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To the Graduate Council:

I am submitting herewith a thesis written by Michael Boyd Akins entitled "The Movement, Sorption, Loss and Chemical Distribution of Arsenic-74 Labeled Disodium Methanearsonate in Some Tennessee Soils." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Science.

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THE MOVEMENT, SORPTION, LOSS AND CHEMICAL DISTRIBUTION
OF ARSENIC-74 LABELED DISODIUM METHANEARSONATE
IN SOME TENNESSEE SOILS

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

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

by
Michael Boyd Akins
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ABSTRACT

Radioactive ^{74}As disodium methanearsonate (DSMA- ^{74}As) was used as a representative compound of the methanearsonate family to study their fate and behavior in soil systems. This compound was produced in the laboratory.

Five samples of 4 Tennessee soils of various chemical, physical, and mineralogical properties were used in this study. Sorption of DSMA- ^{74}As was studied by employment of the batch equilibration technique. Various soil properties (pH, percent clay content, CEC, organic matter content) were related to the soil sorption of DSMA- ^{74}As in this study. Imposed conditions (alteration of soil pH, phosphorus content) of selected soil properties were related to the soil sorption of DSMA- ^{74}As . Using laboratory prepared soil columns the leachability and distribution of DSMA- ^{74}As were determined in the soils and the effect of the imposed conditions were measured.

Determination of microbial or chemical induced evolution of gaseous arsenic under imposed conditions of organic matter and moisture was investigated. The distribution of sorbed DSMA- ^{74}As in the soil was determined by a modified phosphorus procedure.

Soils with high clay content and with kaolinite as their major component sorbed the greatest quantities of DSMA- ^{74}As from solutions containing DSMA- ^{74}As . The effect of organic matter on sorption could not be measured directly, but it appears to have a positive effect on sorption of DSMA- ^{74}As . Cation exchange capacity apparently had no direct effect on sorption. In most cases the amount of DSMA- ^{74}As leached was inversely proportional to the sorption capacity of the soils. The soils with the least amount of clay leached the greatest quantities of DSMA- ^{74}As . Phosphorus reduced the ability of soil to sorb DSMA- ^{74}As quite dramatically in the batch equilibration experiments and in the soil columns. Acid treatments generally increased the ability of the soil to retain DSMA- ^{74}As . Sorption of DSMA- ^{74}As was found to be more dependent upon soil texture and mineralogical composition than pH.

Gaseous arsenic evolution was greatest from soils that had received an exogeneous carbon source and maintained under reduced conditions. The chemical distribution of DSMA- ^{74}As in the soils studied showed that Fe arsenate was the predominant form and Al arsenate was the second most predominant form.

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CHAPTER I

LITERATURE REVIEW

Arsenic in the form of arsenic trioxide, sodium arsenite, lead arsenate, calcium arsenate, and paris green have been used for many years as insecticides, herbicides, soil sterilants, and silvicides. Since the 1960's organic arsenical herbicides, in which the organic group is bonded directly to the arsenic atom, have been used extensively for postemergence control of weeds in cotton and turf management.

Laboratory preparation of disodium methanearsonate (DSMA) can be easily accomplished by following the procedure proposed by Quick and Adams (46). This procedure is an adaptation of a general procedure outlined by Dehn (16, 17). The methanearsonic acid compounds were originally synthesized for their therapeutic value. In World War I organic arsenicals were considered as chemical warfare weapons in Germany (42) and in the United States (59). Disodium methanearsonate was first prepared by Klinger and Kreutz (37) using the Meyer reaction (41). They reacted arsenious acid with sodium hydroxide, added methyl iodide, and then isolated the crystalline sodium methyl arsenate. Uhlinger and Cook (59) also applied the Meyer reaction in the

production of methyldichloroarsine which was used as a poisonous gas in World War I. Disodium methanearsonate was an intermediate step in the synthesis scheme of this gas and essentially follows the same steps that Klinger and Kreutz used except that dimethyl sulfate was substituted for methyl iodide.

Many years passed before the present group of organic arsenicals were used as herbicides. However, the inorganic arsenic compounds have been in use as herbicides since 1897, when they were used for experimental control for a variety of weeds in North Dakota, Vermont, Massachusetts, and water hyacinth in Florida and Louisiana (58). They have been used over a wide spectrum of crops and pests since then. Arsenic and its associated compounds desiccate plants and provide good weed control under various climatic conditions. However, repeated applications of arsenic-containing compounds will result in residue accumulations that are toxic to some crops.

Applications of arsenic compounds to soil in some cases have reduced yields and produced arsenic poisoning symptoms in the plant. Arsenic has a tendency to accumulate in the seed and vegetative parts of plants which are actively growing in soil to which arsenic-containing compounds have been applied (6, 9, 22, 23, 28, 30, 37, 60, 63, 66). The reaction of arsenicals in soils and their effect on plants have been an area of investigation for many years. Vandecaveye,

Horner and Keaton (60) reported that in orchard soils with a long history of lead arsenate spray applications, crops would not grow. The orchard soils in Annapolis Valley had concentrations of arsenic in the plow layer that were detrimental to the growth of arsenic sensitive crops (9). In the cotton belt, where calcium arsenate was used as a dust for boll weevil control, Dorman, Tucker, and Coleman (21) reported that arsenic accumulations in coarse-textured soils reached toxic levels. Greaves (27) found that 50 orchard soils varying widely in chemical, physical, and biological properties accumulated arsenic residue of 5-102 ppm. Sodium arsenite, which had been applied as a defoliant for potatoes at rates of 45-720 kg/ha in Plainfield sand inhibited the growth of subsequent crops of vegetables (potatoes, peas, snap beans, and sweet corn (31)). Schweizer (52) incorporated 50 ppm of DSMA in Bosket silt loam, and a significant reduction in the growth of cotton and rotational crops resulted.

The toxicity problems of arsenicals and their peculiar chemical reactions in the soil have been an area of major effort in an attempt to solve the mysteries of arsenic behavior in soil systems. Generally seven factors are known to influence the fate and behavior of pesticides in soil systems: (1) volatilization, (2) photochemical decomposition, (3) microbial decomposition, (4) plant or organism

uptake, (5) chemical decomposition, (6) movement (leaching), and adsorption (5, 32, 62). Of these seven factors, volatilization and photochemical decomposition are not considered important factors in the loss of DSMA and other arsenicals from the soil (61).

As early as the 1900's arsine evolution caused by microorganisms was reported in the literature (57). McGeorge (39) observed that arsenic present in the soil stimulated ammonifying and nitrifying bacteria found in the soil. Thom and Raper (57) investigated arsine evolution by fungi in agar solutions that contained arsenic. In the isolated pure cultures of fungi, they found that 10 strains of Scopulariopsis were the most active gas producers and that other fungi were positive producers. Some strains of fungi were inhibited by the presence of arsenic. They also took dilute solutions from arsenic-contaminated soils and placed them in agar solutions. Arsine gas was detected in all petri dishes.

Dickens and Hiltbold (20), using ^{14}C labeled DSMA, showed that after 30 days 16 percent of the methanearsonate carbon had evolved as $^{14}\text{CO}_2$ in a loamy sand soil in which organic matter had been added. In another experiment using ^{14}C -monosodium methanearsonate (MSMA), Kearney, Von Endt, and Kaufman (36) found that the evolution of $^{14}\text{CO}_2$ was proportional to the amount of organic matter in the soil. After 3 weeks' incubation the rate of evolution ranged from

10 percent decomposition for the highest organic matter soil (3.9 percent), to 1.7 percent decomposition in the lowest organic-matter soil (1.67 percent). When the same soils were steam sterilized, they produced essentially no $^{14}\text{CO}_2$. In another experiment Kearney et al. used the soil-enrichment technique to isolate pure cultures of a fungus, several actinomycetes, and several bacteria. In cultures containing 100 ppm of MSMA- ^{14}C as the sole carbon source, 20 percent of the radioactive carbon was released after a one week incubation period. In cultures where yeast extract and 10 ppm of MSMA- ^{14}C were added, 20 percent of the organic arsenical was degraded after three days of incubation. In a later study in 1971, Kearney and Woolson (34) conducted a similar experiment with ^{14}C -cacodylic acid (dimethyl arsenic acid) in which they projected that cacodylic acid is metabolized by two pathways: an oxidative pathway leading to C-As bond cleavage and a reductive pathway leading to alkyl arsine production. Bond cleavage ranged from 1 to 13.3 percent in 6 weeks and was stimulated by an exogenous carbon source. Reductive metabolism of ^{14}C -cacodylic acid by Scopulariopsis brevicaulis produced a pungent, volatile substance which was apparently gaseous dimethylarsine.

Cullimore (14) and Audus (4) in their treatises postulated that microorganisms could alter a substance to one that has greater toxicity than the original compound.

Kearney et al. (34, 36), in their two studies on MSMA and cacodylic acid, isolated the residue in the pure cultures that resulted from the microbial activity. In both cases arsenate in the +5 state was identified, but none in the +3 state was found. Disodium methanearsonate has an acute oral LD₅₀ (amount of chemical taken orally to cause death in half of test animals) between 700 to 1,000 mg/kg of body weight for rats (61). One possible degradation product, calcium arsenate, has an LD₅₀ of between 40-100 mg/kg for rats (52).

The fourth factor known to influence the fate and behavior of arsenicals in the soil is plant uptake. Plants resistant to arsenic poisoning store arsenic in their seeds and vegetative parts. Topical and directed sprayings at particular stages of growth with arsenicals have produced detectable concentrations of arsenic in the plants, especially cotton and soybeans. However, these concentrations developing from uptake from the soil vary quite extensively. Variation in plant uptake depends on such soil properties as soil type, soil pH, and amounts of aluminum, calcium, iron, magnesium, and phosphorus present in the soil (1, 2, 21, 22, 23). Jacobs, Keeney, and Walsh (31) found that when sodium arsenite was used as a defoliant for potatoes in a sandy soil, detectable levels of arsenic appeared in edible portions of peas, sweet corn, potato tubers, and peelings, making them unfit for consumption. Woolson, Axley, and

Kearney (69) ascertained that cotton and soybean seeds accumulated more arsenic than corn or sorghum or the winter crops of crimson clover, vetch, and oats. Small and McCants (54) found that the arsenic content of flue-cured tobacco ranged from 4.5-17.5 ppm, and that tobacco grown on sandy soils that had received an application of phosphorus fertilizer contained the greatest amount. Barley plants grown on apple-orchard soils that received large amounts of lead arsenate for insect control stored 10.01-17.50 ppm of As_2O_3 in the tops and 788-1640 ppm in the roots at the blooming stage (60). Ehman (23) applied DSMA to the soil at a rate of 63 lbs per acre, and the resulting residue in cotton seed was 0.73 ppm as compared with 40 ppm when the same rate was broadcasted at square formation stage of the cotton. In another series of experiments involving soils of different texture DSMA was inactivated to such an extent that almost no detectable arsenic accumulations were observed in the crops (22). Ehman attributed the degree of inactivation to differences in soil type, soil pH, length of time between application and planting of crops, and the amounts of calcium, magnesium, iron, and phosphorus present.

The inactivation process has been an area of intensive study and a great deal of speculation. Sorption and deactivation of arsenic have been attributed to the clay fraction and its components. Crafts and Rosenfel (12, 13), in a

series of experiments involving 80 California soils, reported that light soils fixed the least amount of arsenic while heavy soils fixed the most. Notable exceptions to this rule were some red soils which fixed greater amounts of arsenic than the textural class would indicate. Also, a soil high in organic matter of medium textural grade proved to have a higher "fixing" power than would be predicted by texture alone.

The use of calcium arsenate for boll weevil control in cotton produced toxicity problems in some soils and had no effect on others (1, 2, 21). Dorman, Tucker, and Coleman (21) reported that soil-applied rates of calcium arsenate less than 400 lbs per acre caused few problems to crops. Injury did appear when rates exceeded 400 lbs per acre, the degree of injury depending on soil type. Crops grown in sandy loams were most sensitive to arsenic poisoning, while clay loam soils showed no toxicity problems. The clay loam soils contained the greatest quantities of iron, aluminum, calcium, and magnesium.

Wiklander and Fredrikson (64) found that Dala brown soil fixed more arsenic than 3 clay soils or a low-moor soil. There was no consistent correlation with the clay content of the soil. When CaCO_3 was added to a clay soil, the capacity to fix arsenate was increased somewhat while the fixation of arsenite increased considerably. The limit of the capacity

of Fe_2O_3 to fix arsenic was not ascertained, but fixation was less for Al_2O_3 , especially for arsenite.

Albert et al. (2) applied amounts of calcium arsenate which ranged from 25-100 lbs per acre for Norfolk sand and 250-2500 lbs per acre for Davidson silt loam; the amounts for other soil types ranged between these two extremes. Crops grown in coarse-textured soils were seriously injured by relatively light applications of calcium arsenate, while the crops grown in the finer-textured ones were not seriously injured. Residues of calcium arsenate become more toxic to several crops where heavy applications of phosphate fertilizer were applied. In another report Albert (1) found that red clay soils had a much greater arsenic-fixing power than did gray sandy soils. He also found that ferric hydroxide removed much greater amounts of arsenic from solution than did aluminum hydroxide.

Williams and Whetstone (66) analyzed many widely divergent soil types from all parts of the United States for arsenic. Soil samples varied from those taken from areas which were free of added arsenic to orchard soils which had been contaminated. In noncontaminated soils arsenic concentrations ranged from 0.3-38 ppm, and the arsenic present was distributed throughout the entire profile. Concentrations in the contaminated soils ranged from 92-270 ppm, with the greatest portion found in the first three inches. These

observations (that soils with high clay, iron, calcium, and aluminum inactivates large quantities of arsenic applied to the soil) prompted soil scientists to fractionate the different forms of arsenic in the soil. First attempts to fractionate soil arsenic were conducted to obtain that quantity which was readily available to the plant (8, 9, 12, 13, 18, 30, 35, 39, 67, 68, 69). Many workers called this fraction "water-soluble" or "easily-soluble". Various extracting solutions have been used to obtain this fraction and correlate the quantity extracted with arsenic toxicity. Greaves (26, 27) found that water-soluble arsenic and total arsenic content of a soil varied greatly; the effective or "available-to-plant" from "water-soluble" may be very low with relatively high amounts of total arsenic present or high with relatively low amounts of total arsenic present.

Using distilled water as the extracting solution, Arnott and Leaf (3) found that as rate of application of As_2O_3 increased the extractable arsenic increased. This increase corresponds with the increased phytotoxic effect on pine seedlings. Deuel and Swoboda (18) used hot distilled water to extract arsenic from Amarillo fine sandy loam and Houston Black clay. Water-soluble arsenic levels of 8 ppm in the Amarillo soil and 28 ppm in the Houston Black soil were required for a significant decrease in the vegetative growth of cotton. The levels of water-soluble arsenic detrimental

to soybeans were 3 and 12 ppm in the Amarillo and Houston Black soils, respectively.

Vandecaveye et al. (60) analyzed arsenic-contaminated orchard soils and reported that when the readily soluble arsenic in the upper 6 inches of soil exceeded 2 ppm, barley plants were damaged. Bishop and Cheshlom (9) also analyzed arsenic-contaminated orchard soils and reported that levels of total arsenic ranged from 9.8-124 ppm and 2-9 ppm in water-soluble arsenic. Machlis (38) grew sudangrass and bush beans in nutrient solutions that contained arsenic. When the arsenic concentrations were greater than 0.2 ppm inhibition of growth occurred.

Water-soluble arsenic is only a part of the total arsenic in the soil. The remaining arsenic is associated with the components of the soil. Hiltbold and Johnson (29), using a sequential extraction for phosphorus, analyzed for arsenic in Chesterfield sandy loam. NH_4Cl extracted 30 percent, neutral 0.5N NH_4F -14 percent, saturated NaCl -13 percent, 0.1N NaOH -8 percent, 0.5N H_2SO_4 -8 percent, dithionite and citrate-8 percent, neutral 0.5N NH_4F -18 percent of the total arsenic. In the phosphorus extraction procedure the previously mentioned solutions were used in sequence to remove exchangeable calcium, extract aluminum phosphate, as a wash solution, iron phosphate, calcium phosphate, iron oxides and occluded phosphates, and aluminum phosphate, respectively.

Jacobs, Keeney, and Walsh (30) extracted added arsenic (320 $\mu\text{g As/g}$ and 80 $\mu\text{g As/g}$) from Plainfield sand and Waupun silty clay loam with Bray P-1 solution (0.03N NH_4F and 0.025N HCl) and 1N NH_4OAc (pH 7). Bray P-1 removed considerably more arsenic than did NH_4OAc , and more arsenic was extracted from coarser-textured than finer-textured soils. Organic matter was not significantly related to arsenic retention, but significant relationships were obtained for free iron oxides or clay. The ability of the soil to sorb was related to the free iron-oxide content. In another series of experiments sorption isotherms showed that Superior clay loam > Waupun silty clay loam > Plainfield sand for sorption of arsenic, and that sorption increased with free Fe_2O_3 content. Removal of amorphous Fe and Al components by treatment with ammonium oxalate eliminated the arsenic sorption capacity of Plainfield and reduced Waupun and Superior by 59 and 35 percent, respectively. Fractionation of the added arsenic was accomplished by two methods, Chang and Jackson (11) and Williams, Syers, and Walker (63). NH_4Cl removed 20, 14, and 3 percent of added arsenic from Plainfield, Waupun, and Superior, respectively. With the Chang and Jackson procedure, NH_4F -arsenic was the dominant fraction in Plainfield, but NaOH -arsenic was dominant in Waupun and Superior, while with the Williams procedure NH_4F -arsenic was the dominant fraction for all three soils.

Kearney, Woolson, and Axley (35) found that arsenic residues in 58 surface soil samples taken from soils with a history of arsenic application averaged 165 ppm arsenic, while nearby soils averaged 13 ppm. Most of the residual arsenic was found as iron arsenate by a modified phosphorus procedure. Water-soluble arsenic was detected in soils from two areas which had high concentrations and little rainfall. Other forms, Al- and Ca-arsenate, predominate when the amounts of "reactive" aluminum or calcium were high and "reactive" iron were low. Plants were tolerant to large arsenic applications (670 ppm) to soils which were high in reactive aluminum.

Woolson, Axley, and Kearney (69) correlated the response of corn against available arsenic estimated by six methods. The phytotoxicities of Na, Fe, Al, and Ca-arsenate compounds in Lakeland loamy sand to corn plants were compared. The phytotoxic effect on corn plants was as follows: $\text{Na} > \text{Al} > \text{Ca} > \text{Fe}$ -arsenate. Iron arsenate and aluminum arsenate, were the predominant forms in most soils. However, in some soils where the aluminum and calcium forms were predominant, the soils had high "reactive" aluminum or calcium contents and low iron contents. Where "easily soluble" arsenic appeared in detectable quantities, corn had greater than 60 percent growth reduction.

Kearney and Woolson (38) established concentrations of 1, 10, and 100 ppm of ^{14}C -cacodylic acid in three soils of varying iron and aluminum content. At 2, 4, 8, 16, and 24 weeks after addition of cacodylic acid, soils were analyzed for ^{14}C and arsenic present in the water-soluble, calcium, iron, and aluminum fractions of the total arsenic. Initially, cacodylic acid was distributed: water-soluble >> iron > calcium. After 24 weeks, the distribution was: aluminum > water-soluble >> iron > calcium. In contrast, inorganic arsenate (+5) was largely precipitated in the iron and aluminum fractions. Cacodylic acid persistence was a function of soil type.

