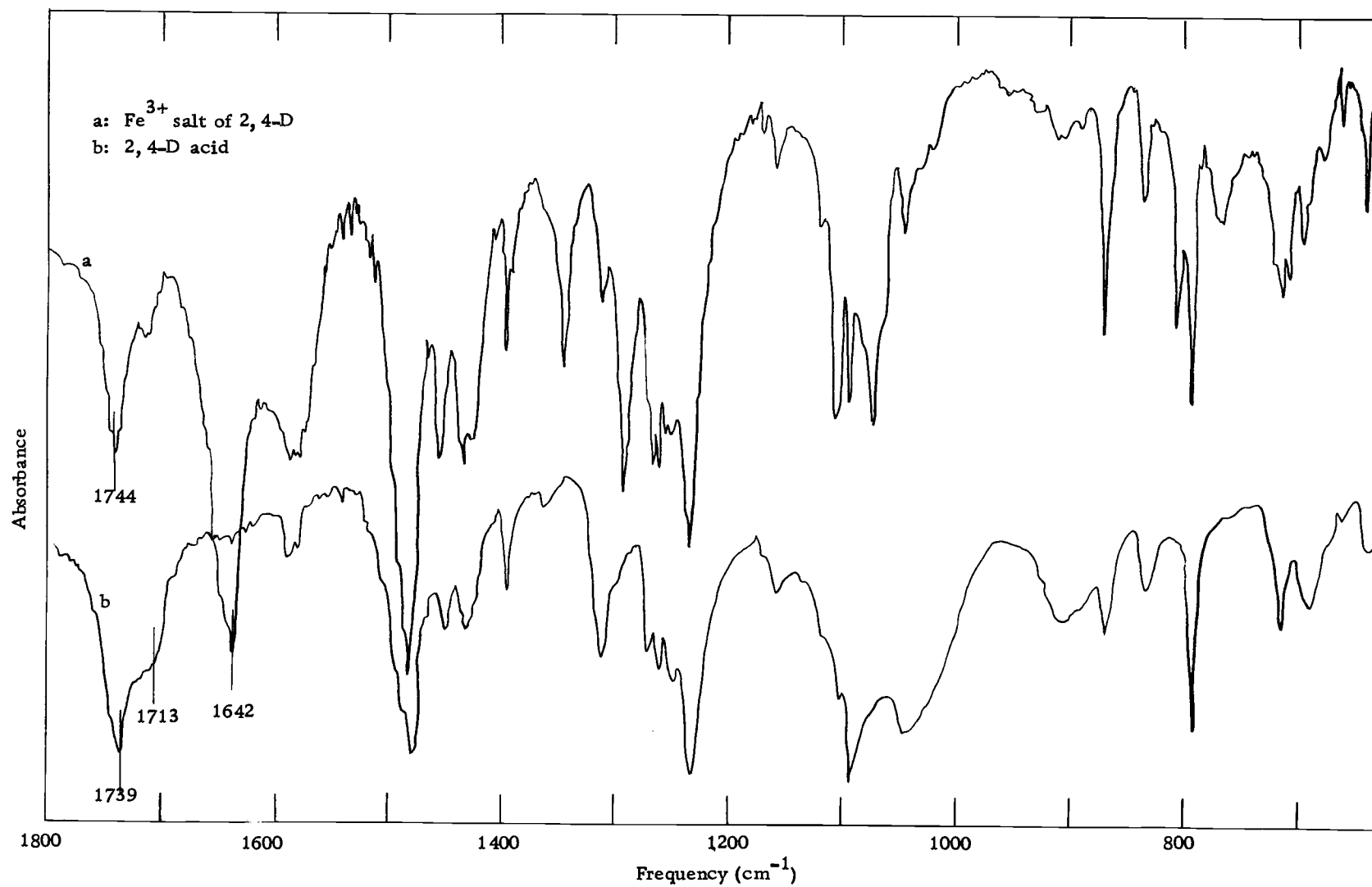


Figure 13. Infrared spectra of 2,4-D acid and its Fe^{3+} salt.

