PREDICTION OF WATER SOLUBLE ARSENIC
IN SEWAGE-SOIL SYSTEMS

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University of Missouri-Columbia

Project Number - A-068-Mo

Agreement Number - USDI-OWRR 14-31-0001-4025 and 5025

July 1, 1973 - June 30, 1975

COMPLETION REPORT

June 1, 1975

The work upon which the publication is based was supported in part by funds provided by the United States Department of Interior, Office of Water Resources Research, as authorized under the Water Resources Research Act of 1964.

ARSENIC CHEMISTRY IN MISSOURI SOILS

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ABSTRACT

Missouri orchard soils were analyzed for total As, Pb, and Cu content. All Cu concentrations were normal, while Pb and As concentrations varied from natural levels to over 2000 ppm for Pb and 350 ppm for As. The Bray tests for available phosphorus were high by 0-8 to 16.8% due to arsenic interference on soils from arsenic contaminated fields.

Fifteen g samples of a Sharpsburg silty clay loam and a Menfro silt loam soil containing 320 and 160 μg As/g, respectively, were equilibrated for 21 days with 30 ml of distilled water or 1% dextrose. After 21 days the samples were freeze dried, divided into 2 groups, one air dry and the other at 26.7% water and exposed to the atmosphere. Eh, pH, As, Fe, Al, Mn, Ca and Pb in solution were determined periodically. After an initial Eh drop in the 1% dextrose equilibration, the As in solution increased rapidly in both soils, but was constant after 12 days.

The As in solution increased more slowly in the water equilibration, but also remained constant after 12 days. At 4 days after freeze drying the As level was near the level observed before reduction.

Both soils were equilibrated with dilute HCl and NaOH for 7 days at 25° C. Values of $pAl + 3pOH$, $pAl + pAsO_4$, $pFe + 3pOH$, $pFe + pAsO_4$, $3pMn + 2pAsO_4$, $3pCa + 2pAsO_4$, and $3pPb + 2pAsO_4$ were computed. The free energies of formation of Mn_3O_4, (-310.6), Mn_2O_3, (-210.82), and MnO_2, (-110.650 kcal/mole), were determined for each equilibration solution. These ion products were compared to those of synthesized arsenates, based on these comparisons both soils were undersaturated with respect to aluminum, ferric, and calcium arsenates, and near equilibrium concentrations of As predicted from lead and manganese arsenates. Lead arsenate applied to the soil may be slowly converted to the more stable manganese arsenate under reducing conditions and reform under highly oxidized conditions.

An experiment was designed to observe and measure biological reduction of arsenic in the soil system to volatile arsenicals. Within 4-7 days, it was possible to measure the evolution of volatile arsenicals.

Platinum electrodes were buried at depths of 7.5, 15, 30, and 60 cm in a Mexico soil that had been treated with 100 ppm As. Variable amounts of sugar, sewage sludge, nitrogen, and water were added. Eh and pH were measured weekly throughout the growing season, and periodically during the rest of the year. The amount of arsenic in Reed's canary grass was measured, and found to decrease from 20 to 2 ppm As as the growing season continued and was independent of treatment.

In order to maintain As insolubility, soil with high As concentration should be maintained as well aerated as possible. If these conditions are maintained, the As will remain fixed as arsenate, have a low solubility and mobility and remain concentrated in the upper 10 cm of the soil. Plowing a soil with As and organic matter concentrated in the surface may result in a system where arsenates could be reduced to arsenite during periods of excessive water.

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CHAPTER 1

INTRODUCTION

There are several sources of arsenic (As) in soil, including minerals, pesticides, feed additives, and industrial contamination. Normal levels of As in soil from mineral sources range from 0.5 to 14.8 ppm As. The most common and widespread As mineral is arsenopyrite (FeAsS). Two other widespread and abundant As minerals are realgar and orpiment (AsS and As_2S_3). Arsenic minerals thought to be in soil that are comparable with variscite and strengite ($AlPO_4 \cdot 2H_2O$ and $FePO_4 \cdot 2H_2O$) are manfieldsite and scorodite ($AlAsO_4 \cdot 2H_2O$ and $FeAsO_4 \cdot 2H_2O$). Arsenic has been added to the soil as pesticides for many years as arsenate of lead, copper, or calcium, and also smaller amounts as organic compounds such as methyl arsonate. The use of these arsenicals has increased the As content of the soil to as much as 800 ppm As. Many farmers use arsenical feed additives for their pigs and chickens, thus the litter of these animals has increased the As content of the soil. Industrial and other man-made products such as As contaminated detergents have added As to soil and ground waters.

With changing land use patterns soils contaminated with As may become residential areas. It has become necessary to evaluate the effect that a changed soil environment would have on the solubility and possible toxicity of As. This type of information may be obtained by examining the forms of As in the soil, the interactions of As with other elements of the soil, and As solubility predicted as a function of Eh and pH levels that exit in the soil system.

The purpose of this study was to determine the stable forms of As in the soil system, based on the stabilities of ferric, aluminum, manganese, calcium, and lead arsenates and to use this information to predict which form will be the most stable under different Eh and pH conditions. This model was applied to two different soils in various stages of anaerobic and aerobic treatment. These ion products when compared to the ion products determined on arsenate compounds prepared in the laboratory provide a means to predict what controls arsenate solubility in the soil system. Perhaps more important by delineating the chemistry of the arsenates, their solubility under different conditions can be predicted.

The pH and oxidation-reduction conditions were measured under field conditions and compared to those created in the laboratory studies. These observations were compared with previous Eh and pH ranges to indicate whether the reported measurements relate to actual soil systems one would expect to encounter in Missouri.

The overall objective was to predict the solubility and possible As toxicity which might exist if these orchard sites were converted to other uses. Some possible uses people may want includes gardens, sewage effluent disposal sites, and home sites.

CHAPTER 2

A SHORT HISTORY OF ARSENIC

Although there are today more than 160 known naturally occurring As minerals (28), man's awareness of the majority of them has only come in recent years. Arsenic trioxide (As_2O_3) is perhaps the oldest known As compound. It was the sublimation product of iron and copper ores, and man was aware of it as early as 2000 BC (12). Hippocrates recognized realgar (AsS) and orpiment (As_2S_3) two naturally occurring As minerals, and used them as salves in the treatment of ulcers (12,27). The following highlights man's growing awareness of As:

2000 BC	Arsenicum, arsenik (As_2O_3). The sublimate from copper and iron ores (12).
400 BC	Hippocrates recognized sulfides of As, and used them as salves in the treatment of ulcers (12,27).
1250 AD	Elemental As first prepared by Albertus Magnus (12).
Middleages	Arsenic trioxide used by professional poisoners (12,27).
1733	First investigation into the chemical nature of As made by Georg Brandt (27).

1775	Scheele volatized arsine as a method to separate As from most other elements (12).
1786	Fowler's solution, 1% arsenic trioxide as potassium arsenite. Still said in 1912 to be the best medicinal in the pharmacopoeia (12).
1815	Professor Gehlen of Munich died of arsine poisoning after breathing one bubble of the gas (27).
1820	Arsenic cancer myth begins in writings of J. A. Paris. Paris wrote more about As as a cure for cancer than as a cause but only the latter idea has been recited (12).
1836	Marsch-Berzelius test for As was based on Scheele's arsine evolution where the As was plated on a shiny copper surface (12).
1839	Gmelin wrote of volatile arsines produced by molds (12).
1842	Bunsen of Heidelberg discovered Cacodyl (27).
1868	First pesticide use of As Paris green, copper acetoarsenite to control Colorado potato beetle (12).
1879	Gutzeit test for As which was also based on Scheele's evolution of arsine where the As formed a yellow compound with mercuric chloride and silver nitrate (16).

1887	Hutchinson's idea was that Fowler's solution produced hyperkeratosis which lead to skin cancer (14). The idea grew by reiteration into medical tradition. Industrial exposure to arsenic trioxide with no undue cancer, negates the idea (11).
1900-3	Royal Commission on Arsenical Poisoning established the world's unofficial tolerance levels without scientific basis, but these are levels with force in courts of law (11,25).
1910	Chemotherapy began with Ehrlich's magic bullet, arsphenamine. Arsanilic acid was characterized (12).
1912	Microorganism isolated which oxidizes arsenite to arsenare (30).
1919	Blue arseno-molybdenum complex used for As analysis (29).
1936	Gaseous loss of As from the soil suggested by Reed and Sturgis (24).
1937	Arsenic spray residues in orchards discovered to make soil unproductive for other crops (15).
1938	Moxon found arsenicals can counteract selenium toxicity (12).

1939-48	Soil microorganisms isolated which reduce arsenate and arsenite to gaseous arsenicals (21,33).
1946	Organic arsenical feed additives found to control diseases in poultry and swine, to stimulate growth, and to improve feed efficiency (7,19).
1952	Silver diethyldithiol carbamate used as absorbing agent for arsine in As determination (32).
1953	Mechanism proposed for biological reduction of arsenious acid to trimenthlyarsine (2).
1955	General use of lead arsenate as a pesticide in orchards stopped.
1956	Arsenic acid emerges as a desiccant for cotton; cacodylates and methane arsonates as desiccants, defoliants, and/or herbicides (4,6,11,13).
1959	France banned organic arsenicals, antimonials and estrogens from use in poultry feeds. Other European countries followed suit.
	England legalizes an Arsenic in Foods Regulation, its first official tolerance (17).

1962	France bars imports of poultry from countries where uses of arsenicals, antimonials, and estrogens are permitted, but exempts poultry livers used in French pâté (10,11).
1963-7	Food and Drug Administration cleared 4 organic arsenical feed additives of carcinogen stigma (5). Arsenic acid permitted as a desiccant for cotton.
1966	Neutron activation analysis used for As determination (23).
1967	Atomic absorption used for As determination (3).

The use of As as a poison in the middle ages in France and Italy is among the more interesting historical events concerning As. It became the vogue in Italy in the 15th century to use As to eliminate one's opponents. One family, Caesar Borgia and his sister Lucrenia poisoned so many of their opponents that they attained ill repute in their own day, Pope Clement VII was thought to have been poisoned in 1534 by the fumes of a medicated torch carried before him in a religious ceremony. Acquo Tofana was executed in 1719 for having poisoned over 600 people with As. After many of her accomplices were hanged, the use of As as a poison in Italy died down (26).

Arsenic poisoning was also a common occurrence in France in the 16th century. One woman, Marie Marguerite

D'Aubray, the wife of the Marquis de Brinvilliers visited hospitals in the guise of charity, but the people she visited became sicker and died. She was caught and executed. Arsenic poisoning in France declined after Penautier, the treasurer of France, and Cardinal de Bonz, who used As to get rid of people who stood in their way to power, had passed on (26).

In the 18 th century, As was used as a drug in the form of Fowler's solution, which was 1% potassium arsenite. This drug was said to cure occasional headaches that were thought to have been caused by malaria. Fowler's solution was also claimed as a remedy for cholera, and when used with mercury, recovery from syphillis was observed. This recovery stopped once the administrations of Fowler's solution and mercury ceased, but would begin again when the compound was once more administered (27).

In 1900, in England, many people died of beer poisoning which was attributed to As in the sulfuric acid used to invert the sugar (27). Tunnicliffe and Rosenheim (31) found 6 ppm Se in the toxic beer, and the sulfuric acid used to invert the sugar was 1.2% Se. Tunnicliffe and Rosenheim were unable to find any As in the milk of a woman whose baby had been poisoned. The lady had drunk some of the beer that was supposed to contain toxic amounts of As. Frost (12) has come to the conclusion that the beer poisoning was caused by Se and not As, but since few people had heard of Se, and almost everyone knew of As, then As was given the blame, and Se was completely overlooked.

Arsenic today is a part of modern agriculture and its use requires that the impact and fate of As be understood. This is particularly important in respect to the mythology surrounding As and fear that many people have concerning it. The present study is a attempt to determine what has happened to As applied to apple orchards and washed to the soil over the past 100 years.

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CHAPTER 3

ANALYTICAL METHODOLOGY

SYNOPSIS

Current colorimetric methods for determining arsenic (As) content of plant, soil, and solution samples were examined. Arsenic was evolved from the solution or digest as arsine in a hydrogen gas stream created by the reduction of zinc with hydrochloric acid. Factors which reduced the rate of hydrogen evolution increased arsenic recovery and 96% of the added arsenic was recovered when the hydrochloric acid was 1.2 N. The method as described provides quantitative estimates of arsenic in plants, soils and solutions when 5 µg/g or more arsenic was present in soil or plant tissue, or 0.250 µg/ml solution. The lower detection limit was 0.5 µg/g for plant tissue and soils, and 0.1 µg/ml solution. Wet oxidation of plant and soil samples using nitric and perchloric acids was compared and found to be more reliable than dry ashing using a slurry of magnesium oxide-magnesium nitrate as a method of solubulizing the As from plant and soil samples.

INTRODUCTION

Numerous methods ranging from simple tests to highly sophisticated instrumental techniques have been devised for the determination of As in a variety of substances. Although there are several methods in which the determination is made directly on the solution or the solid material, most methods involve the use of some variation of the Gutzeit method where the arsine is evolved in a hydrogen gas stream by the action of HCl on Zn.