Woolson, Kearney, and Axley (68) investigated the effects of time on the solubility of sodium arsenate. The amount of arsenic soluble in 1N NH_4Cl , 0.5N NH_4F , 0.1N NaOH , and 0.5N H_2SO_4 solutions were determined. The percent of water-soluble arsenic was proportional to arsenic added and inversely proportional to time, and the iron and aluminum content. Iron arsenate was predominant in Hagerstown silty clay and aluminum arsenate in Lakeland loamy sand. Growth of corn increased with increased time of arsenic in the soil before planting.

Arsenic occupies the same sites on clay surfaces as do other anions. Dickens and Hiltbold (20) reported that kaolinite and limonite adsorbed much more DSMA than did

vermiculite or montmorillonite. The exposed hydroxyl groups and hydrous iron oxides apparently have a great affinity for methanearsonates. The low adsorption by montmorillonite and vermiculite was due to a lack of amorphous material and the exposure of octahedral alumina only at crystal edges. The authors concluded that the methyl group does not affect adsorption.

Rubins and Dean (48) showed that phosphate and arsenate can be adsorbed alternately and mutually replaced on soil colloids. Sieling (53) used activated kaolin to compare sorption of arsenate and phosphate. Phosphate was effective in replacing arsenate, but arsenate was not as effective in replacing phosphates. Kaolin sorbed equal amounts of phosphate and arsenate from dilute solutions. Deb and Datta (15) reported that arsenate competes with phosphate for occupying a place on the positively charged sites of the soil colloid.

Benson (8) reported that the addition of phosphate to arsenic contaminated soils helped subsequent growth of crops. Rumberg, Engel, and Meggitt (49) indicated that uptake of arsenic by oats from a nutrient solution was decreased when phosphate concentration increased. However, several workers (1, 2, 21, 52) reported that arsenic residues become more toxic where heavy applications of phosphate fertilizer were applied. Woolson et al. (68) observed that arsenic residues

in a loamy sand soil become more phytotoxic upon application of phosphorus while in a silty clay loam they became less phytotoxic. Leaching with 0.05M KH_2PO_4 removed 77 percent of the total arsenic from a contaminated Dunkirk fine sand. The forms of arsenic were changed in the process; water-soluble-As content increased from 0 to 5 percent, the aluminum-arsenate fraction decreased, and the iron-arsenate fraction increased, with no change in calcium-arsenate percentage.

Chemical transformations of inorganic arsenic usually involve the reduction from the +5 oxidation state to the +3 state or conversion to arsine gas (AsH_3). Epps, Reed, and Sturgis (24, 47) working with flooded rice soils, reported that reduced arsenic compounds were especially toxic to rice. They were unable to account for all of the arsenic lost in their field experiments and suggested that some may have been reduced to As^{-3} and lost as arsine.

Deuel and Swoboda (19) added NaAsO_2 to flooded soils and found that soluble arsenic levels were related to total arsenic, temperature and the reduced environment obtained. Arsine gas was not detected in any of the soil samples.

The remaining fate awaiting arsenicals in the soil is movement (leaching) out of the system. Hartley (28), White and Bailey (62) have prepared excellent reviews of the factors affecting the movement of pesticides in soil systems.

Ehman (22) leached surface applied DSMA and cacodylic acid through soil samples, one foot in depth. Sixty inches of water removed 9 percent of the applied arsenical from a sandy soil and 6 percent from a clay soil. Hiltbold and Dickens (20) surface applied the equivalent of 100 lbs of DSMA hexhydrate per acre to 10 inch by 38 mm columns that contained Decatur clay loam and Norfolk loamy sand. Each column was leached with 20 successive 30-ml increments of distilled water. The amount of arsenic leached and the quantity in each 1-inch section of soil in the column was determined. No arsenic was leached from the Decatur soil, but 52 percent was removed from Norfolk. One-half of the applied arsenic remained in the surface inch of Decatur and none leached below six inches.

Arnott and Leaf (3) constructed columns of glass cylinders 24 by 2.95 inches, with the inside walls lined with plastic tubing. Chenango silt loam was packed in the columns and received the equivalent of 1,000 or 8,000 lb per acre of As_2O_3 applied to the soil surface and leached with 1 or 5 l of distilled water. No arsenic was leached except for the 8,000 lb per acre and 5 l treatment. Arsenic distribution in the column decreased markedly from a high value at or near the surface to a distinct point where no arsenic was detected. Schulz and Thompson (51) applied sodium arsenite to a well-drained soil. After 2 years only 5

percent of the arsenic was left in the sampled soil. There was no mention of depth of sampling.

McGeorge (39) in an early study with three soils, a red clay, brown clay, and high organic silt, packed in lysimeters showed that in all three cases little arsenic moved from the surface.

The chemical determination of arsenic is a long and laborious process and much care must be taken that experimental error is not great. The use of radioactive-labeled atoms had been widespread since World War II. Although most herbicides have been studied by radioactively tagging one of their atoms, little work has been done with arsenicals. In a series of experiments Kearney and his associates (34, 36) used ^{14}C tagged cacodylic acid and MSMA to study microbiological degradation, chemical distribution forms, and persistence in soil. Ball and Hooper (6) employed ^{74}As tagged sodium arsenite to determine its effects on a pond's ecology. Fredrickson et al. (25) synthesized arsanilic- ^{74}As acid and arsanilic-1- ^{14}C acid for metabolism studies in chickens and swine. Wilkinson and Hardcastle (65) used neutron-rich ^{76}As to determine limits of detection of arsenic compounds in cotton leaves. Analyses were quantitatively reproducible at 10 ng of arsenic per gram of sample.

Thin-layer and paper-chromatographic segregation and identification of herbicidal residues and metabolites are

powerful tools in the hands of the skilled chemist. Kearney et al. (36) separated the degradation products of MSMA by soil microorganisms using the procedure proposed by Stahl (55) for phosphorus identification. The detection limit for sodium arsenate, sodium arsenite, and MSMA was 1.5 μg . Residues isolated from microbial decomposition were MSMA and arsenate.

Overby, Bocchieri, and Fredrickson (44) developed a paper-chromatographic procedure for quantitative estimation of arsenate- ^{74}As , arsenite- ^{74}As , and arsanilic- ^{74}As acid from biological specimens. The supporting column was Whatman Chromatography Paper, grade No. 1, and an isopropyl alcohol-water, 70:30 (v/v) solvent. Detection was by a chromatogram isotope-scanning system and ultraviolet lamp. Separation of the three compounds was accomplished very handily.

Sachs et al. (50) segregated cacodylic acid from arsenate, arsenite, and MSMA by 1-propanol: NH_4OH (7:3 v/v) solvent system. A Bausch and Lomb Spectronic 20 was used for optical density measurements at 540 nm.

Meketukova, Kohlicek, and Kac1 (40) used a methanol-ammonia-water solvent system to separate arsenite and arsenate ions by paper chromatography. The detection system was an ammoniacal silver nitrate (2N AgNO_3 in 10 percent ammonia) solution. Silver arsenite produced a yellow color while silver arsenate produced a pale brown color, and detection was made more sensitive when UV light was applied.

CHAPTER II

I. METHODS AND MATERIALS

Synthesis of DSMA-⁷⁴As

Disodium methanearsonate (DSMA) was prepared by the procedure proposed by Quick and Adams (46). The chemical reactions involved are:



Radioactive ⁷⁴As was incorporated in the first step of the chemical scheme. The carrier-free ⁷⁴As was obtained from Amersham/Searle in the form of arsenic acid in 0.04M HCl which contained less than 1 µg of As per ml and the total volume of solution was less than 1 ml. The solution contained 5 mCi of ⁷⁴As, has a half-life of 18 days and gamma decay energies of 0.593 (60%) and 0.633 (14%) Mev (56). This isotope was contaminated with 0.8 mCi of ⁷³As which was a half-life of 76 days and gamma decay energies of 0.560 (45%) and 0.646 (6%) Mev (56).

The DSMA-⁷⁴As was prepared on two occasions to obtain a theoretical yield of 2 g. Five ml of 10N NaOH and 1.074 g of As₂O₃ were added to a 50 ml round-bottom flask. The ⁷⁴As was added and the mixture stirred until the reaction was

complete. To this solution 1.54 ml of CH_3I was added, warmed, and allowed to reflux for two hours. The solution was stirred and warmed with a Cole-Parmer Mark I magnetic stirrer equipped with a controlled hot plate. The pyrex reflux condenser was made of a 600 mm jacket and a 24/40 adapter. All chemicals were reagent grade. Disodium methanearsonate was isolated from the solution upon addition of 25 ml of methanol followed by rapid cooling. Purification was accomplished by dissolving the crystals in 1-2 ml of hot water and reisolation upon addition of methanol and rapid cooling. The product isolated from solution was a white crystalline solid that formed needles upon addition of methanol and rapid cooling. After drying in the oven overnight at 105°C , yields of 2.0065 and 2.2280 grams of the hexahydrate ($\text{CH}_3\text{Na}_2^{74}\text{AsO}_3 \cdot 6\text{H}_2\text{O}$) were measured which represents 64.0 and 71.2 percent of the theoretical yield, respectively. Melting range for the products was $136\text{--}137^\circ\text{C}$ while the reported melting range is $131\text{--}139^\circ\text{C}$ (61). The R_f value observed for laboratory produced DSMA- ^{74}As by the way of thin-layer chromatography was 0.86 and that for known DSMA 0.84. These values were measured from the second solvent front of the system, because it advanced more uniformly up the plate than did the lead front.

No difficulty was encountered in the synthesis process. This can be attributed to the several trial runs before the

radio-active arsenic was incorporated. The major consideration in selecting the theoretical yield value was to obtain a quantity with enough specific activity so that it could be used for experiments for several weeks. Another factor was to use quantities of starting materials that could be manipulated easily with the equipment available in the laboratory.

II. SOILS

Five samples of 4 Tennessee soils with various chemical, physical, and mineralogical properties were used in the studies. The soils were Hartsells loam, Memphis silt, Iberia silty clay, Halewood loam (Ap horizon), Halewood (B horizon). Selected chemical, physical, and mineralogical properties are shown in Table 1. Throughout the remainder of this study Halewood A and Halewood B will be referred to as separate and independent soils although they are of the same soil type. Treating these soils in such a manner facilitates presentation of the data.

pH Adjustments of Soils

To determine pH effect upon adsorption and movement of ^{74}As labeled DSMA the pH of each of the soils was adjusted to pH's of 4, 5, 6, 7, and 8 by leaching with 0.01N HCl or 0.01M $\text{Ca}(\text{OH})_2$. Number 40 Whatman filter paper 11 cm in

Table 1. Selected Chemical, Physical and Mineralogical Properties of the Soils Used in this Study

SOIL	TEXTURE	MINERALOGICAL ANALYSIS	pH	PERCENT ORGANIC MATTER	PERCENT CLAY	CEC
Halewood ^a						
A horizon	Loam	$K_1V_2V/I_2I_3Q_3Gi_3$	4.9 ^b	5.33	26.60	12.93
Halewood ^a						
B horizon	Clay	$K_1V_2V/I_2IQ_3Gi_3$	5.0 ^b	1.04	50.60	11.46
Memphis ^c	Silt	$M_2I_2K_2Q_3$	6.3 ^b	1.89	10.00	13.78
Iberia ^c	Silty Clay	$M_2K_2Q_1$	6.1 ^b	3.01	49.00	40.80
Hartsells ^c	Loam	$V_1K_2Q_2I_3$	6.7 ^b	0.82	14.25	4.85

^aDepartment of Plant and Soil Science, University of Tennessee, Knoxville, unpublished data.

^bObserved pH (saturated paste).

^cJoseph Rule, Master of Science in Agriculture Thesis, Department of Agronomy, University of Tennessee, 1970, Selectively, Fixation, and Exchange Equilibria of Potassium in Six Tennessee Soils and Soil Fractions.

diameter was placed in the appropriate size Buchner funnel, and fitted into a 500 ml suction flask. The soil was placed in the Buchner funnel to a depth of 2-3 mm. The appropriate solution (either acid or base depending on the soil's initial pH) was added to the Buchner funnel and allowed to leach slowly through the soil. Light suction was applied when necessary. Excess salts were washed out with deionized water, and the pH was checked by a Beckman Model W Industrial pH meter equipped with a glass and a calomel reference electrode. After pH was adjusted to within ± 0.1 pH unit of the desired pH, the soil was air dried and allowed to sit for a few days for pH to stabilize. The pH was checked again, and adjustments were made where necessary. Soils were moistened to a saturated paste and the pH was measured.

Phosphorus Levels and Acid Wash of Selected Soils

Soils (Hartsells, Memphis, and Iberia) which had been treated with phosphorus to obtain 200 or 1000 ppm concentrations in the soil were available in the laboratory. Another treatment was available in which the pH of these three soils had been adjusted to pH 5.0 with acid.

III. ADSORPTION STUDIES

Effect of Time Equilibration

Three 1 g samples of Hartsells, Memphis and Iberia soils were placed in 50 ml centrifuge tubes. Ten milliliters

of 5 or 10 ppm of ^{74}As labeled DSMA was placed in the tubes, sealed, and mixed with a cortex mixer, and shaken with a reciprocating mechanical shaker (265 cycles per minute). Shaking time was varied for 30 minutes, 1 hour, and 12 hours. The tubes were then centrifuged for 20 minutes at 2500 rpm. Five milliliters of the supernatant were pipetted into a counting tube. The activity was determined with a Nuclear Chicago Automatic Gamma Well Counting Instrument Model 4216. The counter was equipped with a thallium-activated sodium iodide crystal, an automatic data printout lister, and background subtractor. Supernatant activity was compared to a DSMA- ^{74}As standard.

Effect of Phosphorus and Acid Wash Treatments

One gram of 1000 ppm P, 200 ppm P, and acid-treated soils were placed in a centrifuge tube, with treatments triplicated. To each tube 10 ml of 10 ppm ^{74}As labeled DSMA was added, mixed, and shaken for 30 minutes. Centrifuging and counting procedure was the same as in the time equilibration experiment.

Effect of Soils

Comparison of the five soils generally followed the same procedure as that used for time equilibration study. Exceptions to the procedure were that Halewood A and Halewood B were used in addition to Hartsells, Memphis, and

Iberia; time of shaking was 30 minutes; only 10 ml of 10 ppm ^{74}As labeled DSMA was added.

Sorption Isotherms and pH Effect

Three 1 g samples of Hartsells, Memphis, Iberia, Halewood A, and Halewood B of each pH were placed in a 50 ml centrifuge tube. In each tube consecutive 2 hours batch equilibration was accomplished with 10 ml of 1, 5, 10, 15, 20, 25, and 30 ppm of ^{74}As labeled DSMA. After each equilibration, 5 ml of supernatant were pipetted into counting tubes and counted. The other 5 ml were drained off and discarded, then 10 ml of the next concentration was added, mixed, and shaken for 2 hours. Centrifuge time was increased with successive equilibrations so that all colloids would be out of suspension. The quantity of ^{74}As labeled DSMA that the soil absorbed was determined by calculating the difference between the activity of the supernatant and the concentration added plus the quantity adsorbed in the previous equilibration step.

IV. LEACHING EXPERIMENTS

Leaching columns were prepared to trace the movement of DSMA- ^{74}As through the soils in this study. The soils were homogeneously mixed with cellulose powder, using the following soil to cellulose powder ratios; 1) Hartsells 1:1;

2) Memphis, Halewood A, and Halewood B 1:2; 3) Iberia 1:4. The ratios were such that all mixtures would leach at the same rate.

Exchange sites on the cellulose powder were deactivated by saturation with potassium acetate. This was accomplished by thoroughly mixing the cellulose powder with a concentrated solution of potassium acetate. The deactivated cellulose was placed in a Buchner funnel and washed thoroughly with distilled water to remove excess salts. After drying in the oven at 105°C (caution: care must be taken so that the cellulose powder will not char), the appropriate amount of deactivated cellulose powder was ground with 1 g of soil to a fine homogeneous mixture with a mortar and pestle.

The columns were pyrex glass test tubes with a hole punched in the bottom. The size of the tubes varied with the ratio of soil to cellulose powder as follows: 1:1 11 mm (inside diameter) × 15 cm (length); 1:2 13 mm × 12 cm; 1:4 13 mm × 15 cm. A small plug of glass wool was placed in the bottom of the tube, followed by a piece of filter paper large enough to cover the plug. The homogeneous mixture of soil and cellulose powder was added to the column. During this addition the sides of the tube were rapped lightly to obtain uniform density throughout the tube. The columns were placed in beakers containing deionized water and then were wetted slowly from the bottom to reduce the number of

air bubbles in the column. Excess water was allowed to drain and 100 λ of DSMA- ^{74}As solution was added to the top of the column then capped with a plug of glass wool. The column was then leached with at least three column volumes (See Table 2) of deionized water in 1 ml increments. The 1 ml increments were collected in counting tubes and counted. After leaching, the soil columns were sectioned into 1 cm segments and also counted. The quantity of DSMA- ^{74}As leached and the distribution of DSMA in the column was determined.

Table 2. Volume of Columns and Quantity of Deionized Water Used in Leaching Studies

Soil:cellulose	Volume (ml)	Volume of leachate (ml)
1:1	3	15
1:2	6	20
1:4	11	30

Leaching of 100 ppm Surface Applied DSMA- ^{74}As

To soils columns consisting of untreated Hartsells, Memphis, Iberia, Halewood A, and Halewood B soils, 100 λ of 1000 ppm of ^{74}As labeled DSMA was surface applied and leached with the appropriate volume of deionized water. The soils treated with phosphorus and acid were leached in the same manner.

Leaching of 10 ppm Surface Applied DSMA-⁷⁴As

One hundred λ of 100 ppm of ⁷⁴As labeled DSMA was surface applied to soils consisting of soils whose pH had been altered to pH's of 4, 5, 6, 7, and 8, then leached with the appropriate volume of deionized water.

V. GASEOUS ⁷⁴As DETERMINATION

An arsine gas trap apparatus was constructed in the laboratory to trap arsine evolving from soil that was maintained under varying moisture conditions. The apparatus consisted of a manifold made of 3/16 inch (I.D.) $\times$ 5/16 inch (O.D.) tygon tubing and size 3/16 inch connector glass Ts. This manifold was attached to a bottle of oxygen. Transmission tubing for a Technicon Auto-Analyzer size 1/16 inch (I.D.) $\times$ 1/8 inch (O.D.) connected a single glass T with a 15 ml polypropylene centrifuge tube in which 1 g (air dried) of soil was placed. Holes were drilled approximately 2 mm above the soil surface for an inlet and outlet for the flow of oxygen. Another 1/16 inch (I.D.) $\times$ 1/8 inch (O.D.) tygon tube attached the outlet hole to a 3 mm (I.D.) $\times$ 4 mm (O.D.) size glass tube in which one end had been heated and drawn out into a sharp point. The sharp point of this glass tubing was submerged in a counting tube which contained 5 ml of arsine trapping solution (1.5 percent HgCl₂ - 0.15 percent KMnO₄ - 2N H₂SO₄ in the ratio of 1:0.15:0.20). Once a week

the system was flushed with oxygen to remove any arsine that had evolved. The rate of flow of oxygen was such that a slow stream of bubbles would move through the trapping solution.

The soil in the tubes was an Etowah silt loam with a pH of 6.6. The soil was air dried so that accurate weighing would be possible. The soil microorganism population would diminish upon reduction of soil moisture, but they would repopulate quickly when moisture was resupplied.