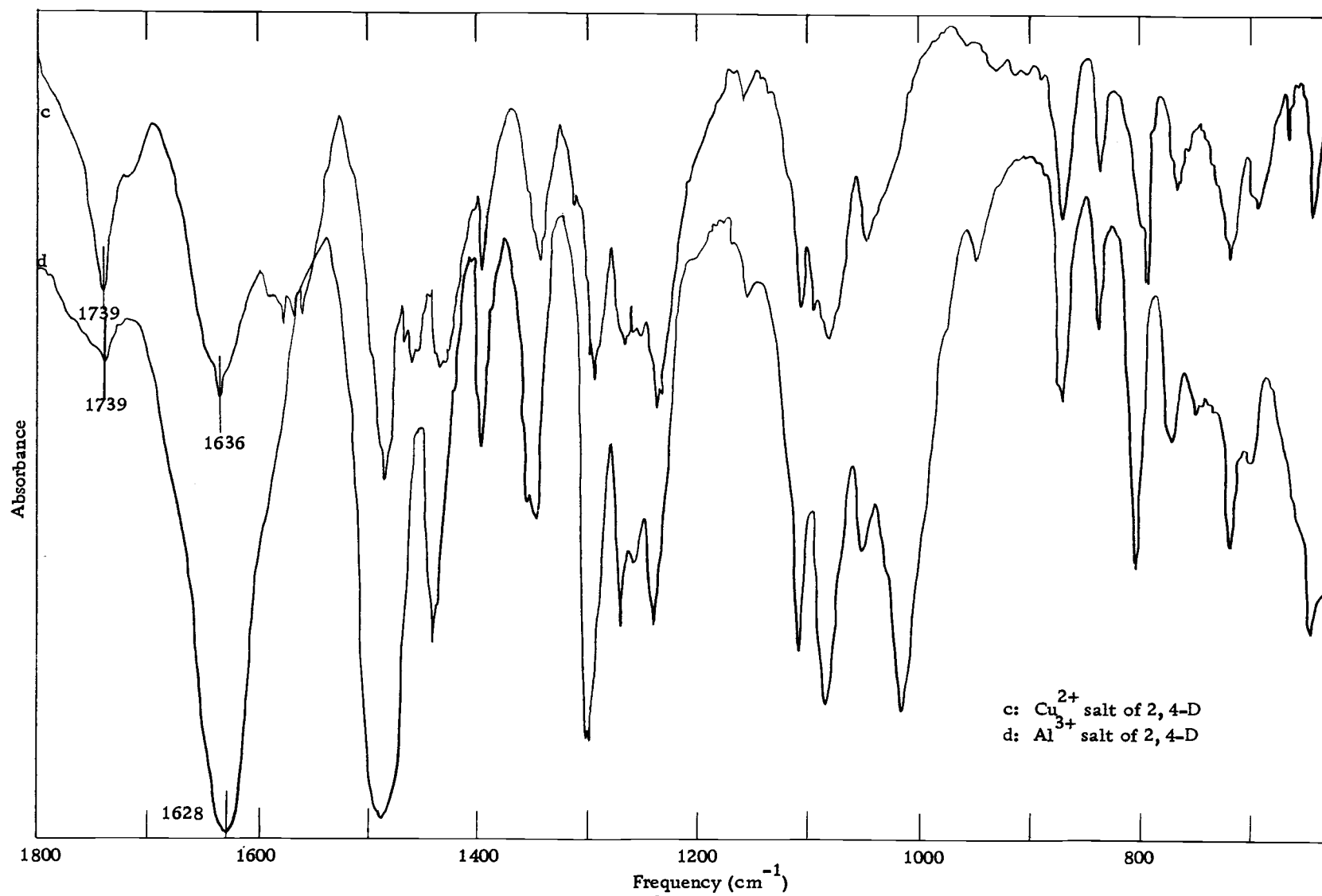


Figure 14. Infrared spectra of Al^{3+} and Cu^{2+} salts of 2,4-D.