Only in recent years, with the advent of instrumental methods of analysis has it been possible to determine micro- and sub micro quantities of As without using a variation of the Gutzeit method. A coulometric method was compared with a colorimetric version of the Gutzeit method and found to give comparable results (29). Polargraphic methods have 1 μg sensitivity, but only 75 ± 4% of the original As was recovered (2,17). Using a deuterium arc or an air-acetylene flame as little as 0.8 μg/ml As has been determined (4), and using nitrogen entrained air-hydrogen flames, As has been determined to a level of 0.1 μg/ml.

In spite of the sensitivity of the above techniques, many investigators continue to use variations of the Gutzeit method. In 1879 H. W. Gutzeit (16) developed a method which consists of evolving arsine from a solution acidified with either HCl or H_2SO_4 into silver nitrate and observing the yellow color formed. By 1901 (5) investigators were using dry paper impregnated with mercuric chloride to absorb the arsine. The test was made more quantitative in 1907 (21) when strips of Whatman paper of uniform width and length were saturated with mercuric chloride and then placed in the line of the evolving arsine gas. A yellow stain resulted, the length of which was proportional to the concentration of the As in solution. How (12) determined that the Gutzeit generator made a complete conversion of the As in solution to arsine.

The development of the blue molybdenum-arsenic complex was an early colorimetric variation of the Gutzeit test. Numerous studies involving this color development have been published (6,20,24,25,28). Arsine is evolved from the sample and absorbed in iodine solution and the blue color developed and its intensity measured at a wavelength of 840 nm with a spectrophotometer.

Later the use of silver diethyldithiolcarbamate (AgDDC) as an absorbing agent for arsine was developed (6,13,26), in which As replaces an equivalent amount of Ag from the AgDDC (3). Arsine was evolved into a pyridine solution containing AgDDC resulting in a red complex, the intensity of which was measured at a wavelength of 530 nm. More recently, due to the unpleasant odor of pyridine, AgDDC was dissolved in a mixture of l-ephedrine and chloroform, and was just as sensitive an absorbing agent for arsine as the AgDDC in pyridine (13).

Many atomic absorption methods for As in which arsine generated by the Gutzeit method is flushed by the hydrogen gas stream directly into the flame with a sensitivity of 0.1 μg As sample have been developed (9, 10,27). The use of sodium borohydride is suggested as an improvement over Zn for evolution of arsine because the sodium borohydride contains much less As contamination than Zn (8,22,23). Schmidt and Royer (22) state that the method also removes the need for stannous chloride, which contains some As impurities.

No methods for arsenic determination in soils and plants were included in the 1965 publication of the American Society of Agronomy entitled "Methods of Soil Analysis" (18). The purpose of this research was to verify the accuracy of current colorimetric methods being used for arsenic determinations.

MATERIALS AND METHODS

Plant and soil samples were oxidized, the arsenic evolved into an absorbing solution, and the amount absorbed determined colorimetrically.

Dry Ashing

One gram of air dried soil ground to pass a 2 mm sieve or plant tissue dried at 65°C for 1 week and ground to pass a 0.84 mm screen was placed in a 70 cc coors evaporating dish. Ten ml of a thoroughly mixed magnesium oxide-magnesium nitrate slurry was added to each sample.

The slurry was prepared by adding 75 g magnesium oxide and 100 g magnesium nitrate to a 1000 ml volumetric flask and diluting to the mark with water. The sample was dried at 105°C overnight, and transferred to a muffle furnace, it was heated to 600°C and held at that temperature for 0.5 hr. The furnace was turned off and the sample was allowed to cool inside the furnace overnight, after which it was removed and 15 ml of 6 N HCl were added. If a residue was present it was crushed with a glass rod until dissolution was complete. The sample was filtered to remove the residue, the residue was washed four times with water, after which the filtrate and the washings were transferred to an arsine evolution flask.

Wet Digestion of Plant Tissues

One gram of plant tissue was placed in a 50 ml calibrated digestion tube and 5 ml of concentrated nitric acid added. The sample was allowed to stand overnight and placed in a specially designed aluminum heating block (7) then carefully heated to 90°C for 0.5 hr. The sample was cooled, 2 ml 72% perchloric acid added, again heated to 90°C and the temperature maintained for one hr. At the end of the hour, the temperature was increased from 90 to 230°C over a period of 1.5 to 2 hr and maintained at this temperature for one hour after the appearance of perchloric acid fumes. The sample was then cooled, diluted to 35 ml with water, and 1 ml 50% potassium iodide (prepared by dissolving 50 g potassium iodide in water in a 100 ml volumetric flask and diluting to the mark) and 1 ml 50% stannous chloride (prepared by dissolving 50 g stannous chloride in 100 ml concentrated HCl) were added to the sample to reduce the arsenate to arsenite. The sample was then gently heated to boiling, and immediately upon boiling, it was removed from the heating apparatus, and allowed to cool to room temperature. Once cooled, it was diluted to 50 ml with water.

Wet Digestion of Soil

One gram of soil was placed in the digestion tube, and 5 ml of 1:1 mixture of concentrated nitric acid and 72% perchloric acid were added. The sample was heated to 90°C for 1 hr and then the same procedure, from the point of perchloric acid addition, used for plant tissue was followed.

Evolution of Arsenic

An amount of solution containing less than 120 μg As was placed in the evolution flask shown in Figure 1a. Enough of the following reagents were added so that the evolution flask contained 15 ml of concentrated hydrochloric acid, 1 ml of 15% potassium iodide solution, and 1 ml of 50% stannous chloride in concentrated hydrochloric acid. The resulting solution was diluted to 125 ml with water and equilibrated for 15 min to insure that all the arsenate had been reduced to arsenite. Four g 30 mesh Zn (0.00001% As) were added and the evolution flask immediately connected to a collection vessel as shown in Figure 1a. The reaction was allowed to procede at least for 2 hr. The collection vessel was removed and the arsenic content determined.

Collection and Determination of Arsenic in Silver Diethyldithiolcarbamate

Silver diethyldithiolcarbamate (AgDDC) was prepared by dissolving 1.7 g of silver nitrate in 100 ml water and 2.3 g sodium diethyldithiolcarbamate in another 100 ml water. The two solutions were mixed by slowly adding the silver nitrate to the sodium diethyldithiolcarbamate on a magnetic stirrer at a temperature below 20°C. The lemon yellow precipitate of AgDDC was filtered, washed thoroughly with water, and dried in a vacuum dissicator. The pyridine solution of AgDDC was prepared by dissolving 1.0 g of AgDDC

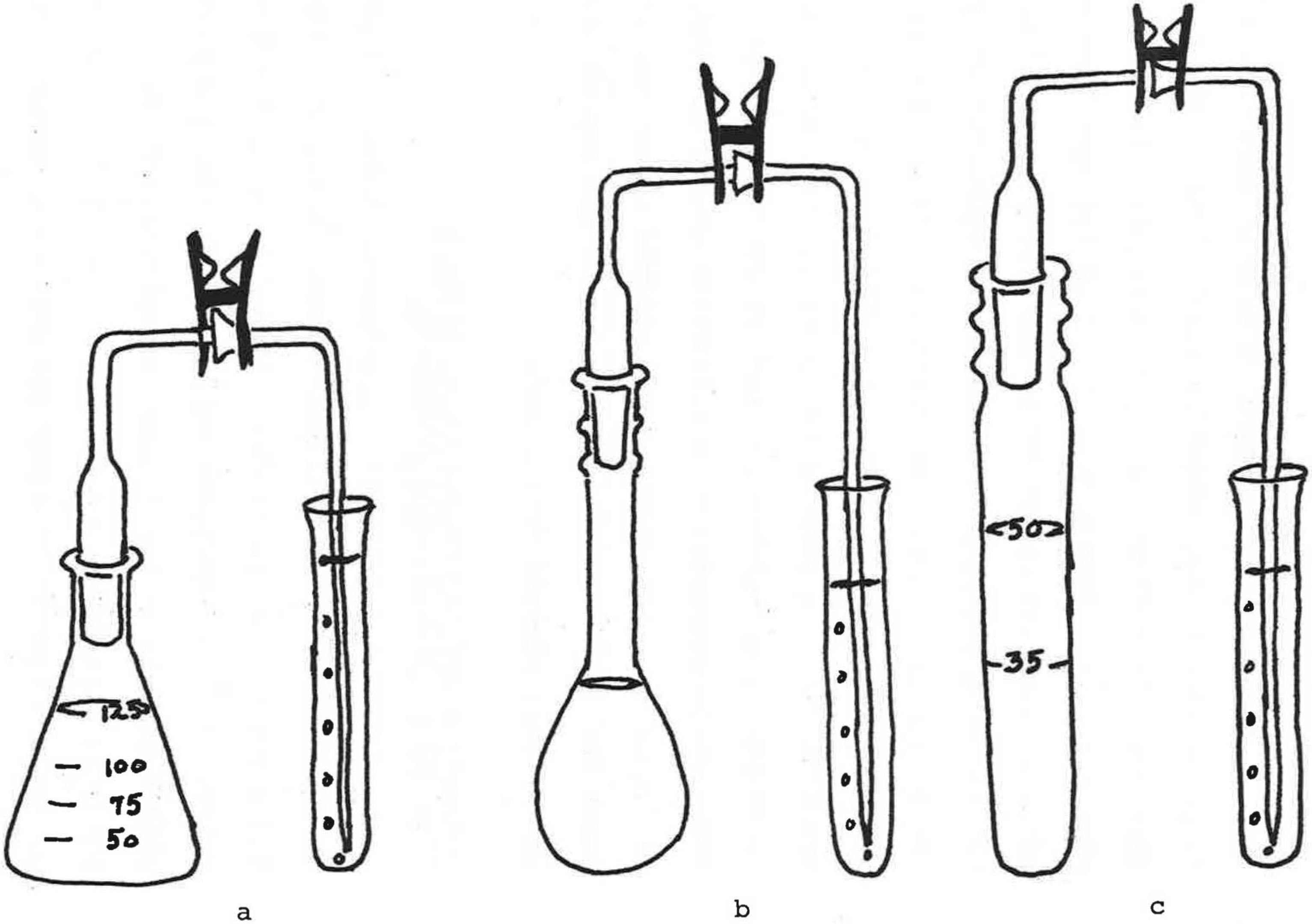

Figure 1. Apparati for arsine evolution: a. 125 ml erlenmeyer flask; b. 100 ml kjeldahl flask; and c. 50 ml calibrated digestion tube, all with 24/40 joints.

in 200 ml reagent grade pyridine. For AgDDC in chloroform, 0.41 g l-ephedrine was dissolved in 200 ml chloroform, and then 0.675 g of AgDDC added and the volume adjusted to 250 ml with chloroform.

When arsine was to be collected in AgDDC solution, a spectrophotometer tube containing 4 ml of AgDDC solution in either pyridine or chloroform was used as the collecting vessel. A cotton plug impregnated with lead acetate was inserted between the evolution flask and the collecting vessel. The reaction was carried out as described, except that a maximum of 32 µg As was used. After the reaction was complete, the cuvette was placed in a Bausch and Lomb spectronic 20 spectrophotometer and the absorbance measured at a wavelength of 530 nm for the pyridine solution and at 520 nm for the chloroform solution. All standards were carried through the procedure in exactly the same manner as samples.

Collection of Arsine in Iodine

The iodine solution was made by dissolving 53.333 g potassium iodide, 14.267 g potassium iodate, and 33 ml concentrated HCl in water and diluting to 1000 ml. This resulted in a 0.4 molar stock solution, from which the working solution was prepared by transferring 20 ml of the stock solution to a 2000 ml volumetric flask, adding 1.6 g sodium bicarbonate and diluting to the mark with water.

Manual arsenic determination. Four ml of iodine solution were placed in a spectrophotometer tube and used as the collection vessel. When the arsine evolution was completed 1 ml of the single solution used for the determination of phosphate was added (19). The solution was prepared by dissolving 10.3 g ammonium molybdate in 400 ml water, adding 70 ml of concentrated sulfuric acid, and diluting to 500 ml. A second solution consisted of 5.4 g of ascorbic acid and 0.068 g potassium antimonyl tartrate diluted to 500 ml with water. The two solutions were mixed 1:1 as needed providing the single solution. One and one-half hour after adding the single solution light absorbance was measured at a wavelength of 840 nm.

Automated determination of arsenic. Fifteen ml of iodine solution was placed in an 18 x 150 mm test tube and used as the collection vessel for arsine absorption. After arsine evolution was complete the test tubes were transferred to the sample changer of the automated system shown in Figure 2.