The loss of ^{74}As was measured under 4 treatments. These treatments were: 1) 1 g of steam - sterilized soil maintained under moist conditions; 2) 0.1 g of organic matter (grounded corn seedling) mixed with 0.9 g of soil and maintained under wet (reduced) conditions; 3) same as number 2 except that the soil was under moist conditions; 4) 1 g of soil maintained under reduced conditions; 5) 1 g of soil maintained under moist conditions. Control samples consisted of 100 λ of 1000 ppm of DSMA- ^{74}As added to 1 g of soil that was placed in 15 ml polypropylene centrifuge tubes. These control tubes were stoppered such that no ^{74}As could escape and then stored. Sixty days after the experiment began the apparatus was disassembled and the concentrations of DSMA- ^{74}As was determined.

VI. ARSENIC EXTRACTION FROM SOIL

Fractionation of arsenic applied during isotherm and pH effects batch equilibration and arsine gas experiments was conducted according to the modified Chang and Jackson procedure as proposed by Petersen and Corey (45). In the Al and Fe extractions, 5 ml of the supernatant was counted. All other fractions were determined by counting the soils, and the difference in soil counts were translated into DSMA- ^{74}As quantities.

VII. THIN-LAYER METHODS

Thin-layer chromatography was carried out on 20 × 20 cm glass plates coated with 0.25 mm of Silica G support and dried overnight at 140°C. The plates were prepared in the laboratory by way of a QRA Model 8CR automatic plate leveller thin-layer chromatography apparatus. A methanol-ammonium hydroxide-10 percent trichloroacetic acid-water (50:15:5:30) solvent system (36, 55) was employed. The visualizing spray (40) was an ammoniacal silver nitrate solution (2N AgNO_3 in 10 percent ammonia), which produced a yellow color when arsenite (+3) was present and a pale brown color when arsenate (+5) was present. Detection was made more sensitive with UV light produced by a Spectroline black light.

VIII. STATISTICAL ANALYSIS

Analysis of variance and F tests were executed by an IBM System/360 Model 65 Computer using an SAS program developed by Barr and Goodnight (7). Duncan's new multiple Range Test was used to compare treatment means when applicable, otherwise the Student's two-tailed t-test with pooled estimate of variance was employed. The experimental design of each section was described in the results and discussion chapter.

CHAPTER III

I. RESULTS AND DISCUSSION

Effect of Equilibration Times on Sorption of DSMA-⁷⁴As

Soil sorption data for the effect of equilibration time on sorption of DSMA-⁷⁴As are presented in Table 3. Means of each of the time combinations were compared by a t-test using a pooled estimate of variance.

Table 3. Effect of Time Equilibration on Sorption of DSMA-⁷⁴As. Values are Expressed in $\mu\text{g/g}$ of Soil and are the Average of Three Replications

Soils	ppm					
	50			100		
	30 min.	1 hr.	12 hr.	30 min.	1 hr.	12 hr.
Hartsells	39.69	42.39 ^{a*}	44.78 ^{b1}	82.53	85.34 ^b	87.98 ^c
Memphis	25.37	38.25 ^c	42.87 ^c	70.28	76.68 ^b	85.49 ^c
Iberia	46.40	46.52	47.52	94.10	93.93	94.96

*Significance levels of t-test, a(0.10), b(0.05), and c(0.01).

¹Means of a soil of the appropriate concentration followed by a different letter are different from the previous value at the indicated level of probability.

For all time combinations of Hartsells and Memphis soils there were at least a significant difference at 10 percent level of probability (P.10) in the sorption of

DSMA- ^{74}As due to differences in equilibration time.

However, for Iberia there are no differences in sorption due to variation of shaking time. Iberia's greater clay content, thus greater surface area, was initially available for sorption and increasing equilibration time apparently did not expose more surface area or release soil components that would increase sorption. On the other hand the increase in sorption with corresponding increase in equilibration time was apparently due to either or both exposure of more colloidal surface or release of some soil component that sorbs DSMA- ^{74}As . These explanations agree with Schweizer's (52) observations that toxicity of DSMA residues in the soil decreased with time and Sieling (53) who reported finding that arsenate sorption by kaolin increased with time. Jacobs et al. (30) stated that sorption forces become more puissant with increasing equilibration time. They reported that the amount of arsenic extracted with Bray P-1 solution and NH_4OAc decreased with an increase in equilibration time.

The purpose of this segment of the study was to determine whether long equilibration times are necessary to obtain maximum sorption. It was concluded that at the level of concentration of DSMA- ^{74}As used in this experiment soils low in clay content would require longer equilibration times to obtain maximum sorption. However, the desirability to obtain maximum sorption must be weighed against experimental time limitations and the type of information desired.

Effect of Selected Soil Properties on Sorption of DSMA-⁷⁴As

The data were analyzed as a randomized complete block design with soils designated as treatments. Duncan's New Multiple-Range Test was employed to compare soil sorption means to determine whether they were significantly different from each other. There were differences in sorption of DSMA-⁷⁴As among the soils at the P.01 level. Soil sorption means and test results are presented in Table 4.

Table 4. Effect of Soil Properties on Sorption of DSMA-⁷⁴As (100 ppm). Values are Expressed in µg/g of Soil and are the Average of Three Replications

Soil	Halewood A	Memphis	Hartsells	Iberia	Halewood B
Treatment mean	61.30 ^d	70.28 ^c	82.53 ^b	94.10 ^a	95.34 ^{a*}

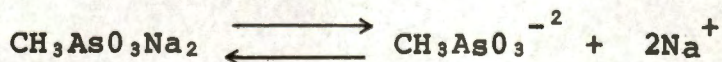
*The means followed by the same letter are not significantly different at the P.01 level.

The greatest amounts of DSMA-⁷⁴As sorbed from solution were by soils with the greatest clay content. The lone exception to this trend was the Halewood A loam soil which has a greater clay content than Hartsells loam or Memphis silt. A possible reason for this discrepancy may be that sorption by Halewood A was time dependent since the equilibration time was only 30 minutes. In another section of

this study where the equilibration time was two hours, Halewood A showed a greater affinity for DSMA- ^{74}As sorption.

Apparently the effect of organic matter on DSMA- ^{74}As sorption was low or masked by other factors. The soil with the 2nd lowest organic matter content sorbed the same amount as the soil with the highest organic matter content. The effect of cation exchange on DSMA- ^{74}As sorption exhibits the same inconsistency. The major contributing factors probably are the amount and type of clay present with its associated components.

It is well known that minerals possessing exposed hydroxyl groups, such as kaolinite and hydrous oxides of Fe and Al, sorb large amounts of phosphate. These minerals would then exhibit similar attraction for arsenic and its associated compounds. Disodium methanearsonate ionizes in solution in the manner



which is quite analogous to that of H_2PO_4^- and HPO_4^{2-} . These anions (phosphates and arsenates) are sorbed by the positively charged sesquioxide films (hydroxy-Al and hydroxy-Fe) on layer silicates and the exposed permanent positive charges on the edges of the layer silicates.

Halewood B clay was a red acid soil (pH 5) and its major clay constituents are kaolinite (>40%) and vermiculite (10-40%). Since the major clay component was kaolinite, and

the soil had a red color, an abundant amount of hydrous oxides of iron would be present. This abundance of hydrous oxides of iron would explain the great affinity Halewood B had for DSMA- ^{74}As . Supporting evidence comes from Dickens and Hiltbold (20) who reported that 1-gram samples of limonite and kaolinite sorbed 100 and 76 percent of DSMA from a solution containing 25 ml of 5.00 ppm As.

Iberia silty clay was a dark, slightly acid (pH 6.3) soil with a clay content of 49 percent of which the major components are montmorillonite (>40 percent), kaolinite (10-40 percent) and a high organic matter content of 3.0 percent. The high montmorillonite content of Iberia was quite evident considering the expansibility of the soil observed in the laboratory. Kaolinite had a much greater affinity for DSMA than did montmorillonite (20) even though montmorillonite possesses a much greater surface area. Montmorillonite had fewer exposed hydroxyl groups, which are necessary for exchange with anions, than kaolinite. Although Iberia had almost the same clay content as Halewood B, its sorption capacity was less (later section) except when relatively low concentrations of DSMA- ^{74}As were involved. Even though the clay was diluted with another clay type that had only a fair affinity for DSMA, its sorption capacity was still quite high. Organic matter may have had a positive effect on sorption.

Halewood A loam was a dark, acid soil (pH 4.7) with a high organic matter content (5.53 percent) and a 26.6 percent clay content. Its major clay constituents are the same as those for Halewood B, but in smaller overall amounts. Its sorption capacity for DSMA- ^{74}As did not fully express itself in this segment of the study, but in later sections a greater sorption capacity was obtained. Halewood A sorption capacity approached that of Halewood B and Iberia at higher pH's which indirectly indicates that organic matter had a high sorption affinity for DSMA also.

Hartsells loam was a light gray, acid soil (pH 4.9) whose clay content (14.3 percent) was comprised of vermiculite (>40 percent) and kaolinite (10-40 percent). It had a low organic matter content (0.82 percent), and its sorption capacity was somewhat lower than for Iberia or Halewood B. Hartsells major clay component, vermiculite, was a 2:1 type clay whose outer surface features were similar to that of montmorillonite. The combination of clay types and lower clay content were responsible for its lower sorption capacity for DSMA- ^{74}As .

Memphis silt, which had the lowest affinity for DSMA- ^{74}As , had a light brown color and a near neutral pH (6.9). Its clay composition (10.0 percent) was comprised of montmorillonite (10-40 percent), illite (10-40 percent) and kaolinite (10-40 percent). The low affinity for DSMA- ^{74}As

parallels the low total clay content and its clay makeup. Illite's outer surface had few exposed hydroxyl groups and thus a low affinity for anion sorption.

Leaching of 100 ppm Surface Applied DSMA-⁷⁴As

There were differences among soils in the amount of DSMA-⁷⁴As leached from the soil columns at the 1 percent level of probability. Duncan's New Multiple-Range Test (Table 5) confirms that Hartsells and Memphis soil sorption means were not significantly different from each other at the P.01 level. There was a tremendous range (90 percent for Memphis to 1.5 percent from Halewood B) in the amount of surface applied DSMA-⁷⁴As leached from the columns. The results are summarized in Table 5.

Table 5. Effect of Soil Properties on the Quantity of DSMA-⁷⁴As Leached from Soil Columns That Received 100 ppm of Surface Applied DSMA-⁷⁴As. Values Are in $\mu\text{g/g}$ of Soil and are the Average of Three Replications

Soil	Halewood B	Halewood A	Iberia	Hartsells	Memphis
Mean	1.48 ^d	13.89 ^c	61.89 ^b	84.24 ^a	90.24 ^{a*}

*Means followed by the same letter are not significantly different at the P.01 level.

The breakthrough increment which contained DSMA-⁷⁴As occurred in the Memphis column at the 6th ml increment and approximately 83 percent of the leached DSMA-⁷⁴As was removed

in the 7th through 12th increments. Six milliliters was roughly equivalent to one column volume of the 1:2 (soil to cellulose powder) columns. The column volume, breakthrough increment, and the percent of leached DSMA-⁷⁴As removed in one column volume for each soil and for each cellulose blank are presented in Table 6.

Table 6. The Column Volume, Breakthrough Increment, and Percent of Leached DSMA-⁷⁴As Removed in First Displaced Column Volume

Column (Soil)	Column Volume (ml)	Breakthrough Increment	Percent of Leached DSMA- ⁷⁴ As in First Displaced Column Volume
Hartsells	3	3	75
Memphis	6	6	83
Halewood A	6	8	69
Halewood B	6	-	-
Iberia	11	12	60
1:1 blank	3	2	97
1:2 blank	6	6	100
1:4 blank	11	11	100

No DSMA-⁷⁴As was detected emerging from the columns until after at least one column volume had been displaced. This observation supports the assumption that uniform displacement of the soil solution occurred when water was added to the top of the column and no DSMA-⁷⁴As should emerge before the soil solution below the surface zone of DSMA-⁷⁴As

application was displaced. The DSMA- ^{74}As advanced downward through the column in a band with high frontal concentration as can be seen in the cellulose blank and soil-cellulose elution curves which are represented in Figures 1 and 2. This band of high frontal concentration represented the quantity of DSMA- ^{74}As which was not sorbed by the soil. The succeeding increments represent the DSMA which had undergone sorption, desorption process with soil surfaces. The tailing of the elution curves in Figure 1 illustrates the release of DSMA- ^{74}As from soil particles surfaces as the equilibrium concentration decreased with continued addition of water. The reduced elution concentrations of DSMA- ^{74}As and the broad elution curves, especially those of Iberia and Halewood A soils, are in contrast to those of the blank columns. The sorption capacity of Iberia and Halewood A soils were greater than those of Memphis and Hartsells (Table 7), and the equilibrium concentrations of DSMA- ^{74}As established between the soil particles and soil solution was shifted in favor of the soil particles. The soil sorption forces allowed only 1.5 percent of the added DSMA- ^{74}As to be leached from Halewood B. The established equilibria between soil particles and soil solutions are illustrated below. The length of the arrows shows the relative distribution in the established equilibrium.

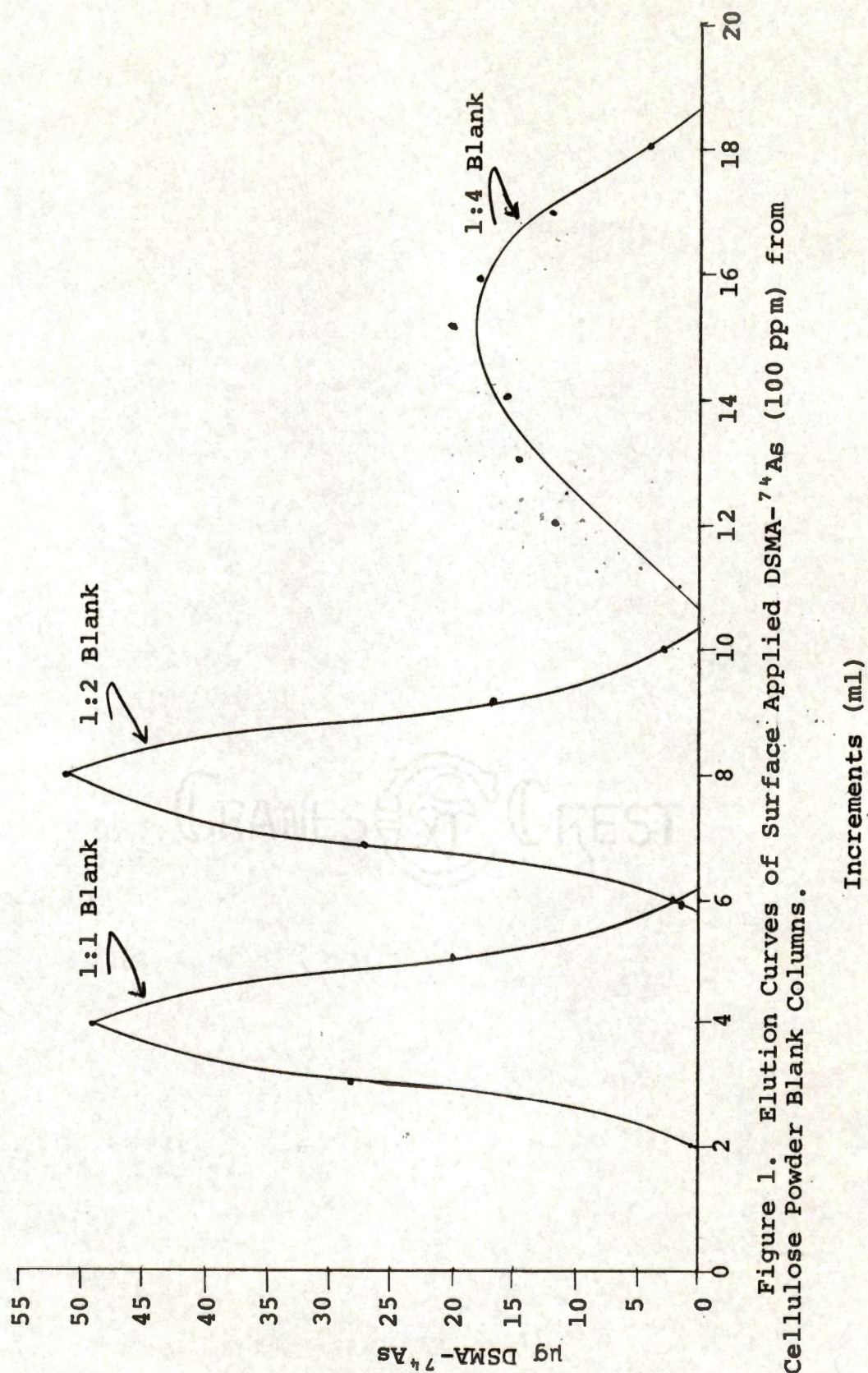


Figure 1. Elution Curves of Surface Applied DSMA-⁷⁴As (100 ppm) from Cellulose Powder Blank Columns.