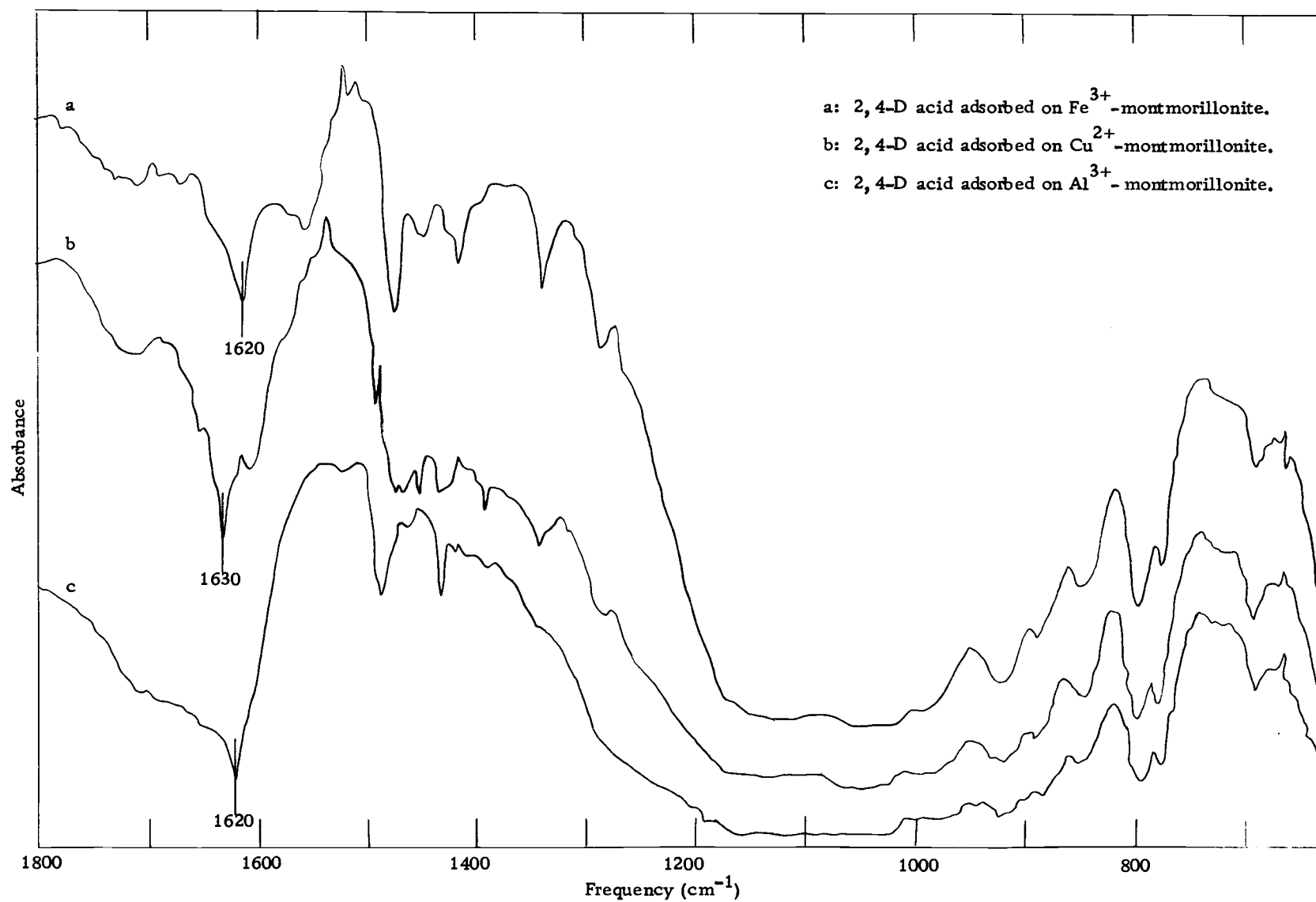


Figure 15. Infrared spectra of 2,4-D acid adsorbed on Fe³⁺, Al³⁺ and Cu²⁺-saturated montmorillonite.

occurred with EPTC added to Cu^{2+} and Al^{3+} clay systems than when alkali metal and alkaline earth cations were present.