The autoanalyzer set-up consisted of a sample changer built by the Scientific Instrument Shop of the University of Missouri-Columbia, a Technicon autoanalyzer proportioning pump, a Bausch and Lomb Spectronic 20 spectrophotometer, and a Perkin-Elmer Model 56 recorder (Figure 2). Sample or water was pumped in 1 min cycles, mixed with the ammonium molybdate and ascorbic acid

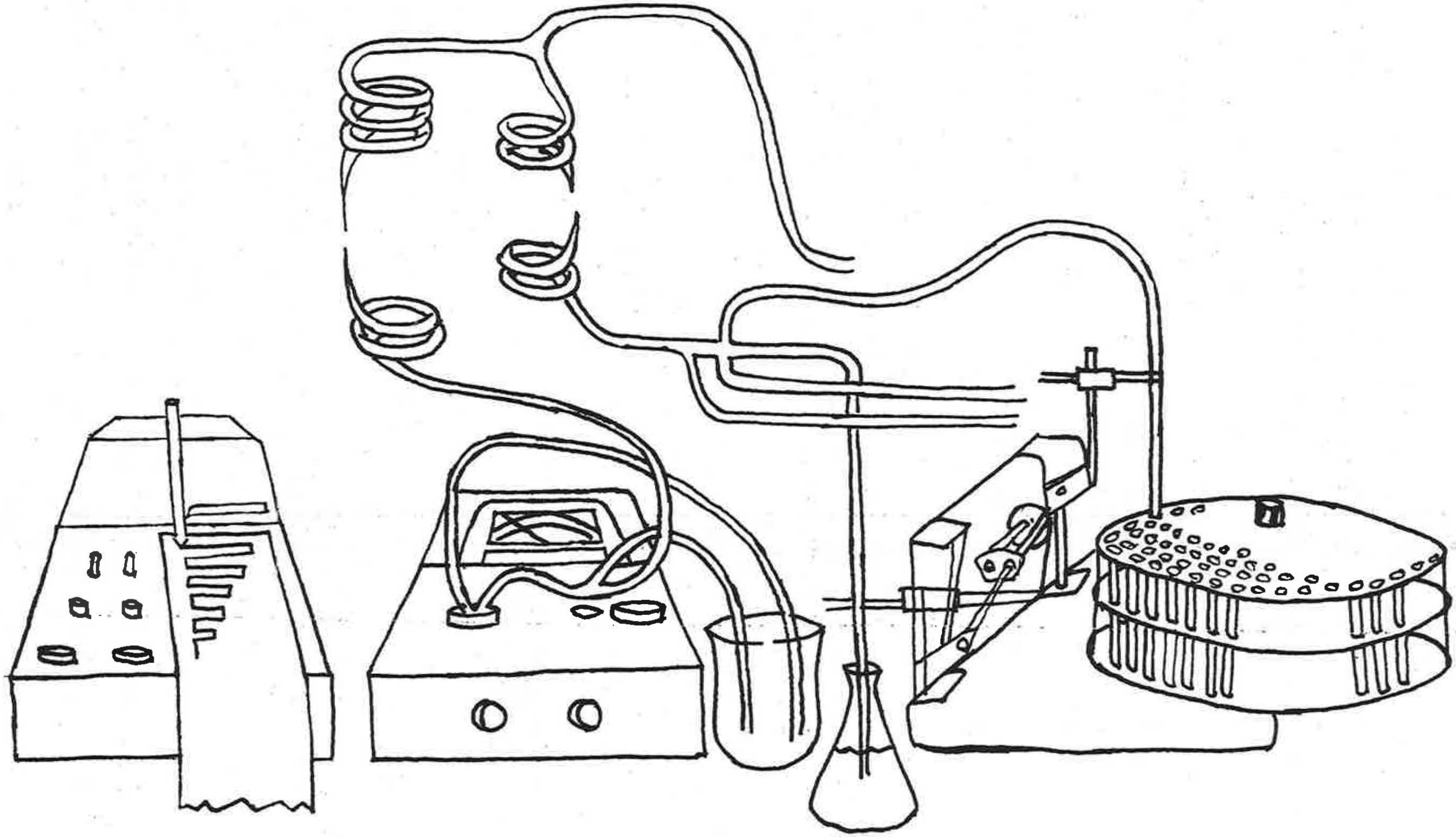

Figure 2. Equipment used in automated determination of arsenic.

solutions, and passed through a delay coil consisting of 14 turns. Then the stannous chloride was added and the sample passed through a mixing coil of 28 turns to allow time for mixing of reagents and for complete color development. Sample and air were pumped at 3.90 ml/min, 0.75% ammonium molybdate in 2.5 N HCl at 0.60 ml/min, 1% ascorbic acid at 1.20 ml/min, and stannous chloride (.5% in 1.2 N HCl) at 0.09 ml/min. After passing the 28 turn delay coil the solution passed a debubbler and then was pumped through the adsorption cell of the Bausch and Lomb spectrophotometer at a rate of 3.90 ml/min. The intensity of the blue molybdenum-arsenic complex was measured at a wavelength of 840 nm and continuously recorded.

RESULTS AND DISCUSSION

Comparison of Dry Ashing and Wet Oxidation

Standards were prepared from a stock solution made by dissolving 4.164 g ($Na_2HaSO_4 \cdot 7H_2O$) in water and diluting to a liter to give 1000 ppm As. Dilutions were made from the stock solution resulting in concentrations of 0.000, 0.067, 0.250, 0.500, 1.000, 2.000, 4.000, and 8.000 μg As/ml in 0.004 M iodine solution. The reason for using sodium arsenate as the standard was because the reaction of arsine with iodine in water is (24),

$$AsH_3 + 4H_2O + 4\ I_2 = 8HI + H_3AsO_4$$

which gives arsenate as a product.

These solutions were placed directly in the automated system and the results shown in Figure 3. The data on any given day follows closely that predicted from Beer's law. Day to day fluctuations of the magnitude shown in Figure 3 are attributed to fluctuations in pumping rates and positioning of the absorbance cell. To account for these variations standards were included at the beginning and end of each batch of samples to be run. The results of digesting standards by wet digestion and dry ashing are listed in Table 1. The percent recovery was calculated by adding the absorbance values of the absolute, and dividing the result into the sum of the absorbance minus blank values of the wet oxidation and the dry ashing from Table 1. The percent recovery of the wet oxidation is 96.7% and of the dry ashing 84.5%. Both the wet and the dry techniques lack sensitivity at lower concentrations. At concentrations above 0.500 µg As/ml the wet method is in very good agreement with the absolute standards, but the dry ashing technique drops off from the absolute as the concentration increases. Thus it is concluded that the wet oxidation is superior to the dry ashing for oxidizing standard additions of As.

The results of ashing duplicate soil samples of Menfro soil and plant tissue samples from Reed's Canary grass are listed in Table 2.

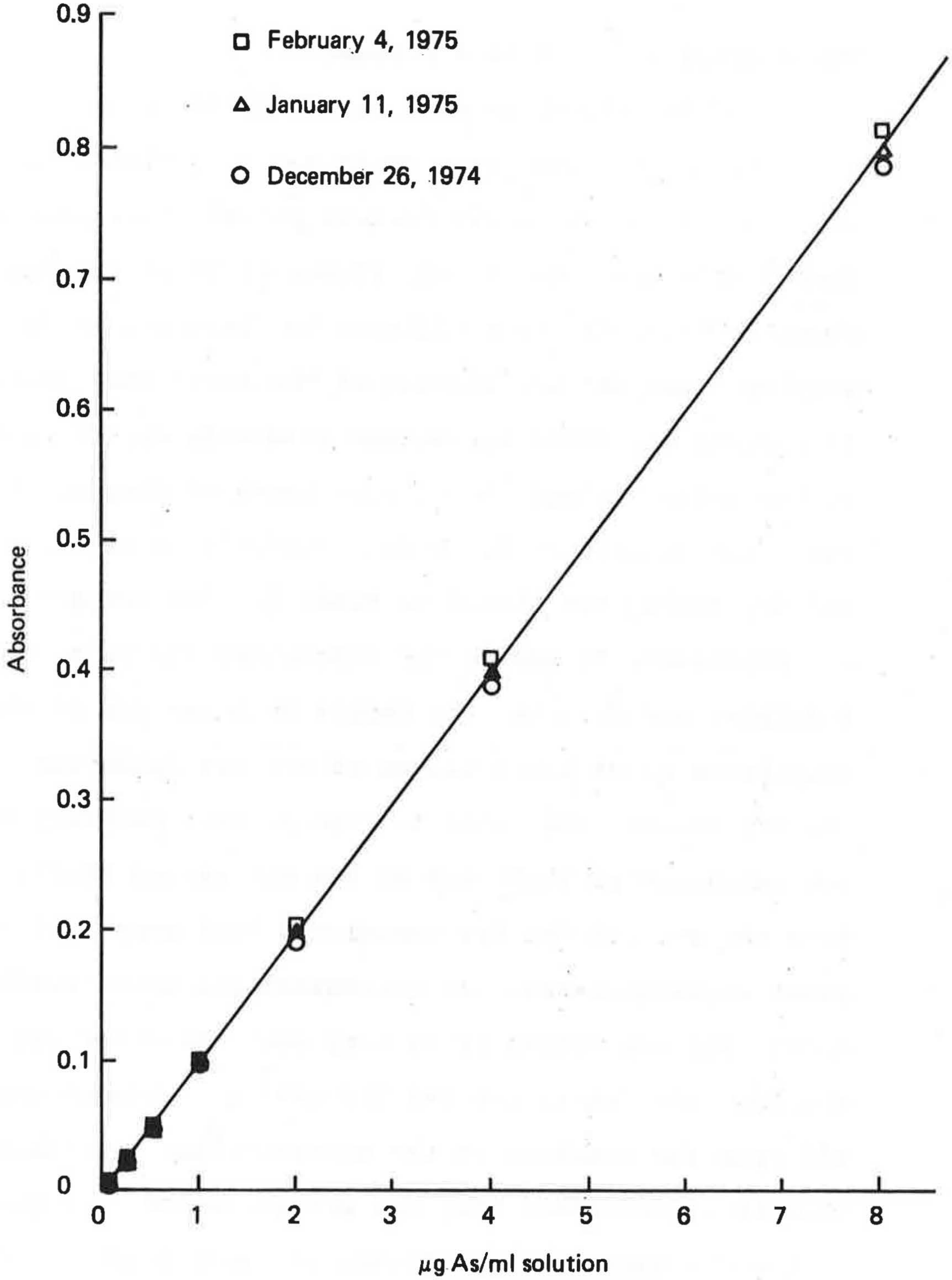

Figure 3. Relationship between arsenic concentration in solution and absorbance at a wavelength of 840 nm.

Table 1. Recovery of arsenic standards, a comparison of wet oxidation and dry ashing methods.

Amount of As	Standards	Ashed	
		Wet	Dry
μg	Absorbance		
0	0.000	0.006	0.011
0.067	0.006	0.010	0.020
0.250	0.023	0.024	0.028
0.500	0.049	0.047	0.045
1.000	0.098	0.095	0.090
2.000	0.198	0.205	0.185
4.000	0.405	0.395	0.345
8.000	0.815	0.795	0.710

Table 2. Comparison of arsenic concentration in Menfro soil and Reed's Canary grass samples as determined by wet digestion and dry ashing.

Sample		Wet Digestion			Dry Ashing		
		1	2	Mean	1	2	Mean
		ppm As					
Menfro soil	(a)*	113	119	116	90	88	89
(0-10 cm) depth	(b)	125	130	128	95	107	101
(10-20 cm) depth	(a)	21	23	22	16	14	15
	(b)	32	29	31	28	20	24
(20-40 cm) depth	(a)	7	8	8	11	12	12
	(b)	11	12	12	15	10	13
Canary grass	(d)†	20	21	21	14	16	15
	(e)	15	17	16	8	9	9
	(f)	6	7	7	10	12	11

*Different samples from the field.

†Different grass samples.

From duplicate arsenic determinations of soils and plants, it appears that the wet oxidation is more reproducable and gives higher values than dry ashing. Coupled with better recovery of As from standards the wet oxidation appears superior as an agent for solubizing the arsenic from solid samples.

Methods of Improving the Efficiency of Arsine Evolution

Initial temperature, percent alcohol, and normality of HCl. It was found that As evolved as arsine by the standard methods was not quantitatively recovered (6,19,22,27). Varying the initial temperature, the amount of isopropyl alcohol, and the normality of the HCl were examined as methods to improve As recovery. For all tests 15 ml concentrated HCl, 4 g 30 mesh Zn, 1 ml 15% potassium iodide, and 1 ml 50% stannous chloride were used to evolve 120 μg As as arsine into 15 ml of the 0.004 M iodine solution. Unless otherwise specified the initial temperature was 25°C, no alcohol added and 15 ml of concentrated HCl in a total volume of 75 ml. Variations in the normality of the HCl were formed by controlling the volume of water added to the flask, which also varied the volume of solution in each flask. Results of these experiments are found in Table 3.

In the temperature studies only the initial temperature was controlled and as it decreased, the

Table 3. Effects of temperature, alcohol content and normality of hydrochloric acid on the recovery of evolved arsine.

Initial temperature	Recovery	Amount of alcohol	Recovery	Normality of HCl	Recovery
°C	%	%	%	N	%
25	60	10	65	5.0	49
20	66	20	71	3.5	71
15	74	30	82	2.9	72
10	76	40	85	2.5	79
5	80	50	80	2.1	85
				1.9	89
				1.2	96

percent As recovered increased. As the concentration of the alcohol was increased the percent As recovered increased to a point and then decreased. As the normality of HCl decreased, the As recovered increased. Although 96% recovery was obtained with 1.2 N HCl, it was thought that this might also be a volume effect, therefore, the test was run using 20 ml of concentrated HCl instead of 15, with the final volume and all else the same. Increasing the normality of HCl from 1.2 to 1.8 dropped the recovery of As from 96 to 92%. The data indicated that the slower the rate of the reaction, the better was the absorption of the arsine by the iodine solution. Controlling the normality of the HCl rather than the initial temperature or the amount of alcohol in solution is the most convenient means of reducing the reaction rate.