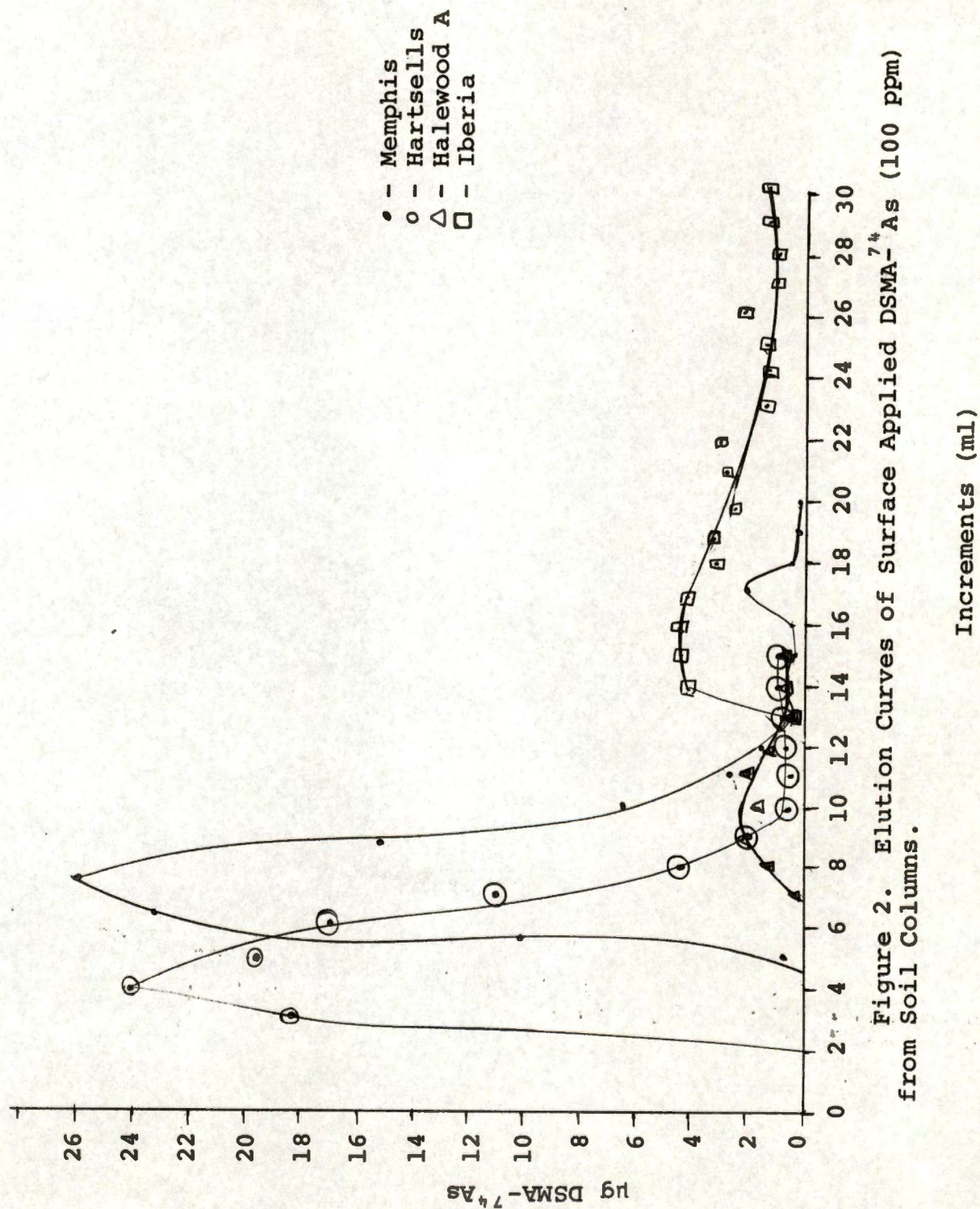
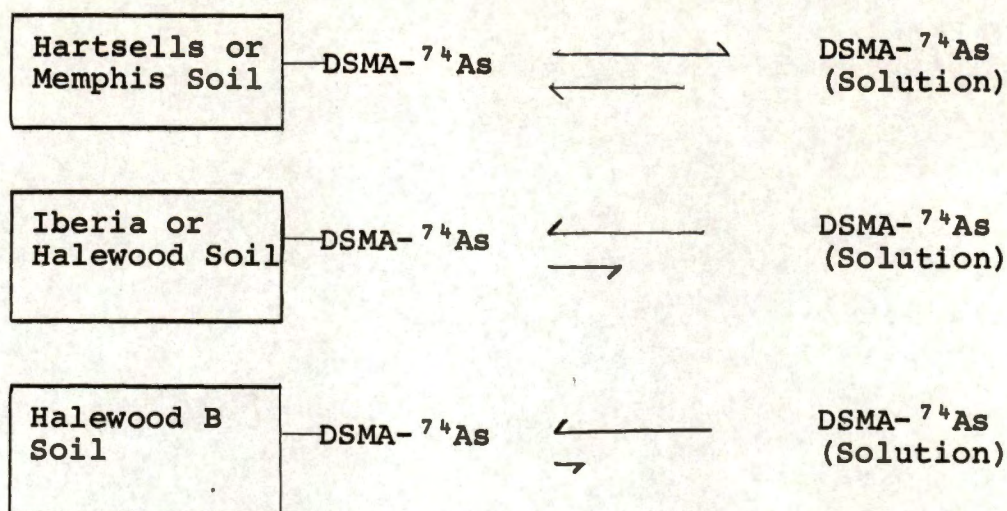


Table 7. The Elution of 100 ppm Surface Applied
DSMA-⁷⁴As from Soils. Values are
Expressed in $\mu\text{g/ml}$ and are the
Average of Three Replications

Fraction (ml)	DSMA- ⁷⁴ As Content of Leachate in μg				
	Hartsells	Memphis	Iberia	Halewood A	Halewood B
1	-	-	-	-	-
2	-	-	-	-	-
3	0.54	-	-	-	-
4	18.27	-	-	-	-
5	24.12	0.78	-	-	-
6	19.73	10.70	-	-	-
7	11.20	22.54	-	0.33	-
8	4.07	26.32	-	1.32	-
9	2.30	14.96	-	1.88	-
10	0.60	6.65	-	1.53	-
11	0.57	2.92	0.13	1.85	-
12	0.80	1.31	4.02	0.99	-
13	0.70	0.28	4.75	1.97	-
14	0.85	0.45	5.22	0.59	-
15	0.53	0.38	5.08	0.89	-
16		0.52	4.23	0.76	-
17		2.66	4.96	0.66	-
18		0.17	3.19	0.45	-
19		0.10	3.30	1.15	-
20		0.10	3.10	0.37	-
21			3.50		
22			1.90		
23			1.98		
24			1.89		
25			2.94		
26			2.09		
27			1.88		
28			1.86		
29			2.21		
30			2.50		



After the columns were leached, the soils were removed, sectioned, and distribution of DSMA-⁷⁴As determined (Table 8). Almost 92 percent of the applied DSMA-⁷⁴As stayed in the 1st cm of Halewood B column. There was a fairly even distribution of DSMA-⁷⁴As throughout the other columns except for the initial segment which had a greater concentration of DSMA-⁷⁴As than would be expected. A possible explanation was that in grinding the soils with the cellulose powder a disproportional amount of the soil, being heavier, settled to the bottom of the mortar during the grinding process. This soil would end up on top of the column.

It was concluded that the rate of leaching of surface applied DSMA-⁷⁴As (Table 7) would differ inversely with the sorption capacity of the soil. The exception in this case

Table 8. Distribution of DSMA-⁷⁴As in Soil Columns
After Surface Application of DSMA (100 ppm) and
Leaching with Water. Values are Expressed
in μg and are the Average of
Three Replications

Depth in cm	DSMA- ⁷⁴ As Content per Column Section (μg)				
	Hartsells	Memphis	Iberia	Halewood A	Halewood B
0-1	10.66	6.94	8.42	24.25	93.94
1-2	2.09	1.01	1.82	10.89	5.58
2-3	3.08	0.88	1.65	9.53	0.11
3-4	1.20	0.50	2.48	11.67	-
4-5		0.43	3.25	10.82	-
5-6			3.67	9.49	-
6-7			3.18		
7-8			3.36		
8-9			4.57		
9-10			5.74		

was the Halewood A soil which retained a greater amount of soil in the column than would be expected, considering the results from the sorption experiments.

A number of authors (3, 20, 22, 39) stated that the amount of arsenicals leached out of soil was inversely related to its sorption capacity. However, their columns were comprised of entirely uniform packed soil. The soil in this experiment was diluted with cellulose powder to obtain uniform movement of effluent through the column. Therefore it is possible that in some columns packed entirely with soil, no DSMA would emerge without necessitating greater quantities of water.

Effect of Phosphorus and Acid
Treatment on Sorption of DSMA-⁷⁴As

The data were analyzed using a randomized complete block design with a split-plot arrangement of treatments where soils were main treatments, and phosphorus and acid treatments were the split-treatments. Analysis of variance and F test showed a difference in sorption of DSMA-⁷⁴As due to soils, phosphorus, and acid treatments, and the interaction of the main treatments and split-treatments at the P.01 level of probability. The data for this section are presented in Table 9.

Table 9. Effect of P and Acid Treatments on the Sorption of DSMA-⁷⁴As. Values are in µg/g of Soil and are the Average of Three Replications

Soil	Treatment			
	Untreated	1000 ppm P	200 ppm P	Acid
Hartsells	82.53 ^a	24.29 ^c	65.47 ^b	88.29 ^{a*}
Memphis	70.27 ^f	20.48 ^h	45.22 ^g	87.34 ^e
Iberia	94.10 ⁱ	71.94 ^j	88.40 ⁱ	94.09 ⁱ

*Means within a row followed by the same letter are not significantly different at the P.01 level.

Addition of phosphorus reduced the soils ability to retain DSMA-⁷⁴As. The 1000 ppm P treatment had the greatest effect in reducing DSMA-⁷⁴As retention in all three soils tested. The reduction in sorption caused by the 200 ppm P treatment was not as great as the 1000 ppm P treatment, but it definitely reduced the ability of the soils to retain DSMA-⁷⁴As. The acid treatment generally increased sorption capacity of Memphis (24.2 percent) and somewhat less so for Hartsells (7.0 percent). The acid treatment did not affect sorption of DSMA-⁷⁴As in Iberia. The means of the split-treatment (P and acid treatments), and main treatments (soils) along with the significance of Duncan's New Multiple-Range Test are shown in Tables 10 and 11.

Table 10. Sorption of DSMA-⁷⁴As as a Function of P and Acid Treatments. The Values were Averaged Across Soils and are Expressed in $\mu\text{g/g}$ of Soil

Treatment	1000 ppm P	200 ppm P	Untreated	Acid
Mean	38.90 ^d	66.36 ^c	82.30 ^b	89.91 ^a

* Means followed by the same letter are not significantly different at the P.01 level.

All the split-treatment means were significantly different from each other at the P.01 level as were the main treatments means.

Table 11. Sorption of DSMA-⁷⁴As as a Function of Soils. The Values were Averaged Across P and Acid Treatments and are Expressed in $\mu\text{g/g}$ of Soil

Soil	Memphis	Hartsells	Iberia
Mean	55.83 ^c	65.15 ^b	87.14 ^{a*}

* Means followed by the same letter are not significantly different at the P.01 level.

These results illustrate the competition of phosphorus and arsenic for the same sorption sites in the soil. The competition of arsenic and phosphorus had been investigated by several authors (1, 2, 21, 31, 52). Albert and his coworkers (1, 2), Schweizer (52), Jacobs et al. (31),

reported that additions of phosphorus to arsenic-containing soils increased symptoms of arsenic toxicity in the crops with the degree of injury depending on the texture of the soil. Generally, arsenic toxicity to plants was more pronounced upon addition of phosphorus in soils low in clay content and had less effect in soils with high clay content. Sieling (53) investigated the relative replacing abilities of phosphate and arsenate ions on activated kaolin. He found that phosphate could replace arsenate quite effectively, but arsenate was not as effective in replacing phosphate. Arsenates replaced only a small percentage of the sorbed phosphate even when the concentration of arsenate was five times that of phosphate.

The increase in sorption of DSMA- ^{74}As in the acid washed soils was probably due to increased reactive aluminum and iron content of the soil. Iron and aluminum becomes more soluble as the pH of the soil decreases. The pH dependent charge of the soil also had a positive effect on the sorption of DSMA- ^{74}As . Since ionized DSMA is doubly negatively charged, an increase in the positive charge in the system would force an increase in sorption of DSMA- ^{74}As .

Effect of P and Acid Treatments on Leaching
of 100 ppm Surface Applied DSMA-⁷⁴As

The same statistical analysis was executed in this experiment as in the Effect of P and Acid Treatments on Sorption of DSMA-⁷⁴As section. At the P.01 level there were differences in the amount of DSMA-⁷⁴As leached due to soils, P and acid treatments, and the interaction of soils-P and acid treatments. The data for this section are in Table 12.

The 1000 ppm treatment of P increased the amount of DSMA-⁷⁴As leached from all the columns. In fact practically all of the added methanearsonate was leached out. The 200 ppm P treatment caused a significant increase in the amount of DSMA-⁷⁴As leached (See Table 13), while the acid treatments showed a significant decrease in the amount of DSMA-⁷⁴As leached from the columns.

Table 13. The Elution of DSMA-⁷⁴As (100 ppm) from Soils Treated with P and Acid. Values are in $\mu\text{g/g}$ of Soil and are Averaged Across Soils (Main Treatments)

Treatment	Acid	Nontreated	200 ppm P	1000 ppm P
Mean	67.44 ^d	78.39 ^c	84.41 ^b	98.30 ^a

* Mean followed by the same letter are not significantly different at the P.01 level.

These results illustrate the effect of P and acid treatments on the capacity of soil to retain DSMA-⁷⁴As.

Table 12. The Elution of Surface Applied
DSMA-⁷⁴As (100 ppm) with Water from
Columns Whose Soils were
Treated with Phosphorus
and Acid

Fraction (ml)	Soil	DSMA- ⁷⁴ As Content of Leachate in μg^*			
	Hartsells	Nontreated	1000 ppm P	200 ppm P	Acid
1	"	-	-	-	-
2	"	-	-	-	-
3	"	0.54	25.08	9.00	-
4	"	18.27	52.33	24.13	0.53
5	"	24.12	13.87	28.69	5.71
6	"	19.73	3.89	15.11	12.41
7	"	11.20	0.37	6.18	12.68
8	"	4.07	-	1.97	8.71
9	"	2.30	-	1.15	5.62
10	"	0.60	-	0.90	5.74
11	"	0.57	-	0.69	3.76
12	"	0.80	-	0.66	2.43
13	"	0.70	-	0.70	1.91
14	"	0.85	-	1.60	2.47
15	"	0.53	-	1.52	1.74
Memphis					
1	"	-	-	-	-
2	"	-	-	-	-
3	"	-	-	-	-
4	"	-	-	-	-
5	"	0.78	2.92	3.05	1.46
6	"	10.70	23.07	15.32	6.21
7	"	22.54	40.75	25.40	7.04
8	"	26.32	19.94	29.75	10.18
9	"	14.96	7.02	16.31	9.80
10	"	6.65	3.25	4.41	6.61
11	"	2.92	0.31	2.77	4.31
12	"	1.31	0.35	1.06	3.34
13	"	0.28	0.05	1.76	2.19
14	"	0.45	0.10	0.17	1.39
15	"	0.38	0.16	-	1.39
16	"	0.52	-	-	1.64
17	"	2.66	-	-	0.74
18	"	0.17	-	-	1.92
19	"	0.10	-	-	0.27
20	"	0.10	-	-	0.19

Table 12 (continued)

Fraction (ml)	Soil	DSMA- ⁷⁴ As Content of Leachate in μg^*			
	Iberia	Nontreated	1000 ppm P	200 ppm P	Acid
1	"	-	-	-	-
2	"	-	-	-	-
3	"	-	-	-	-
4	"	-	-	-	-
5	"	-	-	-	-
6	"	-	-	-	-
7	"	-	-	-	-
8	"	-	-	-	-
9	"	-	-	-	-
10	"	-	-	-	-
11	"	0.13	10.80	-	-
12	"	4.02	22.21	0.98	-
13	"	4.75	8.62	8.18	0.10
14	"	5.22	4.38	7.51	4.02
15	"	5.08	4.20	7.92	4.31
16	"	4.23	4.51	7.37	5.78
17	"	4.96	3.18	5.97	4.88
18	"	3.19	5.80	5.44	4.64
19	"	3.30	4.90	4.36	4.33
20	"	3.10	3.50	3.36	3.87
21	"	3.50	5.32	3.51	3.60
22	"	1.90	3.68	3.41	3.23
23	"	1.98	5.53	2.11	2.50
24	"	1.89	7.62	1.95	2.32
25	"	2.94	4.58	1.61	2.64
26	"	2.09	1.02	1.33	2.43
27	"	1.88	-	0.63	2.12
28	"	1.86	-	0.28	1.82
29	"	2.21	-	0.27	1.83
30	"	2.50	-	0.20	1.62

*The average of three replications.

These effects are graphically shown in Figures 3 through 5. The 1000 ppm P treatment elution curve has a sharp peak and is very similar to that of the cellulose blank curves (Figure 1, page 42). The 200 ppm P elution peak was broader and not as sharp as the 1000 ppm treatment, but is narrower than the nontreated soil. The elution curves of the acid treated columns are short, broad ones which showed the increased sorption capacity of the acid treated soils. Generally, the leaching results parallel those of the sorption section, that is, addition of phosphorus decreased the sorption capacity of the soil and the acid treatments increased the sorption capacity of the soil.

The distribution of the DSMA-⁷⁴As in the soil columns show the effect of the different treatments on the sorption capacity of the columns (Table 14). Almost all of the DSMA-⁷⁴As was removed from all the 1000 ppm P treated columns while for the 200 ppm P the amount of DSMA-⁷⁴As removed was greater than the nontreated columns for all soils. The acid treatment showed a definite increase in the sorption capacity of the soils for DSMA-⁷⁴As. The leaching was stopped after three column volumes although measurable quantities of DSMA-⁷⁴As were still detectable for all three soils that was not treated with 1000 ppm P. Whether the acid treatment columns would hold more DSMA-⁷⁴As than the nontreated ones if more leaching was applied is a matter of

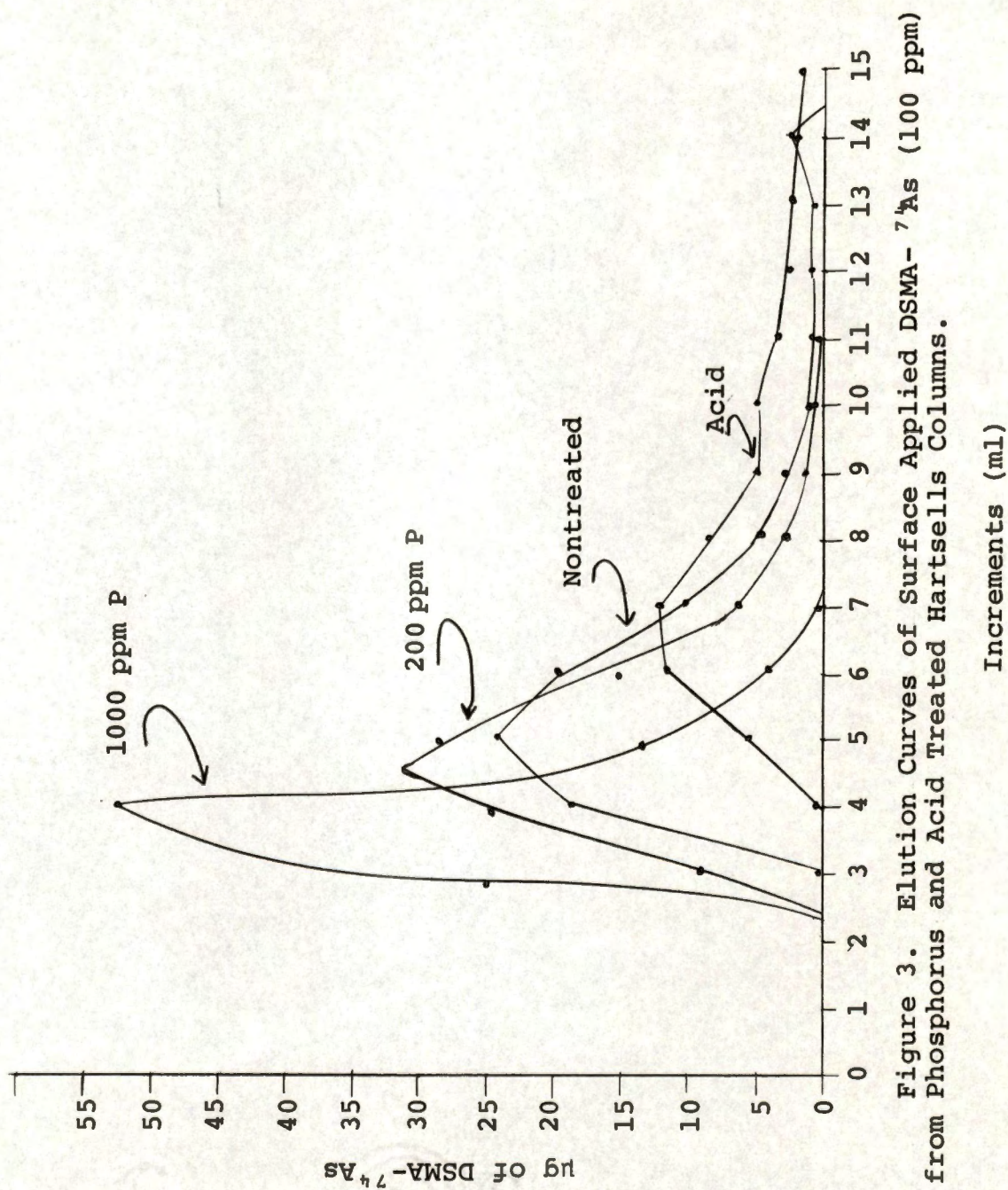


Figure 3. Elution Curves of Surface Applied DSMA-⁷⁴As (100 ppm) from Phosphorus and Acid Treated Hartsells Columns.