According to Badger's rule (Pauling, 1960), the formation of a hydrogen bond between hydroxyl and electronegative atoms tends to decrease the OH-vibration frequency. This rule also applies to the C=O vibration. Upon the complex formation of 2,4-D with the cation-saturated montmorillonite, the bonding through the C=O, whether directly to the cation or through a water bridge tends to lower the C=O stretching force constant, and consequently lower the observed carbonyl stretch.

SUMMARY

The movement and adsorption of 2,4-D acid in selected Oregon soils was studied as a function of pH, organic matter, and the presence of acidic cations.

A decrease in the movement and an increase in adsorption of 2,4-D acid could be induced by the presence of Fe^{3+} , Al^{3+} , and Cu^{2+} cations on the exchange sites. The reduced 2,4-D mobility was attributed predominantly to the decreased pH of the soil with acid cation saturation. However, evidence was observed to indicate the formation of a complex between the 2,4-D and the hydrated Fe^{3+} , Al^{3+} , and Cu^{2+} . Water solubility of the 2,4-D salts of Fe^{3+} , Al^{3+} , and Cu^{2+} increased from 195 to 354 to 1069 ppm respectively, but the 2,4-D concentration in the soil solution did not exceed the solubility of any of these salts.

Equilibration of the natural and the Fe^{3+} , Al^{3+} , and Cu^{2+} -saturated soils with 50 ppm of 2,4-D at 25°C for 24 hours showed the 2,4-D adsorption to decrease in the following order: $\text{Fe}^{3+}\text{-soil} > \text{Al}^{3+}\text{-soil} > \text{Cu}^{2+}\text{-soil} > \text{natural soil}$. Studies of the effects of pH and extractable aluminum on the 2,4-D adsorption indicated that the 2,4-D adsorption was directly associated with the degree of dissociation as governed by the pH. After the 2,4-D adsorption maximum had been achieved, the desorption studies showed that 40%, 60%,

81%, and 57% of the total adsorbed 2,4-D was desorbed from the natural soil and the Cu^{2+} , Al^{3+} , and Fe^{3+} -saturated soil, respectively.

In summary, the pH and organic matter content appear to be the most important factors which affect 2,4-D adsorption in most soils. It is felt that cations such as aluminum and iron which are often associated with the organic matter may serve as active adsorbent sites within the soil. Because of the adsorption phenomenon, higher rates of 2,4-D should be applied for better weed control in acidic soils with a higher organic matter content. Since microbial degradation studies have shown that 2,4-D degrades rapidly, application of higher rates of 2,4-D should not accumulate in the soil phase.

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Table 19. Chemical properties of the Lookout silt loam soil.

Soil series	Fe ₂ O ₃ , %	Extractable aluminum, meq/100gm	Exchangeable calcium, meq/100gm	Exchangeable magnesium, meq/100gm	Exchangeable potassium, meq/100gm	Cation exchange capacity, meq/100 gm	Organic carbon, %	Organic matter, %	Soil pH			Soil fractionation		
									Soil paste	1:10 H ₂ O	1:10 KCl	Sand, %	Silt, %	Clay, %
Lookout silt loam	0.68	0.49	9.34	4.34	1.13	15.99	0.87	2.01	6.55	6.90	5.65	24.65	56.97	18.38

VITA

Eugene Cheng-yen Kuo, son of Chung lin Kuo and Yu zu Kuo, was born in Giaw lin County, Canton, China on May 17, 1943. He attended elementary school at Hsinbu, Hsinchu, and was graduated from high school at Hsinchu, Taiwan in June, 1961.

He attended Provincial Taipei Industrial Institute, Taiwan, one year, transferring to the Department of Agricultural Chemistry, National Taiwan University in September 1962, from which he received the degree of Bachelor of Science in Agriculture in June 1966. After one year's ROTC service on an isolated Penghu island, he entered the Graduate School of Oregon State University, U.S.A. in September 1967. Since that time, he has served as Research Assistant in Soils while working towards the master's degree.

He was married to Judy J. I. Hwang on August 5, 1969.