Reaction vessels. Various reaction vessels were examined in the evolution of arsine to learn which would give the best recovery of the evolved arsine (Figure 1). The comparison was among a 125 ml erlenmeyer flask, a 100 ml kjeldahl flask, and a 50 ml (25 x 200 mm) digestion tube, all fitted with 24/40 joints. Each flask was set up so that the final concentration of HCl was 1.2 N, and the volumes were adjusted as follows: for the erlenmeyer, 125 ± 5 ml; for the kjeldahl, 100 ± 5 ml; and for the digestion tube, 50 ml. The arsine was evolved into 15 ml of 0.004 M iodine solution, and the blue molybdenum-arsenic color was measured at a wavelength of 840 nm. The results of the experiment are listed in Table 4. For the erlenmeyer flasks, the As recovery was 98%, for the kjeldahl flask 90%, and for the digestion tubes 93%. From the results it was concluded that all of the reaction vessels give recovery above 90%, but since recovery from the erlenmeyer flask was 98%, it would be used in this study.

Comparison of silver diethyldithiolcarbamate with iodine as arsine absorbing agents. Standards additions of 0, 1, 2, 4, and 8 μg As were placed into the evolution flasks, and the arsine was evolved into one of the three solutions, AgDDC in pyridine, AgDDC in chloroform with l-ephedrine, and 0.004 M iodine, using 4 ml of each solution. After the reactions were completed, the molybdenum blue color was developed in the iodine solution and the absorbance of each solution measured and the results listed in Table 5. Absorption of arsine into 4 ml of 0.004 M iodine solution results in a more sensitive method than absorption into either the pyridine of the chloroform solutions. For this reason, and because of the strong odor of both the pyridine and the chloroform, it was decided to use the iodine solution as the absorbing agent throughout this study.

Table 4. Recovery of arsenic added as sodium arsenate and evolved from erlenmeyer flasks, kjeldahl flasks, and digestion tubes.

Amount of As	Standard	Erlenmeyer flask	Kjeldahl flask	Digestion tube
µg	Absorbance			
0	0.000	0.000	0.000	0.000
0.5	0.065	0.059	0.050	0.054
1.0	0.120	0.110	0.095	0.102
2.0	0.230	0.219	0.180	0.194
4.0	0.425	0.412	0.380	0.405
8.0	0.815	0.820	0.785	0.790

Table 5. Comparisons of arsine absorption by silver diethyldithiolcarbamate dissolved in pyridine or chloroform containing l-ephedrine and 0.004 M I_2 solution.

As evolved	AgDDC		0.004 M I_2
	pyridine	chloroform	
μg	Absorbance		
0	0.000	0.000	0.000
1	0.033	0.032	0.059
2	0.065	0.066	0.110
4	0.135	0.245*	0.219
8	0.272	0.265	0.435

*The solution was slightly cloudy at the time of measurement.

CONCLUSION

From this study, it has been concluded that reliable colorimetric arsenic determinations can be made. Plant and soil samples can be oxidized using wet digestion with nitric and perchloric acids. The 1.2 N HCl used reacts slowly enough with the zinc so that quantitative recovery of arsine is obtained. The arsine thus evolved should be absorbed by iodine, and determined by the molybdenum blue method. The method gives quantitative estimates of arsenic in plants, soils and solutions.

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CHAPTER 4

DISTRIBUTION AND OCCURRENCE OF LEAD, ARSENIC, AND COPPER IN MISSOURI SOILS

SYNOPSIS

Arsenic, lead, and copper levels were determined in soils from several orchards and former potato fields and compared to naturally occurring levels of these elements in the soil. No copper accumulation was found in any of the samples tested. The potato fields were free of arsenic and lead contamination. In the orchard soils, lead and arsenic was concentrated in the top foot and varied from very high to naturally occurring levels. The Bray tests for available phosphorus were high by 0.8 to 14.8% due to arsenic interference on soils from the arsenic contaminated fields.

INTRODUCTION

From the late 19th century to the middle of the 20th century arsenicals were used as general pesticides in orchards and potato fields throughout the country. Calcium, lead, and copper arsenates were used, but either no records or incomplete records of date and amounts applied were kept. Because of the uncertainty involved regarding the form of arsenate used in many of the locations, the soils at all sampling sites were analyzed for Cu, Pb, and As in the soil. These levels were compared with the levels of uncontaminated soils. Results of research (1,4,5,10,12,16,25) which surveyed soils for total As content have been summarized by Woolsen, Axley, and Kearney (26). They concluded that untreated soils ranged from 0.5 to 14.0 ppm As and soils contaminated with As varied from 1.8 to 830 ppm As. Jones and Hatch (15) reported levels of 30.3 to 1383 ppm Pb in contaminated orchard soils, which otherwise had normal levels of 7.6 to 16.8 ppm Pb. The overall level of Pb in the earth's crust is 15 ppm (22), and several reports confirmed that the natural level of Pb in soils ranged from 5-25 ppm Pb (3,7,8,11,17,18,20,22, 27). The concentration of Cu in the earth's crust has been determined to be between 45 and 70 ppm, with the soil content at 20 ppm (13). Other reports confirm this as the natural level of Cu in soils (2,6,20,27).

MATERIALS AND METHODS

Sampling

Soil samples were taken at various depths and at different distances from the trunk of the tree and the As concentration determined. A Menfro soil near McBaine that had been converted to pasture without plowing three years earlier, and that had been an apple orchard for about 75 years with a history of lead arsenate treatment, was selected to test the sampling procedure. The sampling pattern used around individual trees is represented in Figure 1. Samples were taken with a Giddeon core sampler at distances of 0.91, 2.10, and 3.05 m from the trunk of the tree at 0-10, 10-20, and 15 cm increments to a depth of 110 cm. Sampling at other orchard sites was done with a Hoffer tube to a depth of 30 cm and divided into 0-5, 5-10, 10-20, and 20-30 cm increments. The samples from these sites were taken at 0.91, 2.13, and 3.05 m from the tree trunk and combined by depth. Figure 2 is a map of the state showing the location of the sampling sites. Two samples were taken from each site, and each sample was run in duplicate.

Arsenic Determination

One g of soil was oxidized with nitric and perchloric acids, the arsine evolved into iodine, and the As content determined as outlined in Chapter 3.

Lead Determination

One g of soil was placed in a 50 ml calibrated digestion tube and 5 ml of concentrated nitric acid were added. The sample was digested for two hours at 105°C, evaporated to near dryness, cooled, diluted to 50 ml with water, and filtered through Whatman #2 paper. Lead was

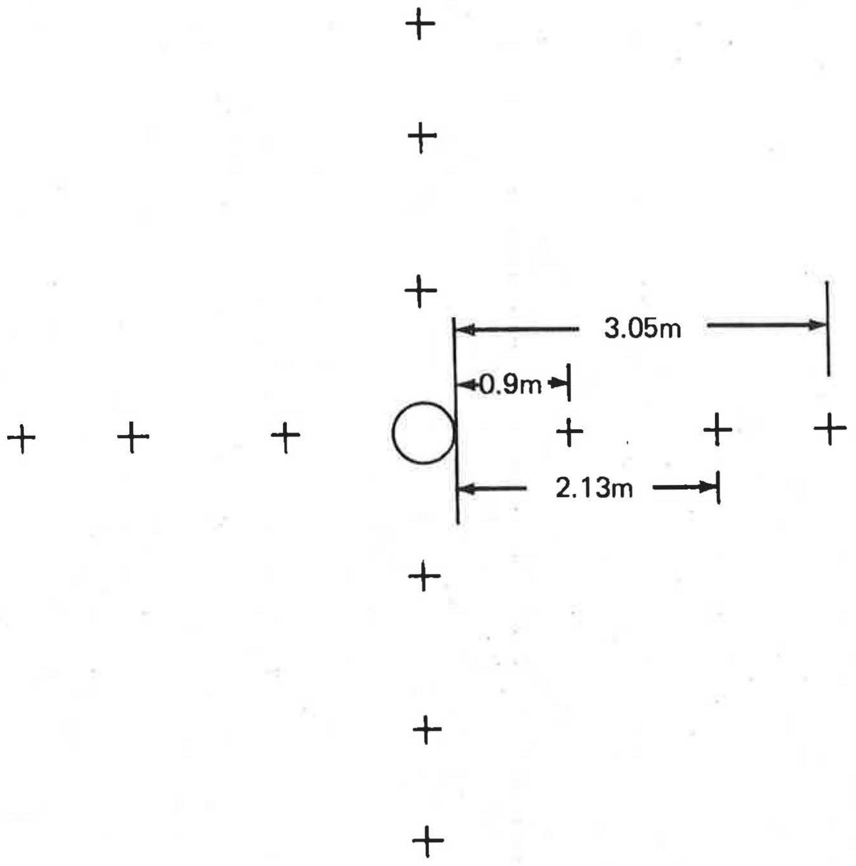

Figure 1. Position of soil samples around orchard trees.

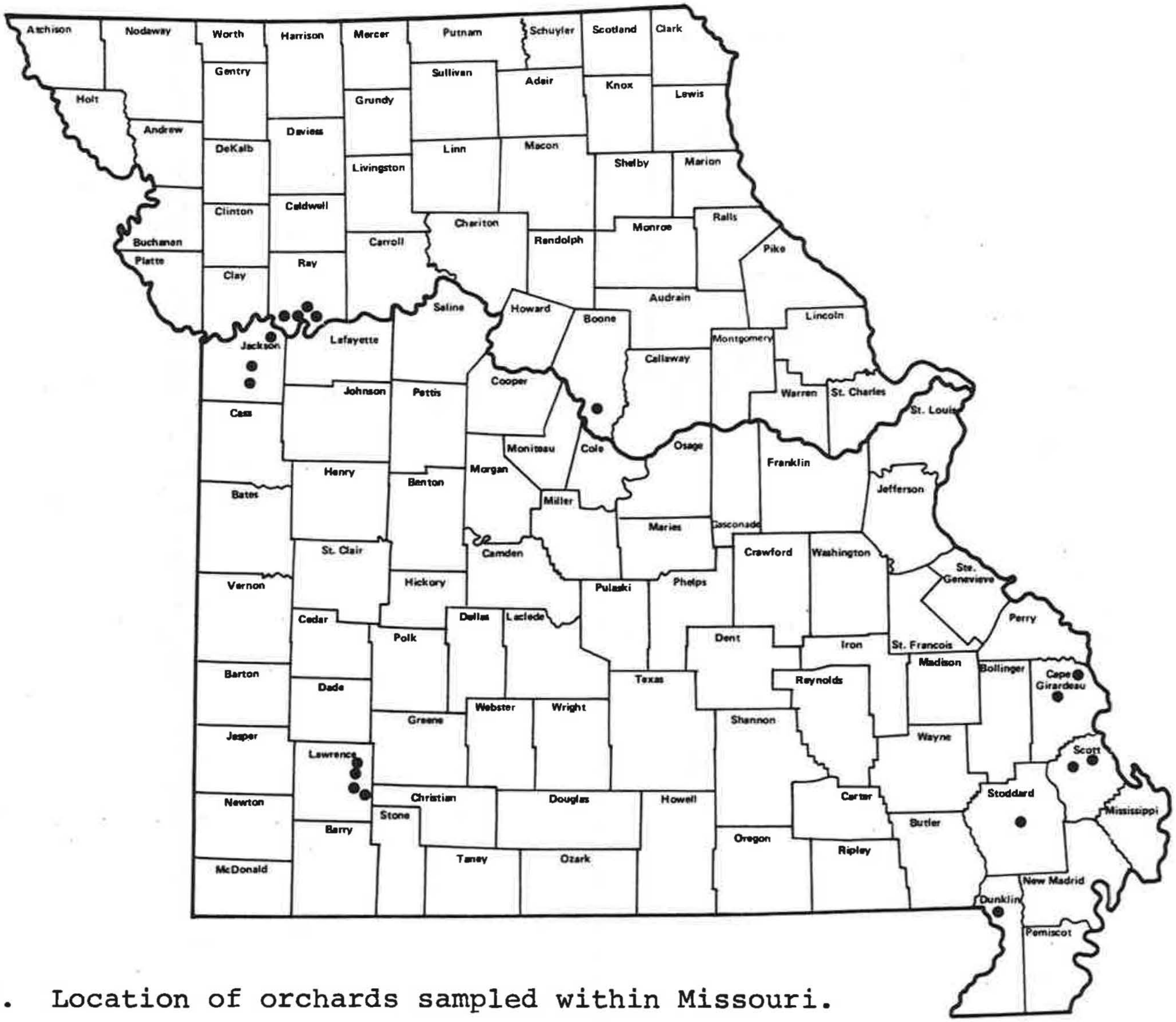

Figure 2. Location of orchards sampled within Missouri.

then determined by atomic absorption spectrophotometry at a wavelength of 283.3 nm.[1]

Copper Determination

The Cu content of the samples prepared for Pb analysis was determined by atomic absorption spectrophotometry at a wavelength of 324.8 nm.