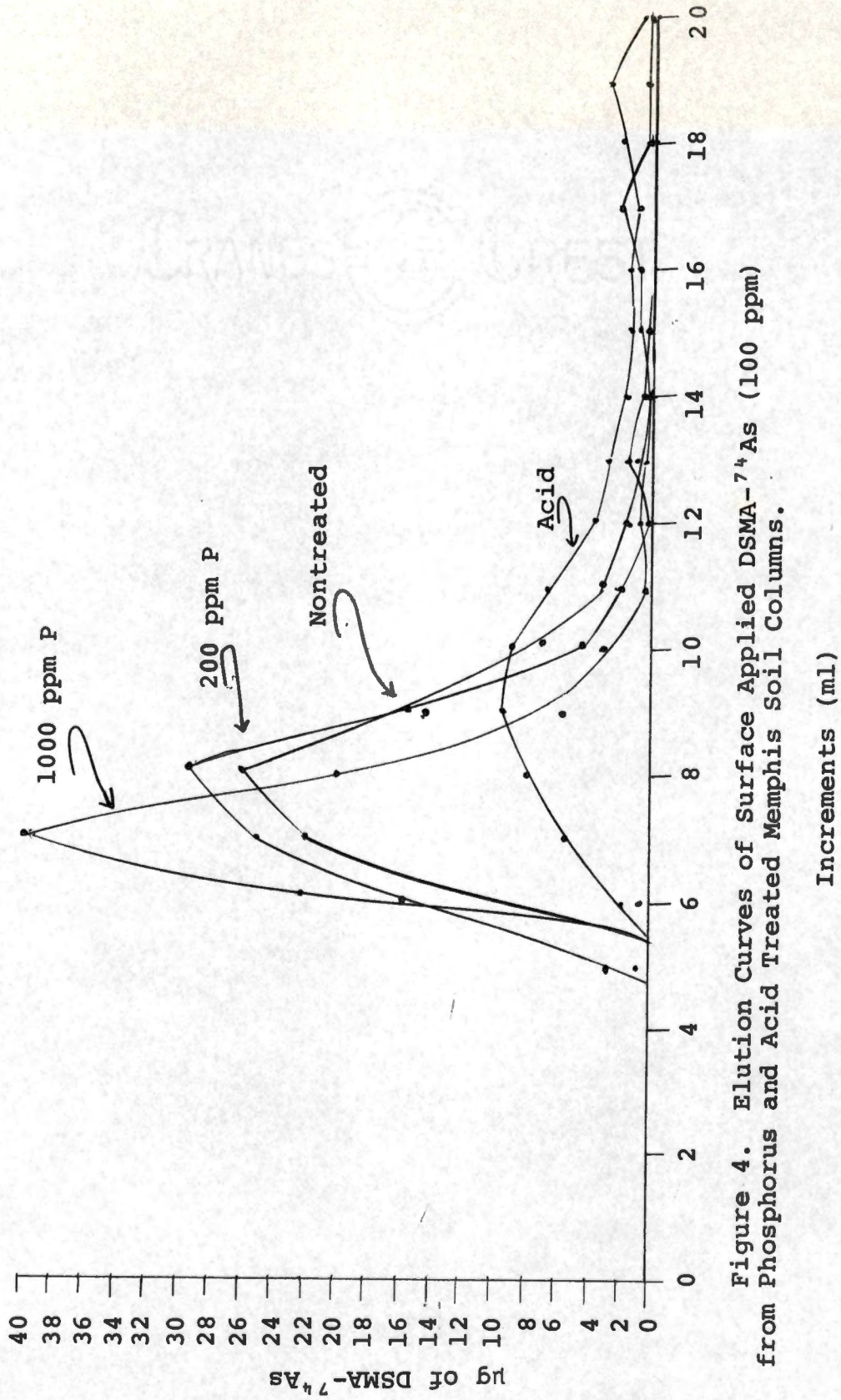


Figure 4. Elution Curves of Surface Applied DSMA-⁷⁴As (100 ppm) from Phosphorus and Acid Treated Memphis Soil Columns.

Increments (ml)

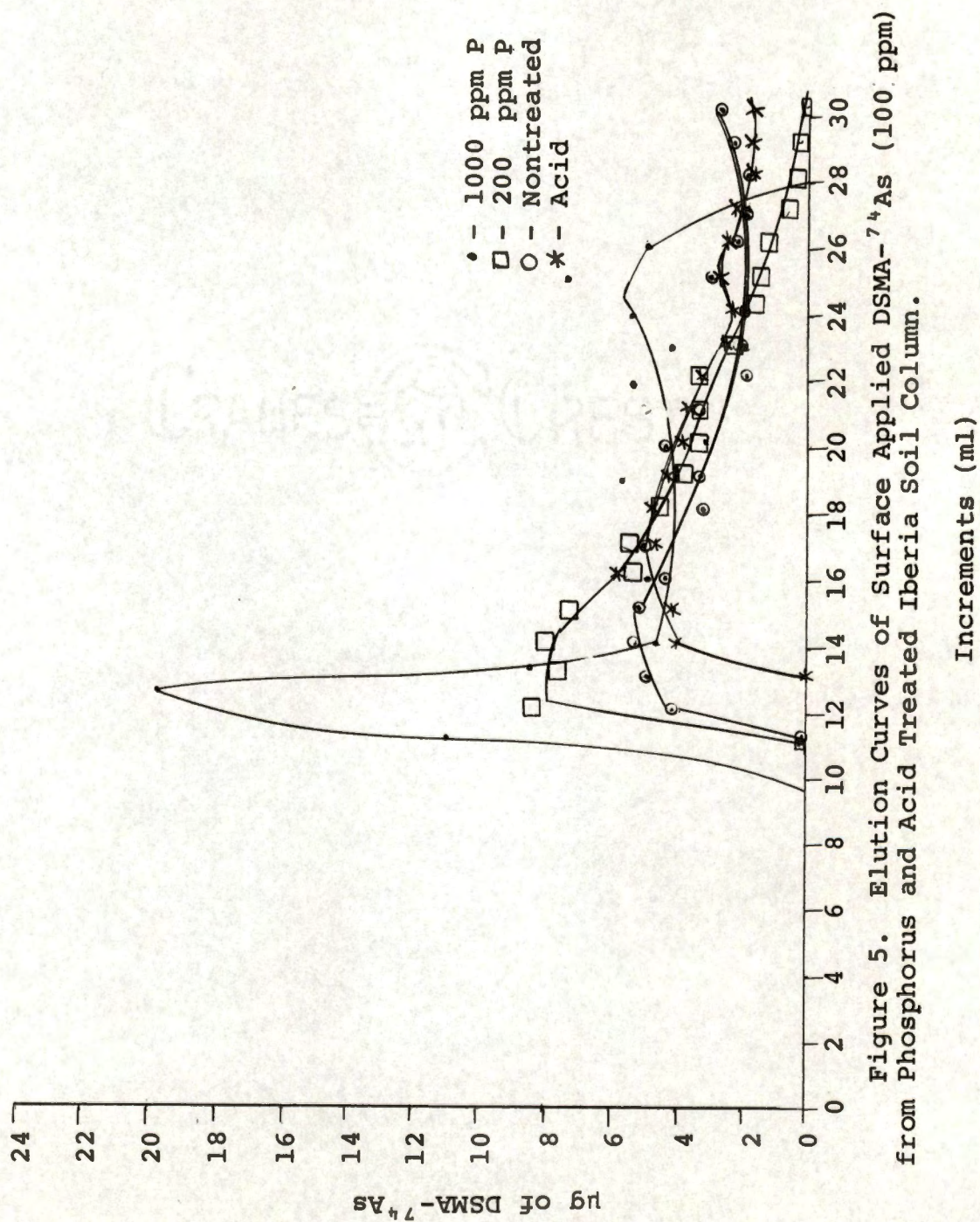


Table 14. Distribution of DSMA- ^{74}As in Soil Columns After Surface Application of DSMA- ^{74}As (100 ppm) and Leaching with Water

Depth (cm)	Soil	DSMA- ⁷⁴ As Content of Leachate μg*			
		Nontreated	1000 ppm	200 ppm	Acid
Hartsells					
0-1		10.66	0.61	3.01	22.24
1-2		2.09	0.28	1.40	6.00
2-3		3.08	0.61	3.40	2.72
3-4		1.20			3.68
Memphis					
0-1		6.94	0.38	1.42	6.03
1-2		1.01	0.17	1.42	7.07
2-3		0.88	0.18	1.15	2.28
3-4		0.50	0.19	0.25	1.03
4-5		0.43	0.32	0.34	1.14
Iberia					
0-1		8.42	0.12	10.76	9.37
1-2		1.82	0.08	1.68	1.88
2-3		1.65	0.09	1.45	1.03
3-4		2.48	0.08	1.29	2.61
4-5		3.25	0.11	0.16	3.40
5-6		3.67	0.10	3.95	4.71
6-7		3.18	0.07	3.07	4.12
7-8		4.36	0.07	2.99	4.39
8-9		4.57	0.06	3.46	5.50
9-10		5.74	0.04	3.15	6.83

*The average of three replications.

speculation, but the evidence indicates that treatment with acid inhibits the movement of DSMA-⁷⁴As. This would indicate that the movement of DSMA-⁷⁴As was dependent not only on the type of clay present, but also on the pH-dependent charge of the soil. At the lower pH more Al and Fe were in the exchangeable form and there was an increase in the positive charge in the system. This had a double-barreled retardation effect upon DSMA-⁷⁴As movement. The sorption of DSMA-⁷⁴As by the increased Fe and Al exchangeable forms are probably the greatest factor in the retardation of the movement of DSMA-⁷⁴As. However, there was the factor of attraction of negative ions to the positive ions sorbed on the clay surface. As anions sweep along the surface of clay, the negatively charged ions are attracted to the partially neutralized cations adsorbed on the clay surface, thus retarding their movement downward through the column.

II. SORPTION ISOTHERMS AND pH EFFECT

This experiment was arranged in a randomized complete block design with a split-plot arrangement of treatments where soils were designated as main treatments and pH as split-treatments. Analysis of variance and F test were determined for differences in sorption of DSMA-⁷⁴As among soils, and among pH's. This analysis was performed at each DSMA-⁷⁴As concentration level to determine the concentration

dependence of soils and effects of pH. Duncan's New Multiple-Range Test was used to compare the treatment means whenever applicable.

At all concentration levels there were differences in sorption of DSMA- ^{74}As among soils, pH, and the interaction term of soils and pH. Data for this segment of the study are summarized in Table 15. The soil sorption means for pH averaged over soils, soils means averaged over pH, and the significance of Duncan's New Multiple-Range Test are presented in Tables 16 and 17.

In Figures 6 through 10, the amount of DSMA- ^{74}As sorbed by soils versus the amount in equilibrium solution are plotted for each pH. At pH 4 (Figure 6), Hartsells and Memphis soils sorbed practically the same quantity of DSMA- ^{74}As at each concentration level. The other soils separate nicely in the order of sorption: Halewood A < Iberia < Halewood B. Sorption results at pH 5 (Figure 7) are: Memphis < Hartsells < Halewood A < Iberia < Halewood B. However, Iberia and Halewood A sorption were almost equal until the 150 ppm level, where Iberia sorption became increasingly greater than Halewood A. Figure 8 shows that at pH 6 sorption of DSMA- ^{74}As followed the order: Halewood B > Iberia > Halewood A > Hartsells > Memphis. At this pH the magnitude of sorption of

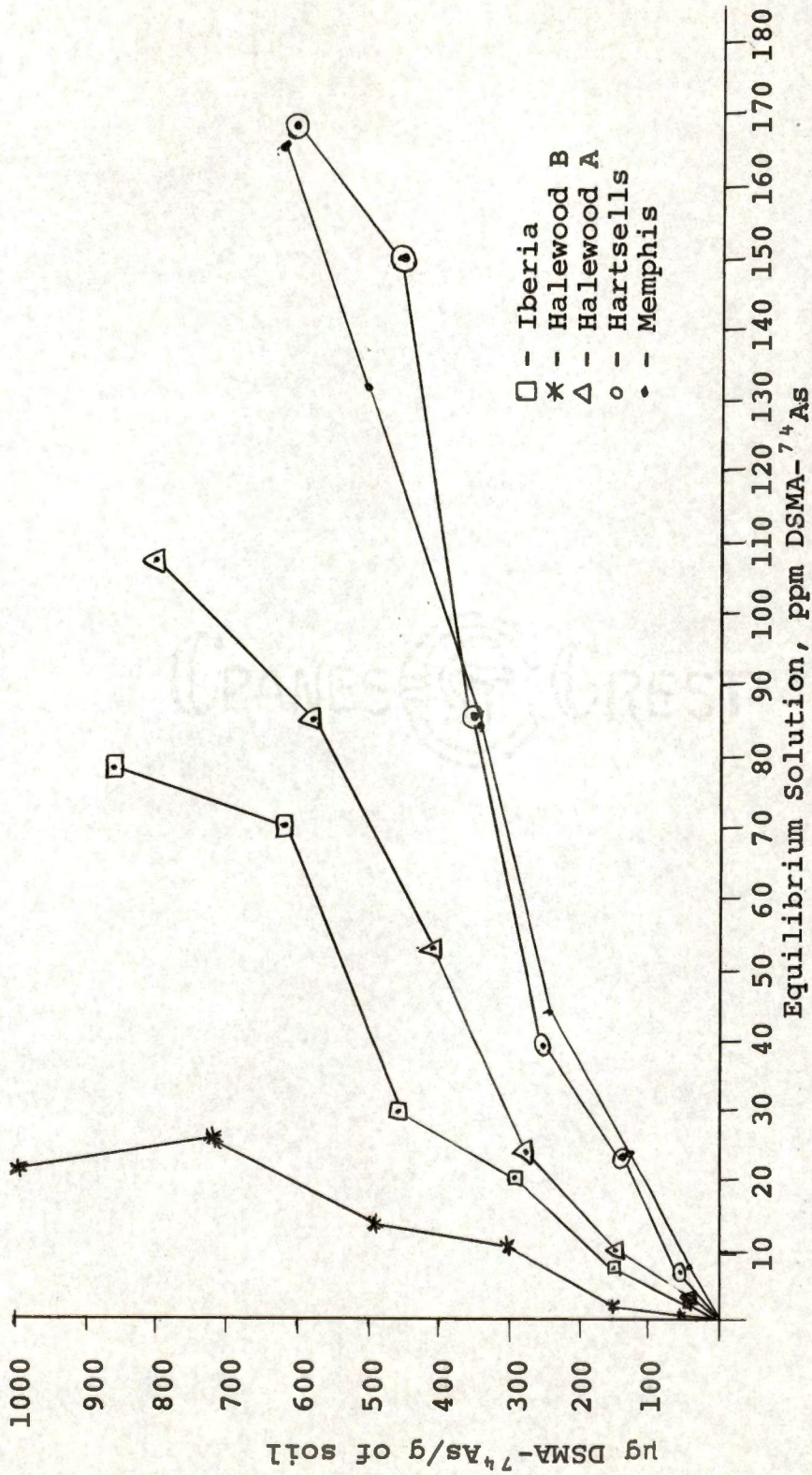


Figure 6. The Sorption of DSMA-⁷⁴As by Soils at pH 4 as a Function of Equilibrium Concentration.

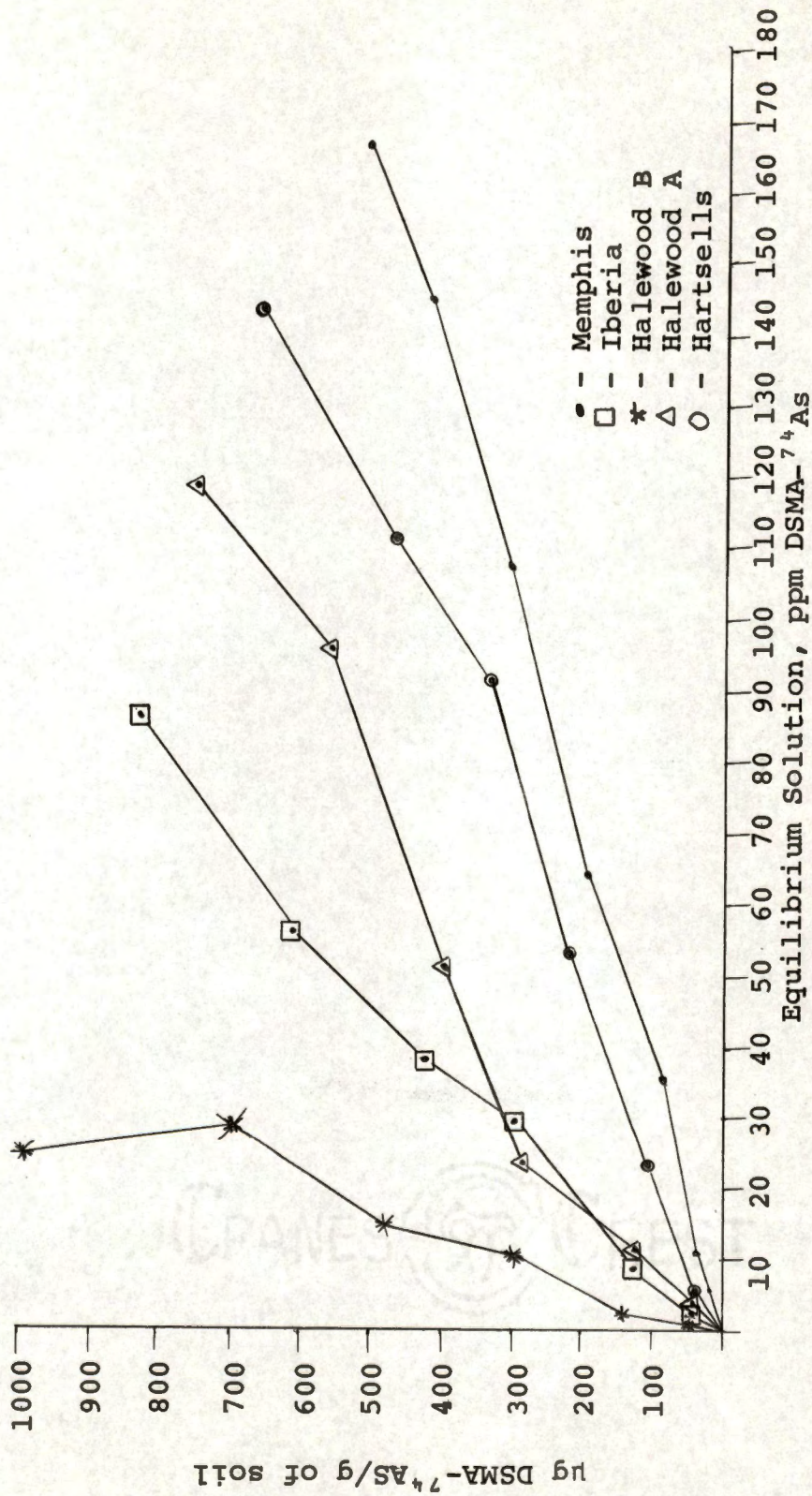


Figure 7. The Sorption of DSMA-⁷⁴As by Soils at pH 5 as a Function of Equilibrium Concentration.