RESULTS AND DISCUSSION

Arsenic Concentration as a Function of Depth and Distance from the Tree Trunk

Figure 3 shows the relationship between As concentration at various depths in the soil and distances from the tree trunk. The As concentrations at a depth of 0-10 cm are 166, 153, and 156 ppm, and at a depth of 10-20 cm, they are 37, 30, and 36 ppm for distances of 0.91, 2.13, and 3.05 m, respectively from the tree trunk. These results indicated that As concentration in orchard soils did not vary as a function of distance from the trunk of the tree.

The concentration of As below 20 cm is equal to the level of naturally occurring As, with an average of 9.7 ppm (Figure 3). This showed that the As remains in the upper horizons of the Menfro soil. On the basis of these analyses it was concluded that making a composite

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[1] Analyses for Pb on these samples were carried out by Mr. Ellis Benham.

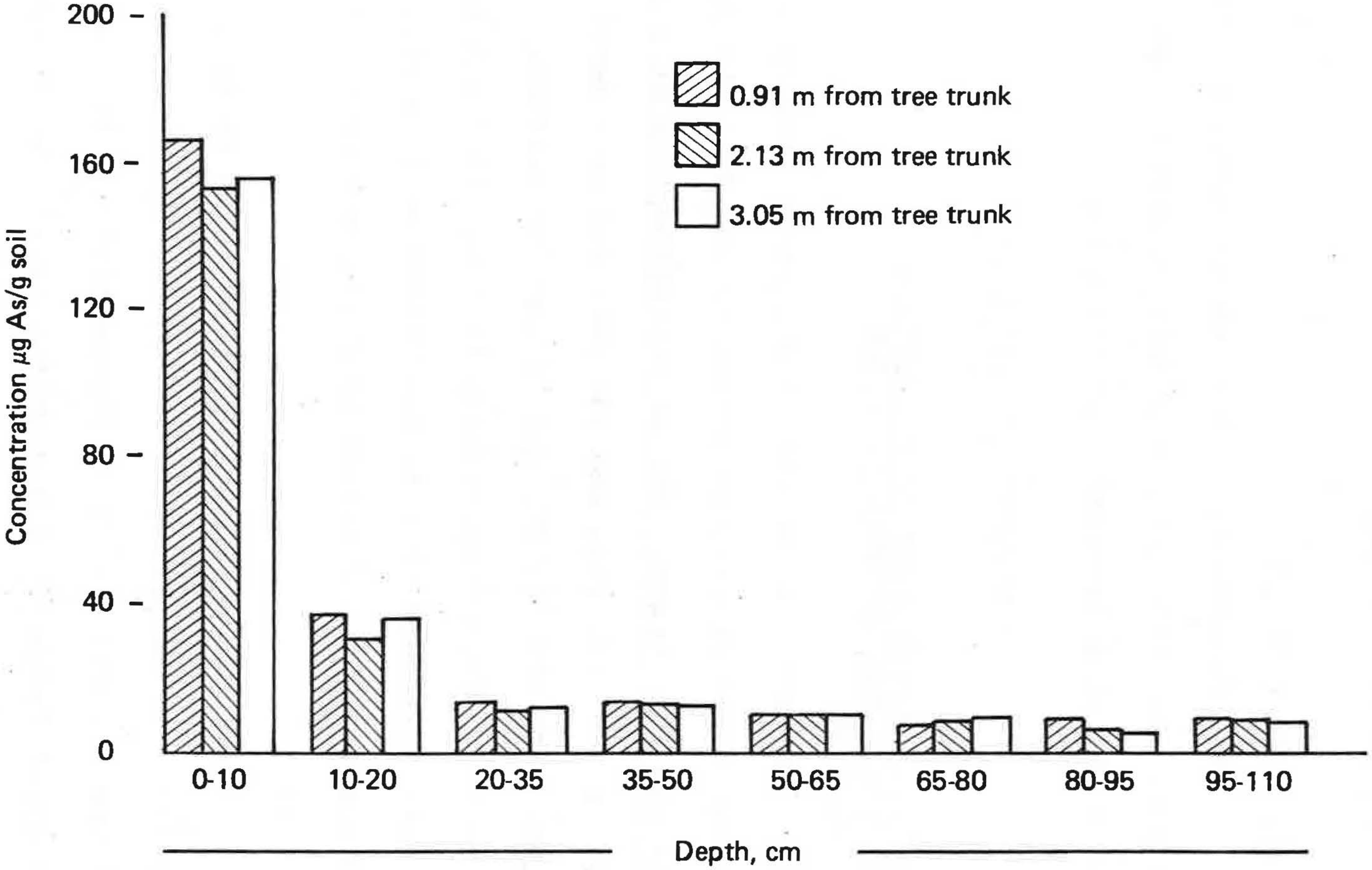

Figure 3. Arsenic concentration in a Menfro soil with depth and distance from the tree.

of three distances from the tree trunk by depths of 0-5, 5-10, 10-20, and 20-30 cm would give samples representative of the orchard to be sampled.

Level of Lead, Arsenic, and Copper Found in the State of Missouri

Based on the results of As concentration in the Menfro soil and on results of other tests of Pb distribution in contaminated soils (21,22,23,27), it was concluded that Pb and Cu would also be concentrated in the upper horizons. Table 1 lists the results of the analyses for the elements throughout the state. Samples 1-4, with Pb levels above 400 ppm and As levels above 100 ppm, were considered to be highly contaminated. Samples 5-12 were mildly contaminated with Pb, and samples 5-7 were mildly contaminated with As with the exception of sample 6b. Samples 13-17 appeared to have no As or Pb contamination.

Standard deviations were determined on the analyses of Pb, As, and Cu in all samples. The standard deviation of the Pb samples above 100 ppm is 170, and for the samples below it is 12. The S.D. of 170 represents the variability of Pb in the 0-10 cm layer according to lead arsenate treatment, and the S.D. of 12.0 relates to naturally occurring Pb in the soil. The S.D. of all As determinations was 23.5, taking into consideration contaminated and non-contaminated soil. For Cu, the S.D. over all samples was 1.3.

Table 1. Levels of lead, arsenic, and copper in Missouri soils.

Sample	Location	Soil Type	Depth	Lead	Arsenic	Copper	Lead/Arsenic	Current Use
	County		cm	—— µg/g soil * ——				
1	Unity Village	Sharpsburg	0- 5	2020	295	14	6.85	Apple orchard
	Jackson	Silt loam	5-10	540	210	7	2.57	
			10-20	80	65	6	1.23	
			20-30	35	15	5	2.33	
2	Carver Orchard	Newtonia	0- 5	910	182	12	5.00	Apple orchard
	Lawrence	Silt loam	5-10	160	126	6	1.27	Vegetable farm
			10-20	50	35	4	1.43	
			20-30	65	13	4	5.00	
3	Head Orchard	Baxter	0- 5	515	120	10	4.29	Apple orchard
	Lawrence	Gravelly loam	5-10	365	84	6	4.35	
			10-20	215	77	13	2.79	
			20-30	104	28	7	3.71	
4	Gudeas Orchard	Knox	0- 5	475	106	28	4.48	Apple orchard
	Jackson	Silt loam	5-10	220	88	6	2.50	
			10-20	50	46	5	1.09	
			20-30	25	27	7	0.93	
5	Stephens Orchard	Crawford	0- 5	235	55	14	4.27	Peach orchard
	Jackson	Silt loam	5-10	210	65	7	3.23	
			10-20	100	30	6	3.33	
			20-30	20	10	5	2.00	

Table 1 (continued)

Sample	Location	Soil Type	Depth	Lead	Arsenic	Copper	Lead/Arsenic	Current Use
	County		cm	—— μg/g soil*		———		
6a[†]	Pioneer Orchard Cape Girardeau	Hagerstown Silt loam	0- 5	230	85	7	2.71	Apple orchard
			5-10	32	22	5	1.45	
			10-20	22	16	5	1.38	
			20-30	25	18	6	1.39	
6b[‡]	Pioneer Orchard Cape Girardeau	Hagerstown Silt loam	0- 5	26	11	8	2.36	Peach orchard
			5-10	23	11	8	2.09	
			10-20	19	10	6	1.90	
			20-30	19	15	7	1.27	
7	Diebold Orchard Scott		0-30	177	80	12	2.21	Apple orchard
8	Russell Orchard Stoddard	Memphis Silt loam	0- 5	162	18	4	9.00	Apple orchard
			5-10	74	53	4	1.39	
			10-20	27	8	5	3.38	
			20-30	34	17	6	2.00	
9	Maples Orchard Lawrence	Newtonia Silt loam	0- 5	150	23	5	6.52	Apple orchard
			5-10	80	9	4	8.89	
			10-20	28	7	4	4.00	
			20-30	29	7	6	4.14	
10	Lindsay Orchard Scott		0- 5	131	20	6	6.55	Apple/peach orchard
			5-10	78	24	6	3.25	
			10-20	36	43	6	0.84	
			20-30	22	20	6	1.10	

Table 1 (continued)

Sample	Location	Soil Type	Depth	Lead	Arsenic	Copper	Lead/Arsenic	Current Use
	County		cm	—— µg/g soil* ——				
11	Wiley Farm	Newtonia	0-30	58	6	4	9.67	Pasture
	Lawrence	Silt loam						
12	Rau Orchard	Knox	0- 5	43	16	6	2.69	Apple orchard
	Cape Girardeau	Silt loam	5-10	33	15	6	2.20	
			10-20	27	14	4	1.93	
			20-30	22	16	5	1.38	
13	Miller's Orchard		0- 5	22	14	6	1.57	Peach orchard
	Dunklin		5-10	22	15	6	1.47	
			10-20	22	15	6	1.47	
			20-30	23	12	6	1.92	
14	Edwards Farm	Cass	0-30	19	11	4	1.73	Corn/soybeans
	Ray	Loam						
15	Gooch Farm		0-30	16	10	4	1.60	Corn/soybeans
	Ray							
16	Offutt Farm		0-30	17	11	5	1.55	Corn/soybeans
	Ray							
17	Artman Farm		0-30	18	10	3	1.80	Corn/soybeans
	Ray							

*Field replicates.

†Treated with lead arsenate.

‡Not treated with lead arsenate.

Several of the sites had undergone a change of crop, from apples to pasture, apples to peaches, or apples to more apples. If plowing had occurred with the crop change, this was taken into consideration, in obtaining the sample. Sites that had undergone crop changes without plowing are: #5 Stephens Orchard, apples to peaches and #13 Miller's Orchard, apples to peaches. Samples in which the crop had been changed and plowing had occurred are: #7 Diebold Orchard, apples to apples; #11 Wiley Farm, apples to pasture; and #14-17, potatoes to corn and/or soybeans. Plowing would distribute the pollutants evenly throughout the profile, therefore these samples were sampled in one depth increment of 0-30 cm.

With the Pb and As spread evenly throughout the soils, problems with the growth of crops have been observed. These sites are the Diebold Orchard in Scott county, the Russell Orchard in Stoddard county, and the Carver Orchard in Lawrence county.

The Diebold Orchard is on land that slopes from 0-7%, with some low spots. In the low spots, either the new trees will not grow, or they do not grow very well and are small in comparison with the other orchard trees. The Russell Orchard has a strip running northeast to southwest in which little to nothing grows. The land slopes from 0-8%, and at a low level spot, nothing has grown for 2-5 seasons. The land has been with the current owner for less than 10 years, and the treatment prior to that time is not known. A section of the Carver Orchard has been changed to a vegetable garden within the past 3 years, and has not produced a good vegetable crop yet. Before the change, it was a productive part of the apple orchard. It is on level ground, and when the samples were taken in late 1973, it was completely barren. The owner explained that it had been in this condition for most of the growing season. All of these orchards have high levels of As and Pb contamination, and certain areas within each orchard could be subject to waterlogging for short periods of time. Since each orchard previously grew productively, it may be that the waterlogging effect was small when As was 0-5 cm from the surface and did not affect the growth of the crop. Perhaps waterlogging increases the solubility of Pb and As that has been added to the soil to toxic levels for crop growth. The solubility of various arsenates is discussed in Chapter 5, and the effects of waterlogging on arsenate solubility is discussed in Chapter 6.

Samples 6a and 6b from the Pioneer Orchard in Cape Girardeau county are approximately 300-500 meters apart. Sample 6a has been treated with lead arsenate 5 times yearly since 1952. Sample 6b was pasture until about 1971, at which time peach trees were planted.

Sample 6b has never received lead arsenate treatment. Comparison of 6a and 6b show that the 0-5 cm horizon of 6a is contaminated with Pb, but both the 0-5 and the 5-10 cm horizons show As contamination (Table 2).

The relationships of the concentrations of Pb, As, and Cu of the Pioneer Orchard are shown in Figure 4, along with those of the Head Orchard which has about twice the level of Pb and As contamination in the 0-5 cm horizon. The Head Orchard has not been treated with lead arsenate since the mid 1950's, prior to that, it had a history of 40 to 50 years of treatment with lead arsenate. The Pioneer Orchard, on the other hand, has had lead arsenate treatments yearly since the mid 1950's. Comparisons of Pb and As levels in the two orchards as a function of time can be made. In the Head Orchard the As concentration is about evenly dispersed to a depth of 20 cm, whereas the Pb concentration steadily decreases with depth. This is not the case for the Pioneer Orchard where the Pb and As concentrations are near normal in the 5-10 cm horizon. This suggests that lead arsenate dissociates in the soil, and that the arsenate ion is more mobile than the lead ion. The relative mobility of Pb and As in the Head Orchard does not follow the general pattern in Table 2, but it still affords comparison over the time span discussed.

Table 2. Relative mobility of lead versus arsenic in contaminated Missouri soils.

Sample	Name	As (0-5) / As (5-10)	Pb (0-5) / Pb (5-10)	Pb/As (0-5) / Pb/As (5-10)
1	Unity Village	1.43	3.74	2.61
2	Carver	1.44	5.69	3.95
3	Head	1.43	1.41	0.99
*		1.09	1.69	1.55
4	Gudeas	1.20	2.16	1.80
5	Stephens	0.85	1.12	1.32
6	Pioneer	3.87	7.19	1.86
8	Russell	0.34	2.19	6.44
9	Maples	2.56	1.88	0.73
*		1.29	2.86	2.21
10	Lindsay	0.83	1.68	2.02
12	Rau	1.07	1.30	1.21
Mean		1.45	2.97	2.05

*Ratio of 0-5 cm/10-20 cm.

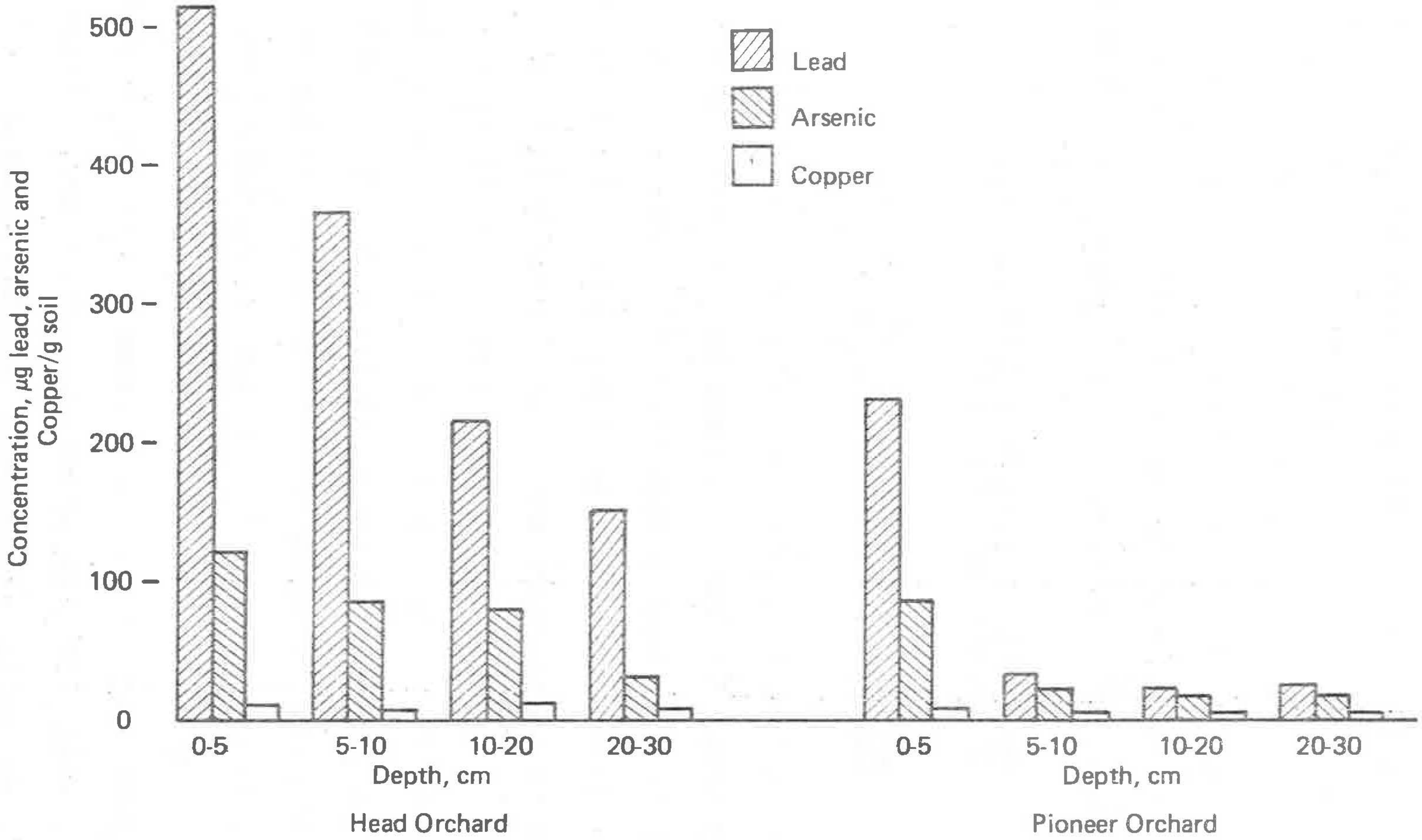

Figure 4. Comparison of lead, arsenic and copper concentrations from an orchard (Head) treated with lead arsenate from about 1910 to 1955 with an orchard (Pioneer) treated with lead arsenate since 1952.

The Pb/As ratios found in Table 2 confirm the postulate that lead arsenate dissociates upon contact with the soil. The relative degree of mobility of Pb versus As in the soil can be arrived at by considering the ratio of Pb concentration in the 0-5 cm horizon to the 5-10 cm horizon versus the As concentration in these horizons. In considering the Sharpsburg silt loam sample,

$$\frac{\text{Concentration As at 0-5 cm}}{\text{Concentration As at 0-10 cm}} = 1.43 \qquad 1$$

$$\frac{\text{Concentration Pb at 0-5 cm}}{\text{Concentration Pb at 5-10 cm}} = 3.74 \qquad 2$$

dividing 2 by 1 yields 2.61, indicating that in the Sharpsburg silt loam, arsenate is 2.61 times as mobile as Pb in progressing from the 0-5 cm horizon to the 5-10 cm horizon. A wide range of mobility of Pb versus As is found in Missouri soils, as listed in Table 2, with an average of As 2.05 times as mobile as Pb in moving from the 0-5 cm horizon to the 5-10 cm horizon. The average decrease in the Pb/As ratio for the heavily contaminated soils in going from the 0-5 cm horizon to the 5-10 cm horizon is 2.35, and in the mildly contaminated soils, it is 2.77. Perhaps Pb forms stable compounds with organic constituents since these samples range from 4-6% organic matter. There are two exceptions among the soils tested, and these are samples from the Head and Maples Orchards both located in Lawrence county on Baxter gravelly loam and Newtonia silt loam, respectively. Probably, the proper conditions do not exist in the 0-5 cm horizon of these soils to fix the Pb more permanently than the arsenic, thus it is more mobile in moving through the upper 10 cm of the profile. However, the mobility of Pb decreases below a depth of 10 cm in these soils.

Several reasons have been offered to explain the mobility of Pb in the soil. Wright, Levick, and Atkinson (27) suggested plant transport as a possible cause, while Swain and Mitchell (23) and Schnitzer and Skinner (21) postulated that Pb forms stable complexes with fulvic acid and other organic molucules. Slinger and Hanson (22) found that Pb forms highly insoluble carbonates and sulfates in the soil. Lead may also be adsorped strongly onto clay particles. Any one or a combination of these reasons may explain the low mobility of Pb in the soil. Marten and Hammond (19) found that chelating agents increased the solubility of Pb in the soil they worked with, which could be the case in the Head and Maples Orchards.

Although As was more mobile than Pb in most soils, it is not very mobile when compared with other elements. After a century from the beginning of treatment on the Unity Village soil, the As had migrated 20 cm or less, with most of it remaining in the upper 5 cm. The insoluble

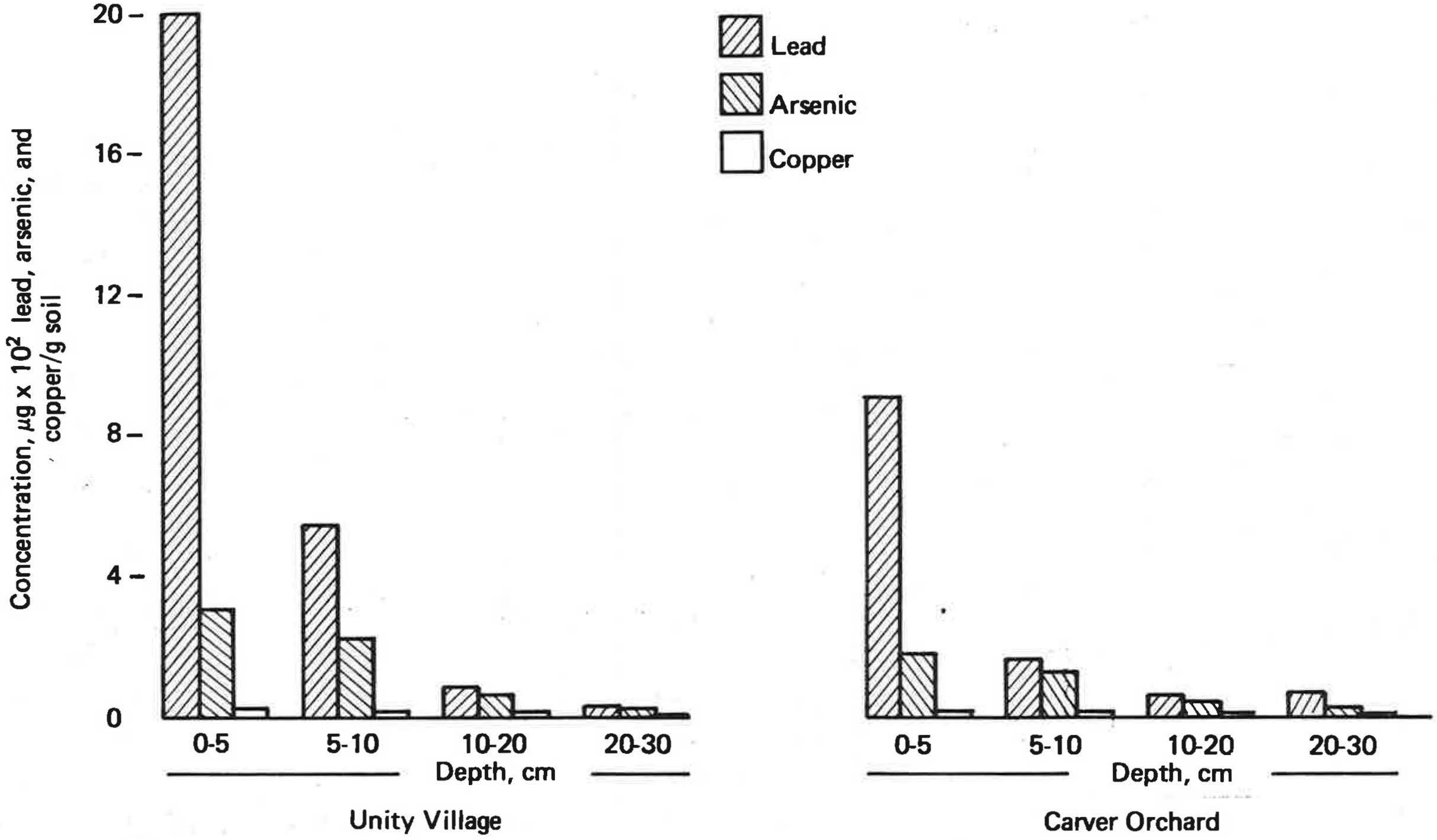

Figure 5. Comparison of lead, arsenic and copper concentrations from an orchard (Unity Village) treated with lead arsenate for 75-80 years with an orchard (Carver) treated for 40-50 years.

compounds that arsenate forms with Fe, Al, Mn, and Ca may account for the immobility of arsenate in the soil. Johnson and Hiltbold (14) showed that arsenate was associated with Al in the soil, and Deuel and Swoboda (9) indicated in the soil they worked with that As was precipated as Fe compounds. This suggests that As forms the Fe and Al compounds readily after being applied to the soil, and that the As will remain near the surface. A detailed evaluation of the forms of stable arsenates likely to occur in soil is presented in Chapters 5 and 6.

Bray P_1 and P_2 Tests for Available Arsenic

In order to determine the effect of As in soils highly contaminated with As on the Bray tests for available phosphorus, both tests were performed on the soils in the survey. The Bray extract was divided and from a fraction of the extract, arsine was evolved and absorbed in iodine solution as outlined in Chapter 3. Phosphorus was determined on a second fraction without any changes from the procedure of the Bray tests. Table 2 shows that a significant error in the estimation of available P can occur in soils that are highly contaminated with As. Unity Village, which has a total As level of 300-350 µg As/g soil, would yield an error of 12.2% for the P_1 test and 14.8% for the P_2 test if consideration were

Table 3. Comparison of Bray 1 and 2 tests in extracting arsenic and phosphorus from soils.