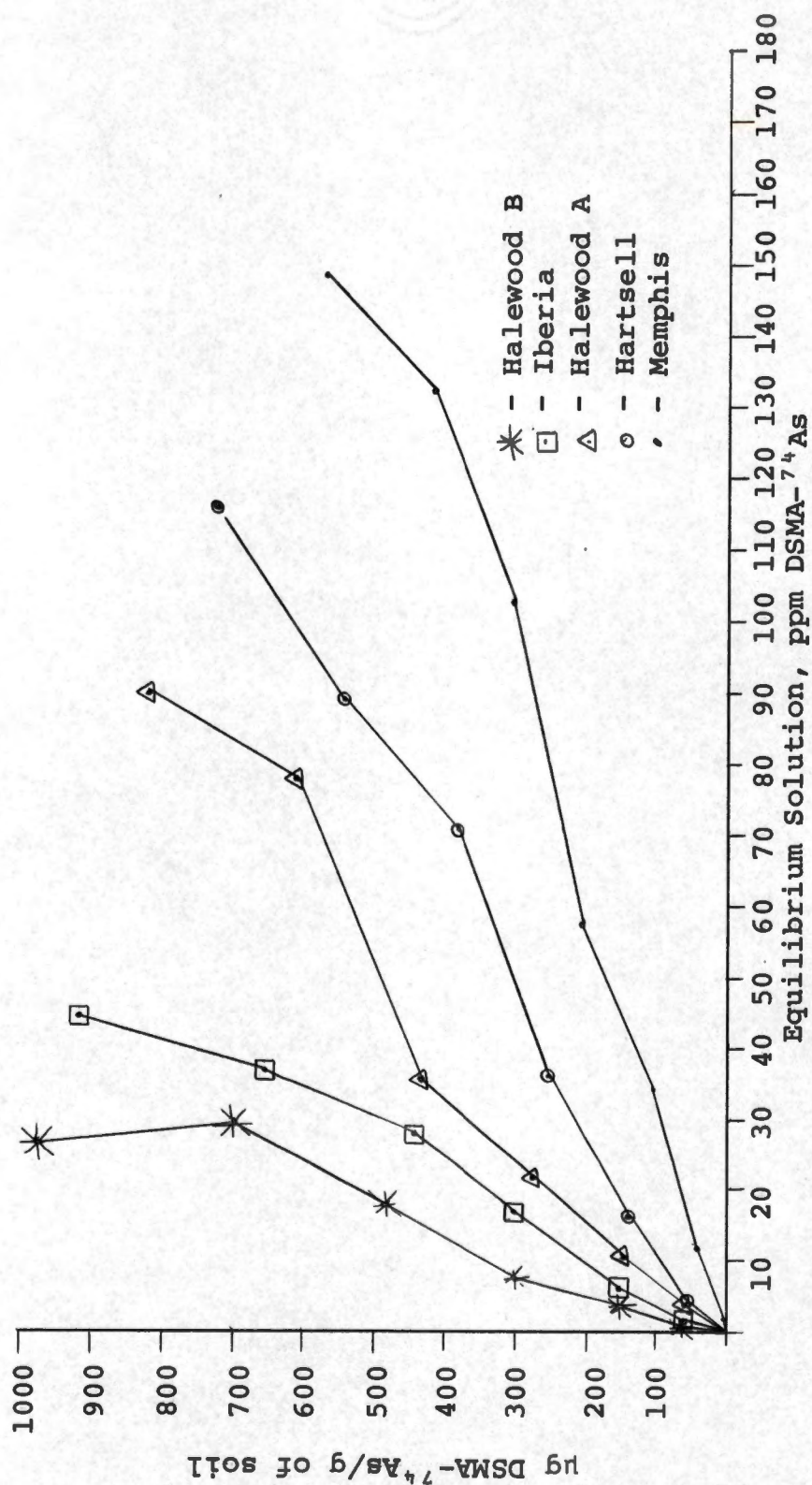


Figure 8. The Sorption of DSMA-⁷⁴As by Soils at pH 6 as a Function of Equilibrium Concentration.

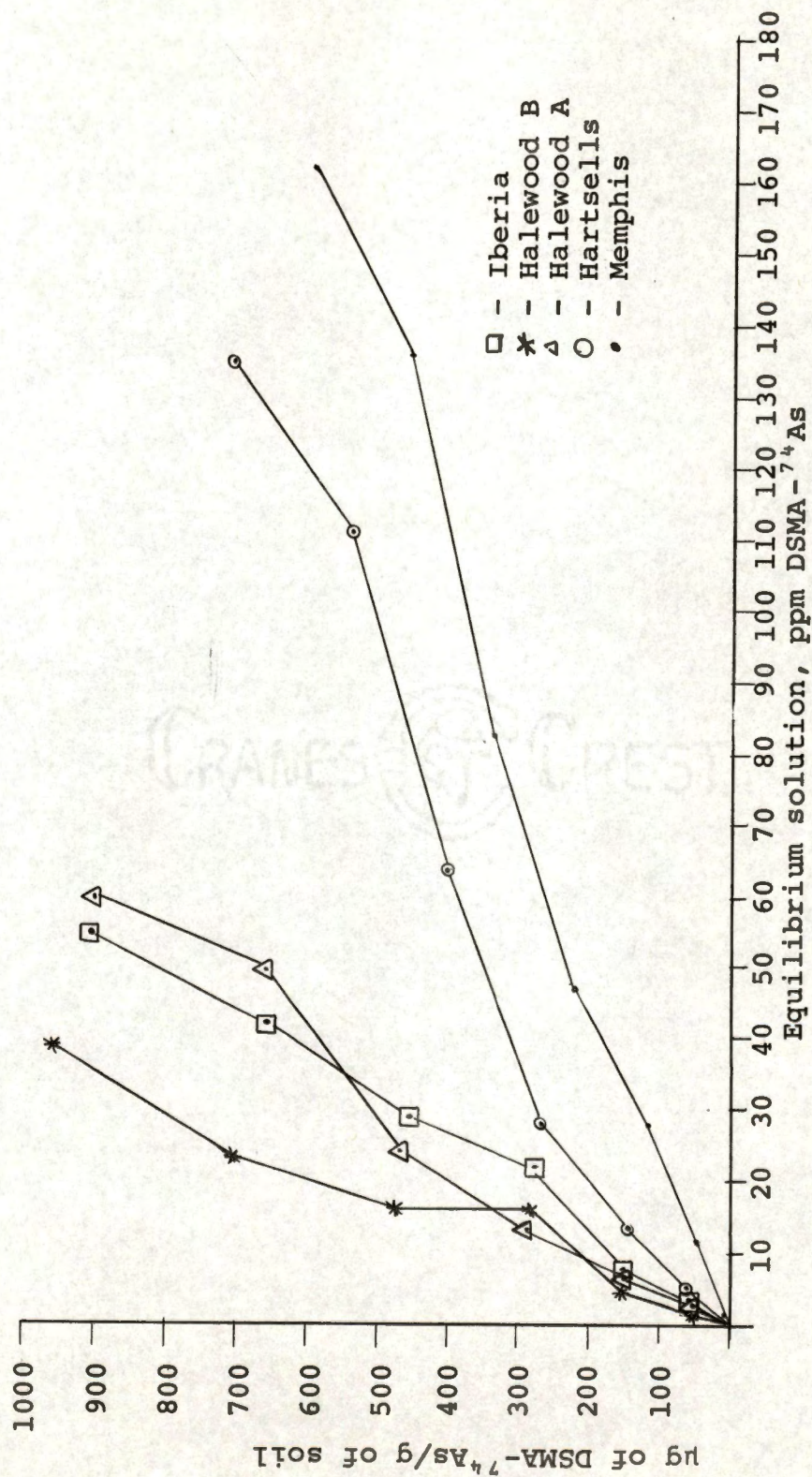


Figure 9. The Sorption of DSMA-⁷⁴As by Soils at pH 7 as a Function of Equilibrium Concentration.

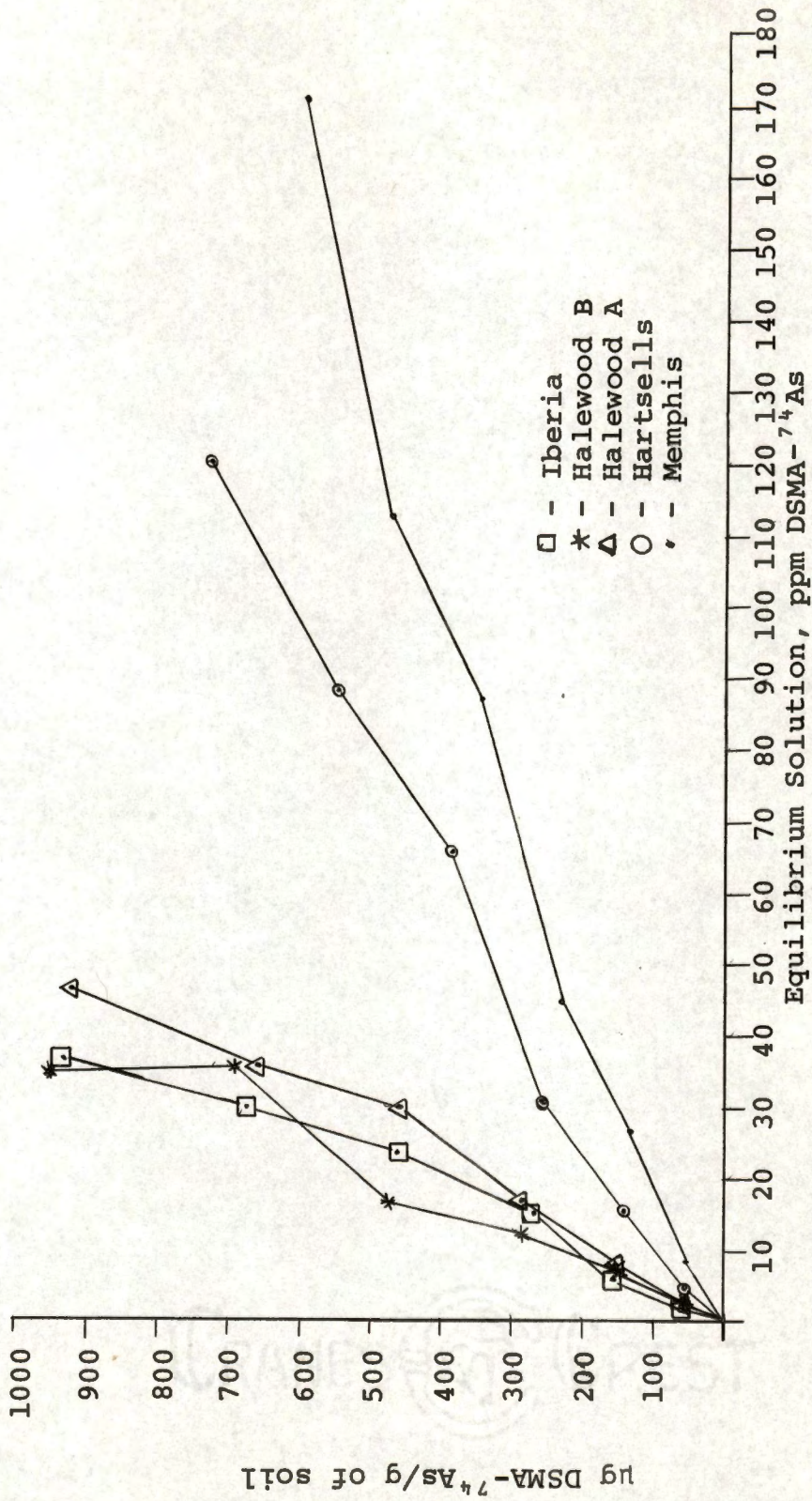


Figure 10. The Sorption of DSMA-⁷⁴ As by Soils at pH 8 as a Function of Equilibrium Concentration.

Table 15. Sorption Isotherms of DSMA-⁷⁴As as A Function of pH.
Values are Expressed in µg/g of Soil and are the Average
of Three Replications

Soil	pH	Concentration Level µg									
		10		50		100		150		Sup.*	
Memphis	4	Sup.	Soil	Sup.	Soil	Sup.	Soil	Sup.	Soil	Sup.	Soil
	5	1.58	8.42	6.48	51.94	22.20	129.74	44.10	235.64		
	6	2.30	7.67	10.48	47.19	34.32	112.87	62.96	199.91		
	7	2.31	7.71	12.20	45.51	34.53	110.98	57.77	203.21		
	8	1.90	8.10	11.27	46.83	28.20	118.63	47.10	221.53		
Hartsells	4	1.03	8.97	8.26	50.71	26.33	124.38	45.00	229.38		
	5	0.47	9.53	7.25	52.28	21.80	130.48	39.30	241.18		
	6	0.80	9.20	5.78	53.42	24.00	129.42	53.81	225.61		
	7	0.88	9.12	4.00	55.12	16.74	138.38	36.74	251.64		
	8	0.61	9.39	4.49	54.90	13.70	141.20	28.20	263.00		
Iberia	4	0.68	9.32	3.94	55.38	16.08	139.30	35.97	253.33		
	5	0.11	9.89	2.21	57.66	7.40	150.26	17.25	282.76		
	6	0.97	9.03	2.53	56.50	9.56	146.94	28.85	268.09		
	7	0.76	9.24	2.09	57.15	6.83	150.32	17.55	272.77		
	8	0.61	9.39	1.93	57.46	7.42	150.04	22.10	277.94		
Halewood A	4	0.39	9.61	1.42	58.19	5.53	152.66	15.70	276.96		
	5	2.28	7.72	3.28	4.44	9.70	144.74	22.20	272.54		
	6	1.97	8.03	3.80	54.23	11.20	143.03	22.35	270.68		
	7	0.25	9.75	4.40	55.35	10.60	144.75	21.60	273.15		
	8	0.20	9.80	3.01	56.79	6.70	150.09	13.80	286.29		
		0.45	9.55	2.35	57.20	7.52	149.68	16.70	282.98		

Table 15 (continued)

Soil	pH	Concentration Level µg									
		10		50		100		150		Sup.*	
		Sup.	Soil	Sup.	Soil	Sup.	Soil	Sup.	Soil	Sup.	Soil
Halewood B	4	0.00	10.00	0.18	59.82	1.70	158.12	8.40	299.72		
	5	0.00	10.00	0.09	59.91	2.60	157.31	10.05	297.26		
	6	0.19	9.81	1.22	58.50	4.20	154.39	7.50	296.89		
	7	0.25	9.75	2.04	57.71	4.10	153.61	15.93	287.68		
	8	0.08	9.92	2.25	57.67	7.90	149.77	11.70	288.07		

Table 15 (continued)

Soil	pH	Concentration Level µg				
		200		250		300
		Sup.	Soil	Sup.	Soil	Sup.*
Memphis	4	84.20	351.44	133.55	467.89	171.30
	5	107.74	292.17	144.30	397.87	164.64
	6	103.26	299.95	132.05	418.90	148.56
	7	82.80	338.73	136.18	452.55	162.15
	8	87.14	342.24	113.33	478.91	130.47
Hartsells	4	85.60	355.58	149.60	455.98	172.86
	5	91.20	334.41	111.90	472.51	148.35
	6	70.52	381.12	89.10	542.02	117.54
	7	63.80	399.02	112.60	536.60	135.51
	8	66.04	387.29	88.48	548.81	120.75
Iberia	4	31.60	451.16	68.25	632.91	77.34
	5	37.80	430.29	57.18	622.47	83.10
	6	28.76	444.01	37.68	656.33	44.88
	7	28.80	449.14	42.13	657.01	54.54
	8	23.76	453.20	29.93	673.27	37.08
Halewood A	4	52.00	420.54	82.58	587.96	108.54
	5	56.20	414.48	96.78	567.70	117.00
	6	36.20	436.95	78.25	608.70	90.12
	7	24.20	462.09	54.71	657.38	59.97
	8	29.72	453.26	36.15	667.11	46.68

Table 15 (continued)

Soil	pH	Concentration Level µg					
		200		250		300	
		Sup.	Soil	Sup.	Soil	Sup.*	Soil
Halewood B	4	12.21	487.51	27.75	709.76	21.75	988.01
	5	12.60	484.66	27.00	707.66	22.14	985.52
	6	17.80	479.09	29.75	699.34	26.28	973.06
	7	15.24	472.44	22.98	699.46	39.06	960.44
	8	15.60	472.47	35.50	689.97	34.86	955.11

* Supernatant

Table 16. Sorption of DSMA-⁷⁴As as a Function of pH.
Values are Expressed in $\mu\text{g/g}$ of Soil and are
Averaged Across Soils

DSMA Conc. Level	pH				
	4	5	6	7	8
1	9.51 ^a	9.13 ^d	9.23 ^{c*}	9.22 ^c	9.44 ^b
2	55.66 ^e	54.62 ^f	54.29 ^f	54.62 ^f	55.78 ^e
3	143.24 ^g	138.54 ^h	139.77 ^h	142.67 ^g	143.09 ^g
4	266.49 ⁱ	253.11 ^k	261.84 ⁱ	267.35 ⁱ	268.16 ⁱ
5	411.47 ^m	392.03 ⁿ	410.53 ^m	422.36 ^l	424.03 ^l
6	571.60 ^q	553.01 ^r	486.80 ^s	598.78 ^p	613.14 ^o
7	761.78 ^v	745.22 ^w	801.88 ^u	808.79 ^u	839.34 ^t

* Means within a row followed by the same letter are not significantly different at the P.01 level.

Table 17. Sorption of DSMA-⁷⁴As by Soils. Values are
Expressed in $\mu\text{g/g}$ of Soil and are Averaged
Across pH's

DSMA Conc. Level	Soil				
	Hartsells	Memphis	Iberia	Halewood A	Halewood B
1	9.31 ^b	8.17 ^c	9.44 ^b	9.75 ^a	9.77 ^{a*}
2	54.20 ^f	49.03 ^g	57.47 ^e	56.33 ^{ed}	58.52 ^d
3	135.78 ^k	119.61 ^l	150.14 ⁱ	147.23 ^j	154.54 ^h
4	246.87 ^o	218.30 ^f	280.11 ⁿ	278.01 ⁿ	293.65 ^m
5	369.41 ^s	323.32 ^t	449.97 ^r	438.73 ^r	478.99 ^q
6	512.71 ^x	441.37 ^v	652.76 ^v	616.69 ^w	699.79 ^u
7	673.96 ^o	585.36 ^e	893.36 ^b	831.53 ^c	972.80 ^a

* Means within a row followed by the same letter are not significantly different at the P.01 level.

DSMA-⁷⁴As appears to rise with clay content of the soil. The interesting observation was that at pH 7 (Figure 9) Halewood A sorbed greater quantities of DSMA-⁷⁴As than Iberia up to the 200 ppm level and at the lower concentrations sorbed almost the same quantities as Halewood B soil. The trend for sorption by Iberia, Halewood A, and Halewood B to approach each other was apparent at pH 8 (Figure 10).

The effect of pH on sorption of DSMA-⁷⁴As at two levels of concentration are shown in Figure 11. This figure illustrates the results described for the isotherms and parallels the results of Table 16 that sorption of DSMA-⁷⁴As at low concentrations showed no trend with respect to pH. However, at the higher concentrations sorption of DSMA-⁷⁴As followed the order: pH 5 < 4 < 6 < 7 < 8. The total DSMA-⁷⁴As added versus the amount sorbed by soil at each pH averaged across soils are shown in Figure 12. This figure also shows that sorption of DSMA-⁷⁴As at lower concentrations did not show an apparent pattern with respect to pH, but again at the higher concentrations (levels 6 and 7) sorption follows the order: pH 5 < 4 < 6 < 7 < 8. In comparison, Figure 13, in which the total amount of DSMA-⁷⁴As added versus the amount sorbed by the soils follow the order: Memphis < Hartsells < Halewood A < Iberia < Halewood B. This figure illustrates that soil texture had a greater effect on DSMA-⁷⁴As sorption than does soil pH.

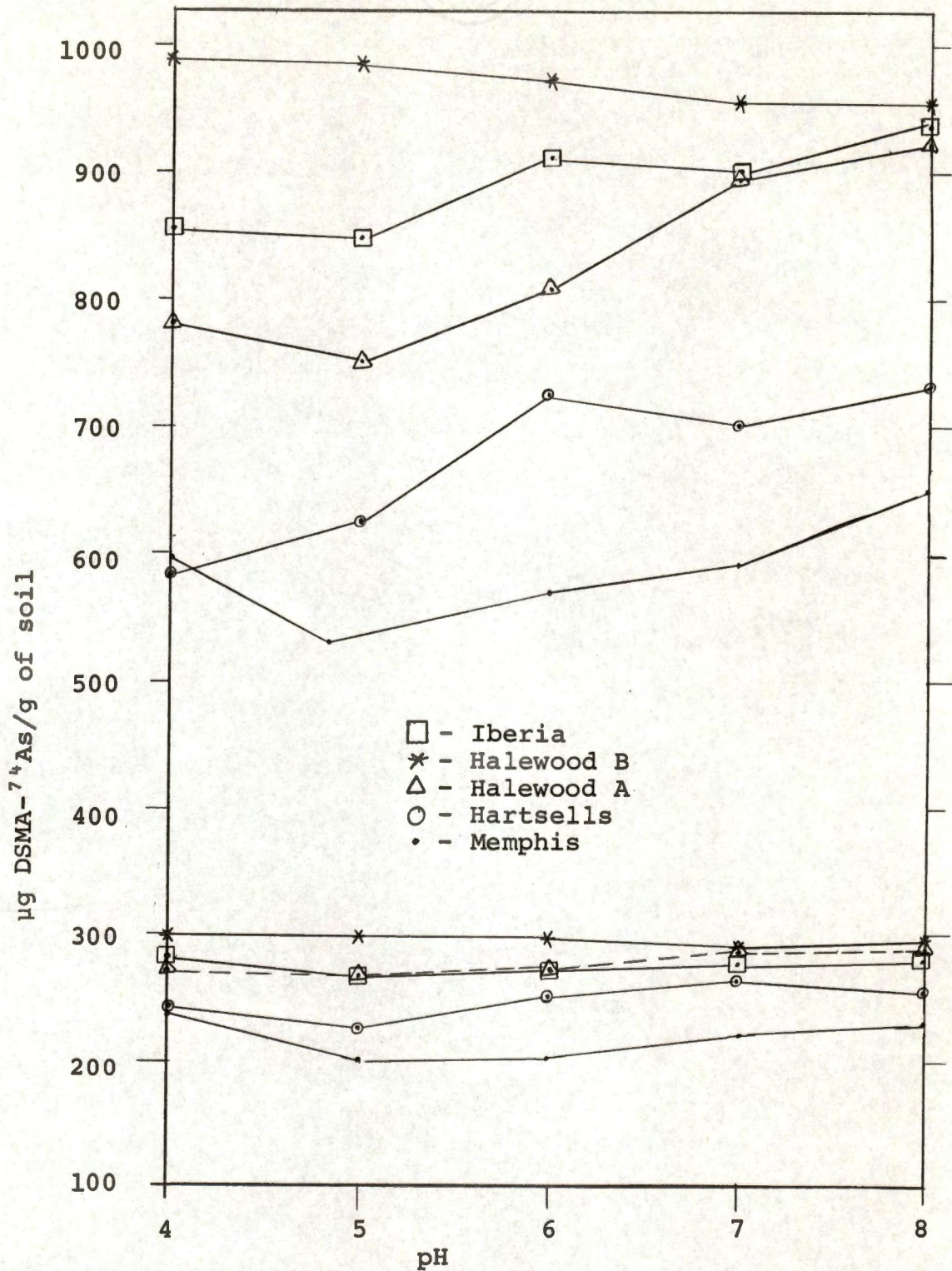


Figure 11. Sorption of DSMA-⁷⁴As at Two Levels of Concentration by Soils at Each pH.

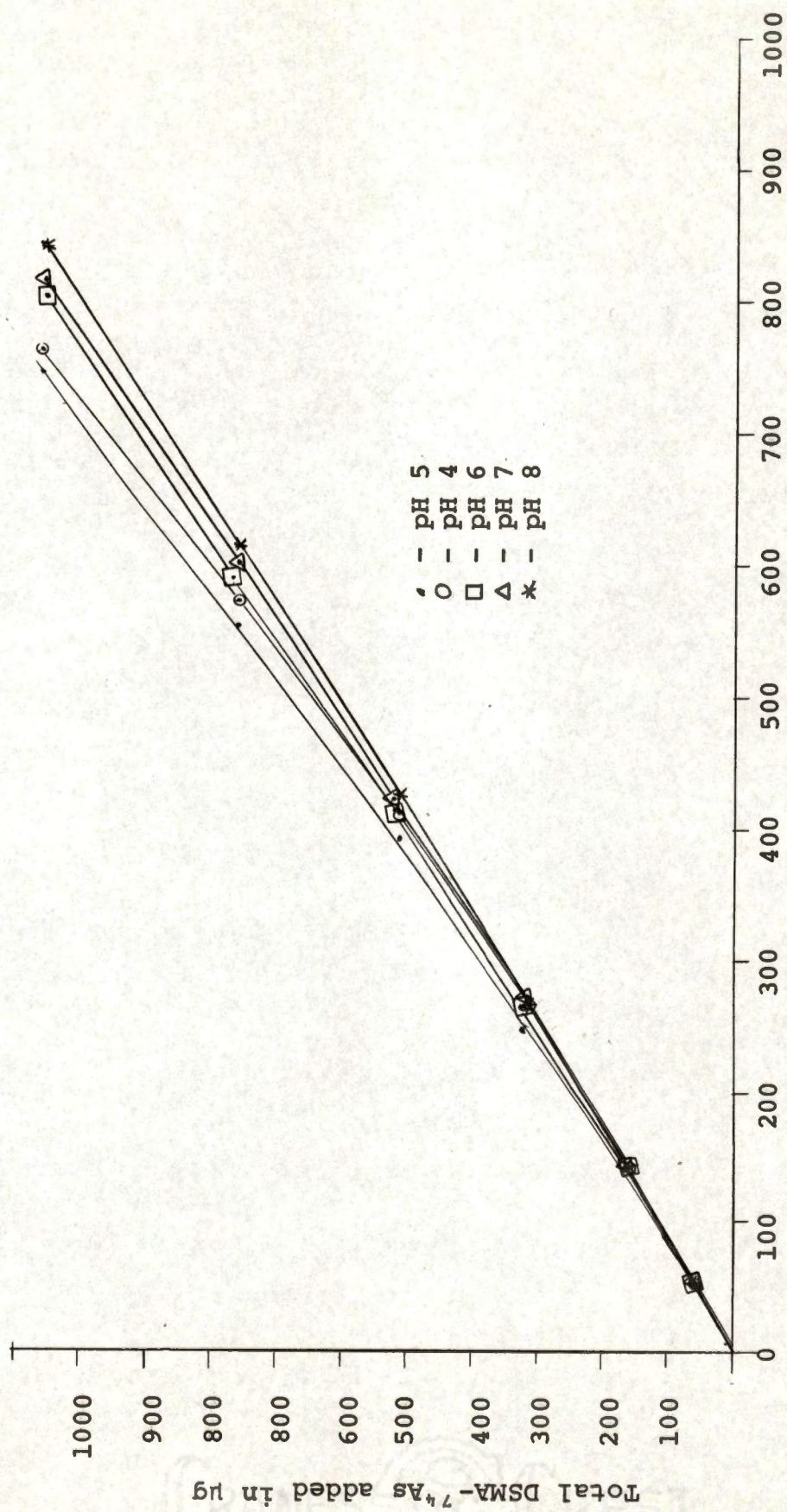


Figure 12. DSMA-74As Sorption as a Function of pH.

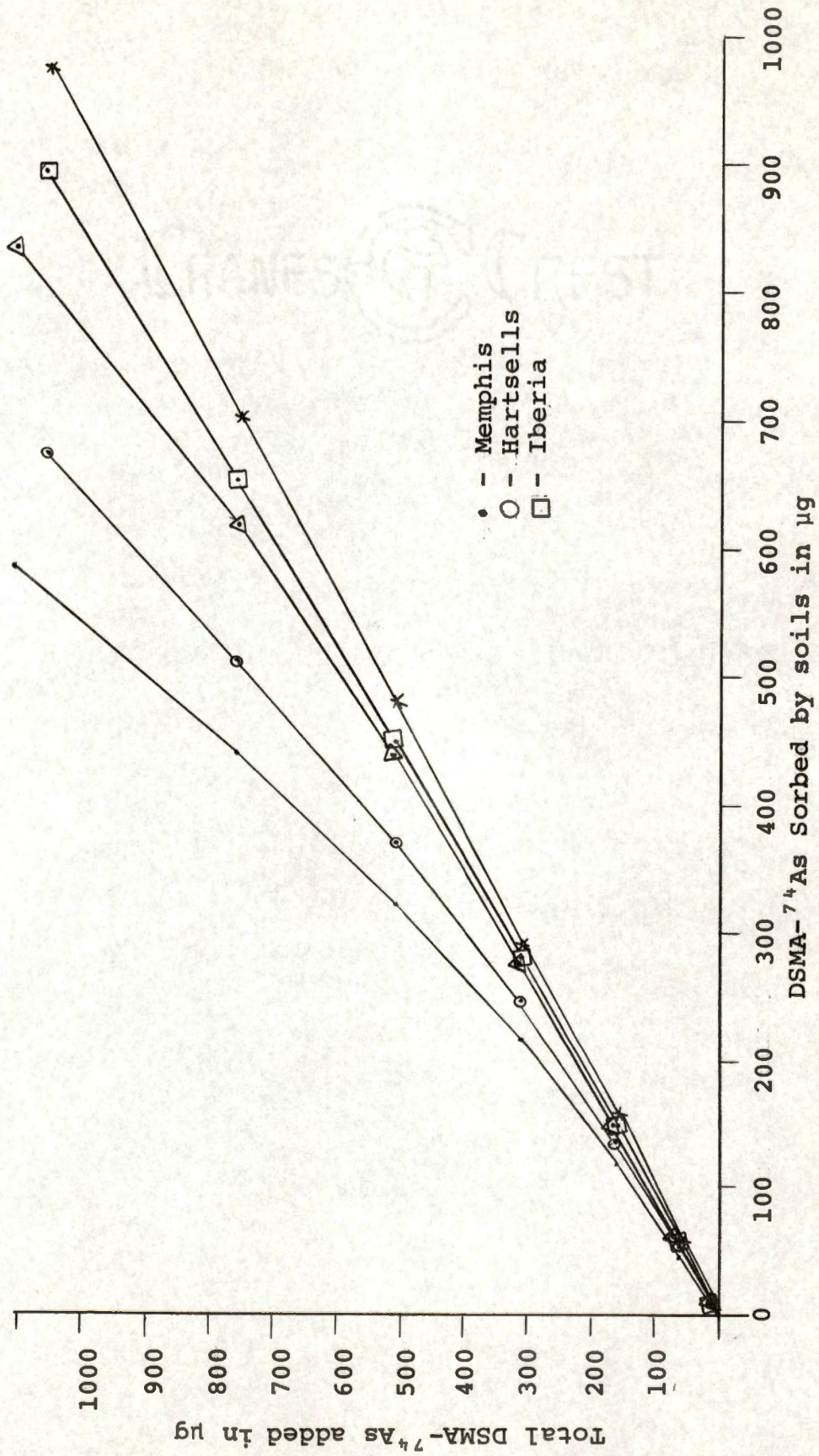


Figure 13. DSMA-⁷⁴As Sorption by Soils.

The greater sorption capacity for DSMA- ^{74}As of soils at higher pH may be explained by the relative availabilities of the sorbing components. Calcium was a readily available sorbing component at the higher pH's because of an excess of Ca^{++} ions. The soils were treated with 0.01M $\text{Ca}(\text{OH})_2$ to raise the pH. Thus a disproportional number of Ca^{++} ions would be in solution and available to form rather insoluble calcium methanearsonate compounds.

The sorption isotherm curves in Figures 6 through 10 do not level off as one would expect on saturation of exchange sites. On the contrary, the curves show a sharp increase in sorption at the higher concentrations of DSMA- ^{74}As . It was observed in the laboratory that as the concentrations of DSMA- ^{74}As increased the soils became more dispersed. Disodium methanearsonate has two atoms of sodium per molecule. This molecule disassociates in solution producing free sodium ions in the system. The higher concentration could cause dispersion and thus expose more colloidal surface area for sorption of DSMA- ^{74}As .

Leaching of 10 ppm Surface Applied DSMA- ^{74}As

The same statistical design and analysis was applied to data in this section that was used in the sorption study. Data for this segment of the study are presented in Table 18. At this relatively low concentration the band of DSMA- ^{74}As

Table 18. The Effect of pH on Leaching of DSMA-⁷⁴As
(10 ppm). Values are Expressed in $\mu\text{g/ml}$ of
Leachate and are an Average of
Three Replications

Fraction	Soil	pH				
		4	5	6	7	8
Hartsells						
1		-	-	-	-	-
2		-	-	-	-	-
3		-	-	-	-	-
4		0.013	0.100	0.035	-	-
5		0.100	0.007	0.333	0.022	-
6		0.013	0.021	0.592	0.035	0.074
7		0.022	0.013	0.531	0.072	0.548
8		0.016	0.015	0.520	0.070	0.800
9		0.015	0.017	0.407	0.108	0.652
10		0.016	0.032	0.418	0.113	0.475
11		0.010	0.009	0.302	0.089	0.301
12		0.016	0.027	0.235	0.090	0.187
13		0.017	0.005	0.145	0.086	0.148
14		0.006	0.019	0.037	0.030	0.131
15		0.013	0.300	0.010	0.005	0.098
Memphis						
1		-	-	-	-	-
2		-	-	-	-	-
3		-	-	-	-	-
4		-	-	-	-	-
5		0.016	-	-	-	-
6		0.004	0.034	-	-	-
7		0.053	0.080	0.103	0.019	-
8		0.044	0.108	0.544	0.006	0.078
9		0.027	0.050	0.821	0.018	0.283
10		0.047	0.117	0.739	0.001	0.433
11		0.029	0.057	0.615	0.027	0.259
12		0.018	0.098	0.542	0.043	0.200
13		0.036	0.047	0.367	0.033	0.198
14		0.018	0.042	0.219	0.039	0.158
15		0.032	0.067	0.181	0.046	0.148
16		0.032	0.045	0.147	0.035	0.140
17		0.024	0.050	0.227	0.025	0.120
18		0.026	0.032	0.098	0.023	0.103
19		0.017	0.076	0.081	0.033	0.104
20		0.016	0.025	0.080	0.025	0.110

Table 18 (continued)

Fraction	Soil	pH				
		4	5	6	7	8
	Iberia					
1		-	-	-	-	-
2		-	-	-	-	-
3		-	-	-	-	-
4		-	-	-	-	-
5		-	-	-	-	-
6		-	-	-	-	-
7		-	-	-	-	-
8		-	-	-	-	-
9		-	-	-	-	-
10		-	-	-	-	-
11		-	-	0.005	-	-
12		-	0.001	0.016	-	-
13		-	-	0.020	-	-
14		-	0.005	-	-	-
15		-	0.006	-	-	-
16		-	0.004	0.004	-	-
17		-	0.011	0.009	-	-
18		-	0.006	0.013	-	-
19		-	0.005	-	-	-
20		-	-	-	-	-
21		-	0.001	0.008	-	-
22		-	0.003	0.057	-	-
23		-	-	0.007	-	-
24		-	-	-	-	-
25		-	-	-	-	-
26		-	0.002	-	-	-
27		-	-	0.007	-	-
28		-	-	-	-	-
29		-	-	-	-	-
30		-	-	-	-	-

Table 18 (continued)

Fraction	Soil	pH				
		4	5	6	7	8
Halewood A						
1		-	-	-	-	-
2		-	-	-	-	-
3		-	-	-	-	-
4		-	-	-	-	-
5		-	-	-	-	-
6		0.004	-	-	-	-
7		0.006	0.080	-	-	-
8		0.025	0.080	-	-	-
9		0.006	0.080	-	-	-
10		0.014	0.066	-	-	-
11		0.004	0.070	-	-	-
12		0.020	0.010	-	-	-
13		0.027	0.006	-	-	-
14		-	0.002	-	-	-
15		0.009	0.007	-	-	-
16		0.002	0.008	-	-	-
17		-	-	-	-	-
18		-	-	-	-	-
19		-	-	-	-	-
20		-	-	-	-	-

Halewood B - No DSMA-⁷⁴As was leached for any of the pH's.

does not overpower the soil particles as they did in the 100 ppm experiments. Thus the quantity leached would be the DSMA displaced from the soil particle by the downward movement of the water. The DSMA- ^{74}As molecule would have undergone a sorption, desorption mechanism similar to that of a chromatographic column. This particular series of experiments was designed to determine the effect of pH and the leachability of DSMA- ^{74}As under acid, neutral, and alkaline conditions.

Analysis of variance showed that at the 1 percent level of probability there was a difference in the amount of DSMA- ^{74}As leached from the columns among soils, pH's and the interaction of soils and pH. The amount of DSMA- ^{74}As leached from the columns as a function of soil properties (Table 19) was in the order: Memphis>Hartsells>Iberia~Halewood A~Halewood B at the P.01 level. This was an inverse relationship to the sorption capacity of the soils. The quantity of DSMA- ^{74}As leached from the column as a function of pH (Table 20) was in the order: 6>8>7~5~4.

Table 19. Amount of DSMA-⁷⁴As Leached from Soil Columns Containing 10 ppm of Surface Applied DSMA-⁷⁴As as a Function of Soil Properties. Values are Expressed in $\mu\text{g/g}$ of Soil and are Averaged Over pH's and Replications

Soil	Halewood B	Iberia	Halewood A	Hartsells	Memphis
Mean	0.00 ^c	0.04 ^c	0.05 ^{c*}	1.69 ^a	1.63 ^b

* Means followed by the same letter are not significantly different at the P.01 level.

Table 20. Amount of DSMA-⁷⁴As Leached from Soil Columns Containing 10 ppm of Surface Applied DSMA-⁷⁴As as a Function of Soil pH. Values are Expressed in $\mu\text{g/g}$ of Soil and are Averaged Across Soils and Replications

pH	4	5	6	7	8
Mean	0.15 ^c	0.24 ^c	1.69 ^a	0.23 ^{c*}	1.20 ^b

* Means followed by the same letter are not significantly different at the P.01 level.

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The results show that DSMA- ^{74}As was leached out the columns to the greatest extent at pH 6, pH 8 and to a lesser degree at pH's 4, 5, and 7. At this lower concentration (10 ppm) only Memphis and Hartsells released DSMA- ^{74}As to any great extent. The inconsistency of the amounts of DSMA- ^{74}As leached from the columns at pH 7 as compared to the quantities leached at pH 6 and 8 prevents any general conclusions to be drawn about the effect of pH on the leaching of DSMA- ^{74}As at low concentrations.

The distribution of DSMA- ^{74}As in the column segments (for this portion of the study) are presented in Table 21. The retention of DSMA- ^{74}As by the column segments was in accord with the leachate results, that is, Hartsells and Memphis columns retained the least amounts of methanearsonate while very little was leached from other soils.