	Depth	Bray Test				P Error	
		P_1	P_2	P_1	P_2	P_1	P_1
	cm	µg As/g soil		µg P/g soil		%	
Unity Village	0- 5	7.1	16.8	24	47	12.2	14.8
	5-10	3.8	16.9	17	22	9.3	11.3
	10-20	2.0	2.9	13	14	6.4	8.6
Carver	0- 5	3.5	7.3	58	82	2.5	3.7
	5-10	2.8	4.6	31	77	3.7	2.5
	10-20	1.3	2.4	19	58	2.8	1.7
Head	0- 5	3.3	7.0	58	82	2.4	3.5
	5-10	2.8	4.4	31	78	3.7	2.3
	10-20	1.5	4.6	17	58	3.6	3.3
Gudeas	0- 5	3.9	10.3	122	122	1.3	3.5
	5-10	2.7	7.5	125	119	0.9	2.6
	10-20	2.4	3.8	122	108	0.8	1.4
Pioneer	0- 5	2.0	4.0	41	68	2.0	2.4
	5-10	1.0	1.5	11	32	3.8	1.9

not given to the available arsenic. From the high of 14.8% error in the estimation of available phosphorus, the error ranges down to a low of 0.8%. It is suggested that in using tests for available P, from areas that are known to have As contamination, that the As also be determined from the Bray extract, thus allowing for a correction factor in the estimation of P.

Nutrient Levels of Soils Surveyed

Table 4 lists the results of soil tests for nutrients of the soils surveyed in this study. These analyses were performed by the Agriculture Experiment Station in Portageville, Missouri. Other than the caution suggested in using the Bray tests for available P, the results of the analyses indicate that the 0-5 cm layer of the orchard soils are high in organic matter, and that the organic matter decreases with increasing depth. The pH values are all acid except for the soils of Ray county which were formerly used to grow potatoes and are now used to grow corn and soybeans. The levels of the other nutrients appear to depend on the treatment that has been applied, and this would vary from one location to the next.

Table 4. Nutrient levels in Missouri soils.*

Sample	Location	Depth	Available P P$_1$	 P$_2$	O.M.	pH	pHs	H	Ca	Mg	K	CEC
		cm	lbs/acre		%			me/100 g	—— lbs/acre ——			me/100 g
1	Unity Village	0- 5	110	215	6.2	5.7	5.0	6.0	4300	250	513	19.0
		5-10	65	72	3.3	5.1	4.4	10.3	2500	230	490	18.0
		10-20	25	35	2.9	4.8	4.2	11.3	2100	230	350	17.8
		20-30	16	19	3.3	5.1	4.5	9.0	3300	350	358	19.3
2	Carver Orchard	0- 5	122	140	5.9	5.2	4.6	8.0	2600	200	372	15.5
		5-10	64	55	3.0	4.9	4.3	7.5	1300	90	268	11.5
		10-20	32	28	2.6	4.8	4.1	8.0	1200	80	220	11.3
		20-30	35	23	2.7	4.9	4.4	6.8	1400	90	211	10.8
3	Head Orchard	0- 5	266	376	5.9	5.9	5.1	4.3	3000	280	432	13.3
		5-10	261	353	2.9	5.9	5.1	3.8	2100	150	352	10.0
		10-20	87	264	2.1	6.2	5.4	2.3	2300	140	305	8.8
		20-30	48	142	2.0	6.1	5.3	2.8	2100	180	222	8.8
4	Gudeas Orchard	0- 5	552	552	5.6	6.3	5.8	3.8	5400	390	600	19.5
		5-10	546	511	2.5	6.0	5.3	4.5	3100	250	600	14.8
		10-20	497	476	1.9	5.9	5.2	4.0	2900	290	600	13.3
		20-30	351	390	1.4	5.9	5.3	4.0	3700	530	600	16.0
5	Stephens Orchard	0- 5	248	291	5.2	5.9	5.3	5.0	3300	260	600	15.3
		5-10	108	142	3.1	6.2	5.6	3.3	3300	200	600	13.0
		10-20	41	60	1.7	6.5	5.7	3.0	3200	200	600	12.5
		20-30	37	37	1.4	6.2	5.6	3.0	3700	340	600	14.5

Table 4 (continued)

Sample	Location	Depth	Available P P1	 P2	O.M.	pH	pHs	H	Ca	Mg	K	CEC
		cm	lbs/acre		%			me/100 g	—— lbs/acre		——	me/100 g
6a	Pioneer Orchard	0- 5	188	312	3.8	6.7	6.1	1.5	3400	230	410	11.5
		5-10	48	147	1.4	6.3	5.7	2.3	2100	200	308	8.5
		10-20	44	83	1.2	6.0	5.4	2.5	2000	240	280	8.5
		20-30	76	124	0.9	5.6	5.0	3.5	2300	370	290	11.0
6a	Pioneer Orchard	0- 5	234	316	2.7	6.8	6.2	2.0	3300	290	592	12.0
		5-10	147	211	2.1	6.5	5.9	2.5	1300	100	366	6.5
		10-20	87	128	1.2	5.3	4.8	5.0	2300	310	288	12.5
		20-30	119	174	0.9	5.0	4.4	6.5	2200	410	240	14.0
7	Diebold Orchard	0-30	273	348	2.4	6.5	6.0	2.3	3900	445	342	14.3
8	Russell Orchard	0- 5	321	319	3.9	5.4	4.7	6.0	1400	330	439	11.5
		5-10	241	243	1.7	5.1	4.5	5.8	900	220	318	9.3
		10-20	87	113	1.2	5.0	4.4	5.3	1100	320	293	9.8
		20-30	83	145	1.3	4.9	4.2	7.5	1300	510	293	13.3
9	Maples Orchard	0- 5	238	245	5.0	5.5	4.9	5.3	1900	160	492	11.0
		5-10	140	156	1.8	5.7	4.9	3.0	1000	110	425	6.5
		10-20	71	76	1.8	5.6	4.9	3.8	1000	120	393	7.3
		20-30	44	55	1.4	5.5	4.8	3.3	1400	170	386	7.8
10	Lindsay Orchard	0- 5	628	609	4.9	5.7	5.2	5.0	2400	260	590	13.0
		5-10	628	609	2.1	5.6	5.0	5.0	2300	210	492	12.0
		10-20	641	628	1.3	5.8	5.1	4.0	2500	260	600	12.0
		20-30	641	628	1.0	5.9	5.3	3.5	3100	410	600	13.5

Table 4 (continued)

Sample	Location	Depth	Available P		O.M.	pH	pHs	H	Ca	Mg	K	CEC
			P_1	P_2								
		cm	lbs/acre		%			me/100 g	—— lbs/acre ——			me/100 g
11	Wiley Farm	0-30	456	444	2.9	6.3	5.6	2.5	1900	185	600	8.8
12	Rau Orchard	0- 5	46	99	3.8	5.5	5.0	4.5	2100	300	187	11.3
		5-10	35	83	2.3	5.7	5.0	4.0	2000	250	124	10.0
		10-20	25	51	1.3	5.7	5.1	3.8	2100	300	99	10.3
		20-30	46	90	0.9	4.9	4.3	6.0	2000	480	147	13.3
13	Miller's Orchard	0- 5	463	488	2.3	6.0	5.3	3.8	1700	790	436	11.8
		5-10	261	335	1.5	4.9	4.2	6.5	1600	590	330	13.8
		10-20	133	229	0.8	4.7	4.0	10.3	1600	715	266	16.8
		20-30	149	250	0.9	4.3	3.9	9.5	1600	690	251	21.5
14	Edwards Farm	0-30	320	435	2.2	7.2	6.6	0.5	6100	310	552	17.5
15	Gooch Farm	0-30	215	355	1.9	6.7	5.9	1.8	4400	220	294	14.0
16	Offutt Farm	0-30	460	522	1.4	7.3	6.6	0.5	5200	280	600	15.5
17	Artman Farm	0-30	289	499	1.4	7.7	7.1	0.0	5200	230	466	14.5

*Analyses performed by Agricultural Experimental Station, Portageville, Missouri.

CONCLUSION

Missouri soils vary widely in As and Pb concentrations, several orchards and former orchard soils are highly contaminated with both, and the degree of contamination appears to depend on the amount of lead arsenate that had been applied. The depth appears to be a function of how long the lead arsenate was used, and how long since the use was discontinued, however neither As or Pb moved more than 20 cm into the soils. Some orchards with high levels of contamination were found to be less productive than they had been earlier, and this may be attributed to an increased solubility of the Pb and As under waterlogged conditions. Care needs to be used in using the Bray tests to determine available phosphorus on soils that have been highly contaminated with arsenic.

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CHAPTER 5

CHARACTERISTICS OF IRON, ALUMINUM, MANGANESE, CALCIUM, AND LEAD ARSENATES

SYNOPSIS

Iron, aluminum, manganese, calcium and lead arsenates were synthesized in the laboratory. X-ray diffraction patterns showed the arsenates to be amorphous. Chemical analyses were used to determine the chemical formula of each arsenate.

Each arsenate was equilibrated with dilute HCl and NaOH for 7 days at 25° C with constant shaking. The values of $pAl + 3pOH$ and $pAl + pAsO$ were 37.19 and 19.89 for $AlAsO_4 \cdot 4H_2O$ and 36.65 and 18.96 for $AlAsO_4 \cdot 2H_2O$. Values of $pFe + 3pOH$ and $pFe + pAsO_4$ were 32.77 and 16.90 for $FeAsO_4 \cdot 2H_2O$, 35.38 and 19.15 for $FeAsO_4 \cdot 1/5Fe(OH)_3 \cdot 2H_2O$, 39.46 and 20.73 for $FeAsO_3 \cdot 1/2H_2O$, 32.69 and 17.08 for $FeAsO_4 \cdot Fe(OH)_3$, 33.69 and 17.78 for $Fe_2(H_2AsO_4)_3 \cdot H_2O$, and 33.80 and 17.72 for $Fe_2(HAsO_4)_3 \cdot H_2O$. Three $Mn_3(AsO_4)_2$ were prepared and found to have $3pMn + 2pAsO_4$ values of 30.19, 33.73, and 33.59. A calcium arsenate, $Ca_3(AsO_4)_2 \cdot 14H_2O$ had a $3pCa + 2pAsO_4$ value of 18.57. A lead arsenate $Pb_3(AsO_4)_2 \cdot 4H_2O$ was prepared, but the value of $3pPb + 2pAsO_4$ was quite variable. Free energies of formations Mn_3O_4

(-310.6), Mn_3O_4 (-210.82), and Mn_2O_3 (-110.65 kcal/mole) were calculated for the reaction of Mn^{2+} with water to form the manganese oxides during the equilibrations of the manganese arsenates.

Arsenate was reacted with freshly precipitated ferric, aluminum, and manganese hydroxides and the results were compared with the Langmuir adsorption isotherm. The reaction of arsenate with freshly precipitated manganese hydroxide followed the Langmuir adsorption isotherm, while the reactions of arsenate with freshly precipitated aluminum and ferric hydroxides did not.

INTRODUCTION

Arsenic has been added directly or indirectly to the soil for many years, as pesticides, soil sterilants, in manure from farm animals which had been fed arsenical additives, and from industrial wastes. It has been assumed that arsenate added to soil forms insoluble complexes with calcium, iron, and aluminum in the same manner as does phosphate. Deuel and Swoboda (5) found that arsenate forms insoluble precipitates with Fe in the soil that they worked with, while Johnson and Hiltbold (7) found that it forms insoluble aluminum arsenates in the soil they worked with.

Arsenic occurs most frequently in nature in the pentavalent state as arsenate (19), and when applied to soils it has usually been as lead arsenate. There are numerous cations in the soil with which arsenate can react to form insoluble compounds. The objective of this chapter is to delineate some of the possible arsenate compounds that may form in the soil under normal conditions, and to use this information as a basis for forming a model of the solubilities of various arsenates in the soil. Because of their importance in soil systems and as plant nutrients, iron, aluminum, manganese, and calcium were examined for their relationships with arsenate. Lead arsenate was included because it was found to be the dominate form of arsenate applied to apple trees in the state.

MATERIALS AND METHODS

Synthesis and Description of Arsenate Salts

In synthesizing the arsenates the cation was added to sodium arsenate over a period of 1.5 hr through a 100 ml buret. The reaction temperature was 95 ± 5° C, and the reaction mixture was stirred with a magnetic stirrer throughout the reaction. An excess of arsenate was always used. Temperature and volume were maintained for 6 hr after addition was complete. The precipitates were placed on a Buchner funnel and washed free of excess salts, air dried, and ground with a mortar and pestle.

Ferric arsenates. F1 was synthesized by adding 100 ml of 0.1 M $FeCl_3 \cdot 6H_2O$ to 100 ml of 0.1 M $Na_2HAsO_4 \cdot 7H_2O$. The solution was maintained at a pH of 6.0 ± 0.5 and an Eh of 300 ± 50 mV with HNO_3 or NaOH. The resulting precipitate was a pale green powder.

F2 was synthesized in the same manner as F1, except that the pH and Eh were allowed to change with the addition of ferric chloride to the solution. After the addition was complete, the pH was adjusted to 6.0 with NaOH. The resulting precipitate was an orange powder.

F3 was synthesized in the same manner as F1, except that 0.1 M sodium arsenite was used in place of 0.1 M sodium arsenate. The resulting precipitate was a yellow powder.

F4 was synthesized according to the procedure of Deuel and Swoboda (5) by adding the sodium arsenate to ferric cholride that had the pH adjusted to 5.5 ± 0.5. This pH was maintained throughout the addition of sodium arsenate to ferric chloride. The resulting precipitate was a brown powder.