Table 21. Distribution of DSMA-⁷⁴As in Columns Treated with 10 ppm of DSMA-⁷⁴As. Values are Expressed in μg Per Segment of Column and are an Average of Three Replications

Depth (cm)	Soil	pH				
		4	5	6	7	8
	Hartsells					
0-1		8.506	6.720	2.336	4.465	1.884
1-2		0.828	2.059	1.574	2.941	1.221
2-3		0.331	0.717	1.392	1.259	0.869
3-4		0.166	0.299	1.134	0.550	0.558
	Memphis					
0-1		4.775	3.724	1.677	4.620	2.247
1-2		2.530	2.123	0.689	2.879	1.486
2-3		1.221	1.494	0.680	1.156	1.053
3-4		0.597	0.999	0.810	0.612	1.388
4-5		0.425	0.410	0.738	0.341	0.816
5-6		-	0.285	0.743	-	0.675
	Halewood A					
0-1		6.038	4.586	5.425	5.420	5.258
1-2		1.513	3.353	3.598	3.152	3.216
2-3		0.303	1.200	0.610	0.464	0.924
3-4		0.087	0.428	0.047	0.044	0.007
4-5		0.064	0.146	-	-	-
5-6		0.051	0.089	-	-	-
	Halewood B					
0-1		10.000	9.048	9.774	9.645	9.906
1-2		-	0.743	0.044	0.164	0.094
2-3		-	0.244	0.016	0.051	-
3-4		-	0.071	0.023	0.034	-
4-5		-	0.060	-	-	-
5-6		-	0.007	-	-	-
	Iberia					
0-1		4.631	6.207	4.111	5.175	4.680
1-2		3.289	2.551	1.613	2.499	2.483
2-3		1.034	0.384	1.180	1.249	1.157
3-4		0.286	1.102	0.941	0.947	0.817
4-5		0.130	0.064	0.624	0.354	0.520
5-6		0.129	0.017	0.363	0.051	0.237
6-7		0.127	-	0.188	0.016	0.097
7-8		0.127	-	0.137	0.002	-
8-9		0.129	-	0.054	-	-
9-10		0.126	-	0.024	-	-

III. GASEOUS ^{74}As EVOLUTION

The loss of ^{74}As from a soil that was maintained under varying conditions of organic matter and moisture as percentage of total ^{74}As applied is shown in Table 22. The mean for each treatment was compared to the control samples mean in which no arsine gas could escape by employment of a two-tailed t-test using a pooled estimate of variance. Loss of ^{74}As was observed from all treatments except the steam-sterilized one.

Table 22. Gaseous Loss of ^{74}As from Etowah Silt Loam

	Treatment				
	1	2	3	4	5
Control					
-	0.00	10.97 ^a	7.89 ^b	8.06 ^b	2.15

*Significance levels of t-test a (0.01, and b (0.05).

The differences in ^{74}As concentration between treatments and control were at least significant at the P.05 level except for treatments 1 and 5. The treatment with greatest loss of arsenic (10.97 percent) was the soil that contained 10 percent organic matter and was maintained under wet (reduced) conditions. The treatment with the second loss of ^{74}As (8.06 percent) was the soil that received no organic matter and was kept under wet conditions. The soil

containing 10 percent organic matter and maintained under moist conditions lost 7.89 percent of the added ^{74}As while the soil having no organic matter and under moist conditions lost only 2.15 percent of the added ^{74}As . The autoclaved (sterilized) soils evolved essentially no ^{74}As . The treatments in which organic matter had been added showed a marked increase in ^{74}As evolution over the corresponding treatments which had received no organic matter. These observations agree with Dickens and Hiltbold (20) and Kearney et al. (34, 36) that an exogeneous carbon source will stimulate microbial decomposition of organic arsenicals.

Moisture conditions also affected evolution of ^{74}As . The greatest loss of ^{74}As in this experiment occurred in the soils maintained under reduced conditions. Reed and Sturgis (47) suspected that arsenic was lost from flooded rice soils as arsine gas, but a later study (24) found that only 1 ppm of the total arsenic present in the soil was lost as arsine. Thom and Raper (57) reported that moldy walls of dwellings which were coated with arsenic-containing plaster evolved gaseous arsine in sufficient quantities (in some instances) to kill the inhabitants. However, Deuel and Swoboda (19) could not detect arsine evolution from soils that were maintained under reduced conditions.

The quantity of arsenic lost was determined by the difference between soil counts of controls and the treatments,

but some problems were encountered with the trapping solution. The permanganate in the trapping tubes oxidized even though the tubes were shielded from light. The solution in the tubes was revitalized with additional permanganate, but the activity in the tubes was at too low a level to be counted. The form of arsine that evolved was not determined and thus it is not known whether the arsine was methylated $[(CH_3)_2AsH]$ or $[CH_3AsH_2]$ or existed as AsH_3 .

IV. As EXTRACTION

The experimental design of this section was a randomized complete block with a split-split plot arrangement of treatments. Soils were designated as main treatments, pH as split-treatments, and arsenic fractionation as the split-split treatments. Analysis of variance and F test showed differences in the amount of arsenic fractionated among extracting solutions, the interaction of soils and extracting solutions, pH and extracting solutions, and extracting solutions and pH and soils. Duncan's New Multiple-Range Test was used to compare means whenever applicable.

The fractionating procedure used in this study was originally used for soil phosphorus and then modified for soil arsenic. In this experiment no distinction was made between the inorganic ^{74}As and the organic bound ^{74}As extracted during the fractionation process. It was assumed

that the soil components that were responsible for fixing inorganic arsenicals would also fix the organic arsenicals in a similar manner. A second assumption was that the extracting solutions would also fractionate the soil bound organic arsenical in a similar manner to that of inorganic arsenic.

There was a difference in the amount of ^{74}As extracted by the fractionating solutions as shown in Table 23.

Table 23. Chemical Distribution of DSMA- ^{74}As Applied in the Isotherm Experiment. Values are Expressed in Percent of Total Sorbed DSMA- ^{74}As

H ₂ O	Al-As	Fe-As	Ca-As	Soil
5.85 ^e	27.48 ^b	43.92 ^a	16.51 ^c	7.32 ^{d*}

* Means followed by the same letter are not significantly different at the P.01 level.

The Fe-As fraction accounted for almost half of the soil bound arsenic while Al-As, the second most predominant form, accounted for almost a fourth of the bound arsenic. Approximately a sixth of the sorbed arsenic was in the form of Ca-As with 6 percent in the H₂O-soluble form and 7 percent was not extracted. The experimental results agree with Woolson et al. (68) that Fe-As was the predominant form of residual arsenic in most soils and that Al and Ca-As forms

were important factors in the fixation of arsenic. Jacobs et al. (30), and Johnson and Hiltbold (29) also found that Fe and Al-As were the predominant forms of fixed arsenic in the soil.

The chemical distribution of DSMA- ^{74}As as a function of soil properties and extracting solutions are presented in Table 24.

Table 24. Chemical Distribution of DSMA- ^{74}As Applied in the Isotherm Experiment as a Function of Soil Properties and Extracting Solutions. Values are Expressed in Percent of Total Sorbed DSMA- ^{74}As

As-Fraction	Soils				
	Memphis	Hartsells	Iberia	Halewood A	Halewood B
H ₂ O	8.42 ^b	10.47 ^a	3.48 ^c	3.49	3.41 ^{c*}
Al	29.44 ^g	41.39 ^d	11.21 ⁱ	37.52	17.86 ^h
Fe	44.32 ^j	36.05 ^l	44.39 ^j	41.05 ^k	53.77 ⁱ
Ca	14.15 ⁿ	9.50 ^p	32.69 ^m	11.76 ^r	14.42 ⁿ
Soil	4.35 ^t	2.80 ^s	8.26 ^r	8.30 ^r	12.91 ^q

* Means within a row followed by the same letter are not significantly different at the P.01 level.

The water-soluble fraction (1N NH₄Cl extractable) was highest in the soils (Memphis and Hartsells) which had sorbed the least amount of DSMA- ^{74}As (lowest clay content also) and lowest in the soils which had a high clay content. This fraction represents that quantity available for plant uptake

and is considered to be very loosely held in the soil. The Al-As fraction (0.5N NH_4F extractable) was the predominant form in Hartsells and was 37.5 percent of the total ^{74}As sorbed by the Halewood A soil. Both these soils were originally acid and thus would contain quite a lot of reactive aluminum. Halewood B, which was also originally acid, contained a low amount of Al-As, but its high reactive Fe content was responsible for the exception. The Fe-fraction (0.1N NaOH extractable) was predominant in 4 out of the 5 soil types with Halewood B, as expected, having the highest value. The Ca-fraction (0.5N H_2SO_4 extractable) was a major factor in arsenic sorption in only one soil, Iberia. Iberia had a high CEC and was originally almost a neutral soil. The bound ^{74}As that was not extracted was retained to the greatest extent by the soils with the higher clay content. This quantity also was roughly inversely proportional to the water-soluble forms, that is, soils with high quantities of the water-soluble form have low amounts of non-extractable As and conversely.

The chemical distribution of DSMA- ^{74}As as a function of pH and extracting solutions are presented in Table 25.

Table 25. Chemical Distribution of DSMA-⁷⁴As Applied in the Isotherm Experiment as a Function of pH and Extracting Solutions. Values are Expressed in Percent of Total Sorbed DSMA-⁷⁴As

As-Fraction	pH		
	4	6	8
H ₂ O	6.37 ^a	5.54 ^a	5.64 ^a
Al	31.24 ^d	24.85 ^c	26.36 ^b
Fe	35.35 ^g	47.47 ^f	48.93 ^e
Ca	20.08 ⁱ	16.27 ⁱ	13.17 ^h
Soil	8.19 ^l	6.62 ^{lk}	7.16 ^k

* Means followed by the same letter are not significantly different at the P.01 level.

There were differences in the amount of H₂O-soluble arsenic among the pH's at the P.01 level. The Al-and Ca-As values were greatest at the low pH while for Fe-As the reverse was true. The Fe-As fraction was the greatest at higher pH values while the arsenic remaining in the soil was evenly distributed over the pH values.

The chemical distribution of DSMA-⁷⁴As as a function of soils-pH-extracting solutions are presented in Table 26. There was no change in the amount of water-soluble As with respect to a change in pH of the soils. The amount of water-soluble arsenic appears to be dependent upon soil texture, while the Al-As fraction generally had its greatest value at pH 4, especially the soils high in reactive aluminum

Table 26. Chemical Distribution of the Sorbed
DSMA-⁷⁴As Added to the Soils in the Isotherm
Experiment. Values are in Percent of
Total Sorbed DSMA-⁷⁴As

As- Fraction	Soil	pH		
		4	6	8
	Memphis			
H ₂ O		8.00	8.83	8.44
Al		34.00	27.95	26.36
Fe		42.83	41.29	48.83
Ca		12.02	17.83	12.62
Soil		5.21	4.20	3.75
	Hartsells			
H ₂ O		12.88	10.20	8.32
Al		42.69	39.83	41.63
Fe		35.26	36.07	36.83
Ca		5.53	11.89	11.07
Soil		4.22	2.00	2.17
	Iberia			
H ₂ O		2.36	3.25	4.83
Al		7.45	10.66	15.53
Fe		22.31	55.49	55.37
Ca		60.91	21.04	16.12
Soil		7.09	9.55	8.13
	Halewood A			
H ₂ O		4.30	2.45	3.72
Al		49.71	32.63	30.21
Fe		32.01	46.91	44.22
Ca		6.74	12.26	16.29
Soil		7.30	5.74	11.87
	Halewood B			
H ₂ O		4.34	2.96	2.92
Al		22.35	13.20	18.03
Fe		44.33	57.61	59.38
Ca		15.18	18.33	9.75
Soil		17.14	11.68	9.90

(Hartsells, Halewood A, and Halewood B). A striking increase in the Fe-As fraction occurs in the Halewood A and B soil from pH 4-6. The Fe-As fraction was the predominant form in all soils except Hartsells and usually the highest values for the Fe-As fraction were at pH 8 and lowest at pH 4.

The Ca-As fraction had its highest values at pH 6 and pH 8. The one notable exception to this was the value for Iberia which shows almost 61 percent of its total sorbed As to be in the Ca-As form. A possible explanation for this observation was that in this case almost all calcium present in the soil was in solution at this pH and therefore was the predominant form. The highest values for ^{74}As that was not extracted were in the soils with the higher clay content, and apparently pH does not influence this fraction.

Fractionation of Sorbed DSMA- ^{74}As
From the Gaseous ^{74}As Experiment

Differences in the quantities of arsenic in the different fractions were related to moisture and organic matter content by comparison of the As-fraction means. The chemical distribution of DSMA- ^{74}As of the sorbed DSMA applied in the gaseous ^{74}As experiment is presented in Table 27.

Table 27. Chemical Distribution of the Sorbed DSMA- ^{74}As Applied in the Gaseous ^{74}As Experiment. Values are Expressed in Percent of the Total Sorbed DSMA- ^{74}As

As-Fraction				
H ₂ O	Al	Fe	Ca	Soil
1.77	22.33	57.52	7.28	9.48

The Fe-As fraction was the predominant form with the Al-As fraction the second most predominant. Almost 9.5 percent of the sorbed DSMA- ^{74}As was not extracted by any of the solutions while the Ca-As fraction contained 7.3 percent of the total sorbed DSMA- ^{74}As , and the water-soluble fraction was very low at 1.77 percent.

The effects of organic matter on DSMA- ^{74}As fixation by the different components are presented in Table 28. A decrease in the Fe-As fraction with a corresponding increase in the Ca-As and non-extractable forms were the most notable observations. Apparently organic matter does contribute to the fixation of DSMA- ^{74}As and perhaps provides an added source of calcium for fixation by the calcium component.

Table 28. Chemical Distribution of Sorbed DSMA-⁷⁴As Applied in the Gaseous ⁷⁴As Experiment as a Function of Organic Matter. Values are Percent of the Total Sorbed DSMA-⁷⁴As

As-Fraction	Sterile	no O.M.	+ O.M.	Control
H ₂ O	0.83	0.37	2.05	6.42
Al	25.48	24.41	19.76	20.17
Fe	62.37	62.15	50.49	57.44
Ca	4.54	4.29	11.44	7.62
Soil	9.98	7.85	14.60	5.01

The effect of moisture on the fractionated arsenic forms are shown in Table 29. The Al-As fraction increased while under reduced conditions.

Table 29. Chemical Distribution of Sorbed DSMA-⁷⁴As Applied in the Gaseous ⁷⁴As Experiment as a Function of Moisture. Values are Percent of Total Sorbed DSMA-⁷⁴As

As-Fraction	Moist	Wet	Control
H ₂ O	1.16	0.35	6.42
Al	20.42	26.27	20.18
Fe	58.94	55.41	57.44
Ca	7.34	6.99	7.62
Soil	11.08	9.31	5.02

The amount remaining in the soil was greater in the moist and wet soils than in the dry control samples. However, the control samples did not have any added organic matter which was a factor in fixing DSMA- ^{74}As as shown in Table 28.

The chemical distribution means of the applied DSMA- ^{74}As are presented in Table 30. As in the previous observations the Al-As fraction increased under reduced conditions, Ca-As and non-extractable forms increased in the treatments in which organic matter had been added.

Table 30. Chemical Distribution of Sorbed DSMA- ^{74}As Applied in the Gaseous ^{74}As Experiment. Values are Percent of Total Sorbed DSMA- ^{74}As

As-Fraction	Treatments					
	1	2	3	4	5	Control
H ₂ O	0.83	-1.88	5.97	2.58	-3.31	6.42
Al	25.48	24.65	14.85	27.89	20.93	30.17
Fe	62.38	55.00	45.59	55.81	68.48	57.44
Ca	4.55	11.15	11.74	2.84	5.74	7.62
Soil	6.97	11.07	18.12	7.55	8.15	5.01

CHAPTER IV

SUMMARY AND CONCLUSIONS

The sorption studies on DSMA- ^{74}As showed that sorption of DSMA- ^{74}As by Memphis and Hartsells were time dependent and that sorption by Iberia was not. It was concluded that in soils with low clay content the exposure of more colloidal surface and subsequent sorption of DSMA- ^{74}As were a function of time.

At the 100 ppm concentration level the soils sorbed DSMA- ^{74}As in the order: Halewood A < Memphis < Hartsells < Iberia < Halewood B. However, it was noted that at longer equilibration times Halewood A sorbed greater quantities than did Memphis or Hartsells. The sorption of DSMA- ^{74}As was related to the soil properties of clay content (percent and types), organic matter and CEC. The conclusions are that soils with high clay content and with its major component being kaolinite would deactivate the greatest quantities of DSMA- ^{74}As . Organic matter effect on sorption of DSMA- ^{74}As could only be related indirectly, but it appears to have a positive effect on sorption. Cation exchange capacity apparently had no direct effect on the sorption of DSMA- ^{74}As .

The quantities of surface applied DSMA- ^{74}As (100 ppm) leached out of columns comprised of the soils used in this study were in the order: Memphis>Hartsells>Iberia~Halewood A~Halewood B. The leaching of DSMA- ^{74}As from soils was inversely proportional to the sorption capacity of the soil.

The effect of phosphorus and acid treatments on the ability of Hartsells, Memphis, and Iberia soils to sorb DSMA- ^{74}As was investigated. It was found that addition of phosphorus at the 1000 ppm and 200 ppm level would reduce the arsenic-retaining capacity of the soils greatly. The acid treatments generally increased the sorption capacity of the soil. Two factors contributed to this observation:

1) as the pH decreased more arsenic sorbing components, Al and Fe, became soluble and; 2) as the positive charge of the system increased the doubly negative charged DSMA- ^{74}As ion would be more readily sorbed onto the clay surface.

At the 100 ppm concentration a greater amount of DSMA- ^{74}As leached from the soils than would be expected considering the results from the sorption section. This leaching illustrates the weak sorption forces that bind the DSMA- ^{74}As in the batch equilibration technique. The shaking exposes a much greater surface area for sorption than would be available if it was not dispersed in that manner.

The isotherm and pH effect section showed that the soils sorbed DSMA- ^{74}As in the order: Memphis<Hartsells<Halewood A<Iberia<Halewood B, and at very high concentrations, in the order of pH: $5<4<6<7<8$. The greater sorption capacity at higher pH's was attributed to the available Ca^{++} in the system. At the relatively low concentration of DSMA- ^{74}As (10 ppm) the leaching results were inconsistent and generally conclusions were not possible.

Gaseous arsenic evolution was found to be a function of organic matter and moisture. The soil that evolved the greatest quantity of gaseous ^{74}As contained 10 percent added organic matter and was maintained under wet conditions. Soils that contained added organic matter evolved more ^{74}As than did soils that in which none were added. Soils maintained under wet conditions evolved more gaseous ^{74}As than soils under only moist conditions.

Arsenic fractionation of the DSMA- ^{74}As sorbed in the isotherm experiment showed that the Fe-As fraction was the most predominant form while Al-As was second. There were higher quantities of Al-As at pH 4 than at pH 6 or 8 and higher quantities of Ca-As at pH 6 and 8 than at pH 4.

Arsenic fractionation of the sorbed DSMA- ^{74}As in the gaseous ^{74}As experiment showed that in the soils containing organic matter an increase in the Ca-As and the amount of DSMA- ^{74}As retained in the soil was observed. Soils that

were maintained under wet conditions had an increase in the Al-As fraction. However, the predominant form in all cases was the Fe-As fraction.

The rates of DSMA-⁷⁴As used in this study were much greater (approximately 100 times for 100 ppm and 10 times for 10 ppm) than would be used in most weed control programs that would utilize this chemical. This increase in rates was necessary to achieve the goals of this study. The leaching results in this study are an exaggeration of the leaching that would occur in the field. This study shows that DSMA would leach in appreciable amounts only under the following conditions: 1) in extremely high concentrations; 2) large amounts of moisture; 3) from soils with low clay content.



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