F5 was synthesized in the same manner as F1, except that the pH was maintained at 4.5 ± 0.5. The resulting precipitate was a dark green solid that became a pale green powder upon crushing.

F6 was synthesized in the same manner as F1, except that the pH was maintained at 5.0 ± 0.5. The resulting precipitate was a pale green powder.

Aluminum arsenates. T1 was prepared by adding 100 ml of 0.1 M $AlCl_3 \cdot 6H_2O$ to 100 ml of 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ with the pH maintained at 4.5 ± 0.5. The resulting precipitate was a white powder.

T2 was synthesized by adding 100 ml of 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ to 100 ml of 0.1 M aluminum chloride with the pH maintained at 4.5 ± 0.5. The resulting precipitate was a white powder.

Manganese arsenates. T3 was synthesized by dissolving 0.5 g Mn in 8N HNO_3 solution diluting to 100 ml and then slowly adding it to 0.1 M sodium arsenate. The pH was allowed to change during the addition of Mn to the arsenate, and was adjusted to 6.0 with NaOH after the addition was complete. The resulting precipitate was a light brownish violet powder.

T4 was prepared in the same manner as T3, except that the pH was maintained at 6.0 ± 0.5 during the reaction. The resulting precipitate was a pale pink powder.

T5 was synthesized by adding 0.1 M $MnCl_2 \cdot 4H_2O$ to the sodium arsenate. The pH was maintained at 6.0 ± 0.5. The resulting precipitate was a pink powder lighter in color than was T4.

Calcium arsenate. T6 was synthesized by adding 0.3 M $CaCl_2$ to 0.2 M sodium arsenate and maintaining the pH at 5.0 ± 1.0. The resulting precipitate was a white powder.

Lead arsenate. T7 was formed by adding 0.3 M $Pb(NO_3)_2$ to 0.2 M sodium arsenate and maintaining the pH at 5.0 ± 0.5. The resulting precipitate was a white powder.

X-Ray Diffraction Analysis of the Arsenate Salts

A 2 ml suspension of each arsenate compound containing approximately 0.2 g of arsenate was placed on a 2.5 x 5.0 cm glass slide and allowed to dry. An X-ray diffractogram of each arsenate was made using a G.E. Model # XDR5 X-ray diffractometer.

Chemical Analysis of the Arsenate Salts

Two hundred mg of each arsenate was dissolved in a minimum of concentrated HCl, and diluted to 1000 ml, as a stock solution. The stock solution was diluted 1:10, 1:100 or 1:1000 as necessary to determine the cation and As concentrations.

The solutions were analyzed for As without evolving the arsine as described in Chapter 3, except for ferric arsenite. It was necessary to convert the arsenite to arsenate, and this was done by evolving the As and collecting it in iodine solution.

All samples were made to 0.05% KCl and 0.5% $LaCl_3$ to compensate for interference in the determination of Al and Ca. Aluminum was determined by flame emission using a nitrous oxide-acetylene flame at a wavelength of 395.3 nm. Iron, lead calcium and manganese were determined by atomic absorption spectrophotometry at wavelengths of 248.3 nm, 217.0 nm, 422.8 nm, and 279.4 nm, respectively.

Determination of Ion Products

Two g of each arsenate were placed in a 50 ml centrifuge tube and 40 ml of dilute HCl or NaOH were added. The initial pH of the added solutions were 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, and 8.00. The arsenates were equilibrated with the solutions in a constant temperature water bath at 25° C for 7 days with constant shaking. After equilibration, the samples were centrifuged, Eh, pH, specific conductivity, total As, and cations in solution were measured.

Activity coefficients were estimated using the extended form of the Debye-Huckel Equation [1]

$$\text{Log } 1/\gamma = 0.509Z^2\sqrt{I}/(1 + aB\sqrt{I}) \qquad [1]$$

Ionic strength (I) was estimated from the empirical relationship derived by Ponnamperuma et al. (14), in which the specific conductance in μ mhos was multiplied by 1.5×10^{-5}. The term $\underline{\gamma}$ equals activity coefficient, $\underline{Z}$ equals charge, $\underline{a}$ equals effective radius of the ion and $\underline{B}$ equals a constant which accounts for variations in electrical properties of water.

Total As, Fe, Al, Mn, Ca, and Pb in solution were considered to be composed of the following:

$$As_t = [AsO_4^{3-}]_c + [HAsO_4^{2-}]_c + [H_2AsO_4^-]_c + [H_3AsO_4]_c + [AsO_2^-]_c \quad [2]$$

$$Fe_t = [Fe^{3+}]_c + [FeOH^{2+}]_c + [Fe(OH)_2^+]_c + [Fe(OH)_{3\ colloidal}]_c + [Fe^{2+}]_c \quad [3]$$

$$Al_t = [Al^{3+}]_c + [AlOH^{2+}]_c \quad [4]$$

$$Mn_t = [Mn^{2+}]_c + [MnOH^+]_c \quad [5]$$

$$Ca_t = [Ca^{2+}]_c + [CaOH^+]_c \quad [6]$$

$$Pb_t = [Pb^{2+}]_c + [PbOH^+]_c \quad [7]$$

Activities of various species were solved for by expressing terms in Equations [2], [3], [4], [5], [6], and [7] in measurable parameters. The computation was done on an IBM 370/168 computer.

Sources and values for constants used to solve the equations derived are presented in Table 1.

Reaction of Arsenate on Freshly Precipitated Ferric, Aluminum, and Manganese Hydroxides

The hydroxides of aluminum and iron were prepared by adding 50 ml of 0.3 N NaOH to 100 ml each of 0.05 M ferric chloride and 0.05 M aluminum chloride and diluting to 200 ml. The 200 ml suspensions contained 0.534 g ferric hydroxide or 0.390 g aluminum hydroxide. Fifty ml

Table 1. Constants used in computations of ion products.

Constant	Form of equation			Source
K1	$(H_2AsO_4^-)(H^+)/(H_3AsO_4)$	=	5.71×10^{-3}	(16)
K2	$(HAsO_4^{2-})(H^+)/(H_2AsO_4^-)$	=	1.74×10^{-7}	(16)
K3	$(AsO_4^{3-})(H^+)/(HAsO_4^{2-})$	=	2.52×10^{-12}	(16)
K4	$(FeOH^{2+})(H^+)/(Fe^{3+})$	=	3.46×10^{-3}	(11)
K5	$(Fe(OH)_2^+)(H^+)/(Fe^{3+})$	=	6.92×10^{-8}	(11)
K6	$(Fe(OH)_{3col}(H^+)^3/(Fe^{3+})$	=	2.69×10^{-14}	(11)
K7	$(AlOH^{2+})(H^+)/(Al^{3+})$	=	1.05×10^{-5}	(15)
K8	$(MnOH^+)(H^+)/(Mn^{2+})$	=	3.55×10^{-4}	(17)
K9	$(CaOH^+)(H^+)/(Ca^{2+})$	=	4.99×10^{-2}	(6)
K10	$(PbOH^+)(H^+)/(Pb^{2+})$	=	1.49×10^{-8}	(16)
E°_{Fe}	$E - 0.059 \log (Fe^{3+})/(Fe^{2+})$	=	0.771	(11)
E°_{As}	$E - 0.030 \log (AsO_4^{3-})(H^+)^4/(AsO_2^-)$	=	0.911	(16)

of 0.2 N NaOH were added to 100 ml of 0.05 M manganese chloride, and diluted to 200 ml, resulting in 0.445 g manganese hydroxide. While each mixture was being continuously stirred with a magnetic stirrer, 25 ml aliquots of each of the suspensions were transferred to 5 centrifuge tubes of 50 ml capacity.

Sodium arsenate, 1.253 g, was dissolved and diluted to 1000 ml, resulting in a 300 ppm As stock solution. Dilutions of 1:2, 1:4, 1:8, and 1:16 were made, and 5 ml of each dilution were added to a 50 ml centrifuge tube containing the hydroxide. The resulting As concentrations were 50, 25, 12.5, 5.25, and 3.13 ppm As. The arsenate-hydroxide mixture was reacted for 16 hr at 25° C, after which the As in solution was determined, and the amount fixed by the freshly precipitate hydroxide calculated.

RESULTS AND DISCUSSION

Ion Products of Iron, Aluminum, Manganese, Calcium and Lead Arsenates

Based on the results of the X-ray analyses, all of the arsenates synthesized were amorphous. The chemical formula was determined by chemical analysis and the results given in Table 2. Water of hydration was determined by difference in the grams of arsenate and cation per gram of solid material.

Table 2. Formulas and chemical analyses of the synthesized arsenates.

Preparation	Fe	Al	Mn	Ca	Pb	AsO_4	H_2O	Formula
	%							
F1	23.05					58.01	18.94	$FeAsO_4 \cdot 2H_2O$
F2	25.80					52.65	21.55	$FeAsO_4\ 1/5Fe(OH)_3 \cdot 2H_2O$
F3	28.90					43.13	27.95	$FeAsO_3 \cdot 1/2H_2O$
F4	41.80					43.09	15.11	$FeAsO_4 \cdot Fe(OH)_3$
F5	11.75					62.40	25.85	$Fe(H_2AsO_4)_2OH \cdot 3H_2O$
F6	18.00					71.66	10.34	$Fe_2(HAsO_4)_3 \cdot H_2O$
T1		11.80				58.11	30.10	$AlAsO_4 \cdot 4H_2O$
T2		13.60				69.71	16.67	$AlAsO_4 \cdot 2H_2O$
T3			36.15			64.09	0.00	$Mn_3(AsO_4)_2$
T4			37.82			62.20	0.00	$Mn_3(AsO_4)_2$
T5			36.49			63.14	0.00	$Mn_3(AsO_4)_2$
T6				18.64		42.70	38.66	$Ca_3(AsO_4)_2 \cdot 14H_2O$
T7					63.98	26.93	9.09	$Pb_3(AsO_4)_2 \cdot 4H_2O$

After equilibration in dilute HCl and NaOH for 7 days at 25° C, ion products corresponding to pAl + 3pOH, pAl + $pAsO_4$, pFe + 3pOH, pFe + $pAsO_4$, 3pMn + $2pAsO_4$, 3pCa + $2pAsO_4$, and 3pPb + $2pAsO_4$ were computed for each arsenate, and are listed in Tables 3, 4, and 5. Free energies of formation of Mn_3O_4, Mn_2O_3, and MnO_2 were calculated and are listed in Table 4. The ion products computed at pH 2 were not used to compute the mean value for the following species: $AlAsO_4 \cdot 2H_2O$, $FeAsO_4 \cdot 2H_2O$, $FeAsO_4 \cdot 1/5Fe(OH)_3 \cdot 2H_2O$, $Fe_2(HAsO_4)_3 \cdot H_2O$ and the three manganese arsenates. These values were not used to compute the mean, because the computed ion products were two or more orders of magnitude different, and may indicate that ion species in solution were not properly considered in the acid or neutral range.

The concentrations of iron and arsenic are shown in Figures 1, 2, 3, 4, 5, and 6 for the equilibration of various solutions with $FeAsO_4 \cdot 2H_2O$, $FeAsO_4 \cdot 1/5Fe(OH)_3 \cdot 2H_2O$, $FeAsO_3 \cdot 1/2H_2O$, $FeAsO_4 \cdot Fe(OH)_3$, $Fe(H_2AsO_4)_2OH \cdot 1/2\ H_2O$, and $Fe(HAsO_4)_3 \cdot H_2O$, respectively. Each system was tested for congruent dissolution. All of the ferric arsenates had a higher As to Fe ratio than would be predicted from a consideration of dissolution of the compound. There were from 3 to 17 times more moles of As in solution than Fe.

Table 3. Ion products of synthesized aluminum and iron arsenates.*

	$AlAsO_4 \cdot 4H_2O$			$AlAsO_4 \cdot 2H_2O$			$FeAsO_4 \cdot 2H_2O$			$FeAsO_4 \cdot 1/5Fe(OH)_3 \cdot 2H_2O$		
Initial pH	Final pH	pAl + 3pOH	pAl + $pAsO_4$	Final pH	pAl + 3pOH	pAl + $pAsO_4$	Final pH	pFe + 3pOH	pFe + $pAsO_4$	Final pH	pFe + 3pOH	pFe + $pAsO_4$
2	3.00	37.73	20.21	2.72	37.88	20.06	1.87	40.49	21.32	1.68	41.68	22.83
3	3.19	37.26	19.95	3.26	36.51	18.74	5.33	33.03	16.79	3.10	38.01	20.48
4	3.00	38.22	20.79	3.34	36.59	19.09	5.61	32.71	16.84	3.59	37.12	20.05
5	3.00	37.57	20.38	3.32	36.37	19.05	5.62	32.74	16.87	4.66	35.58	19.44
6	3.34	36.30	19.18	3.34	36.32	18.92	5.69	32.68	16.93	4.81	34.16	18.16
7	3.36	37.23	19.98	3.33	36.37	18.83	5.70	32.72	16.97	5.17	33.62	18.04
8	3.41	36.00	18.76	3.37	36.49	19.15	5.73	32.74	16.98	5.74	33.80	18.75
Mean		37.19	19.89		36.65	18.96†		32.77†	16.90†		35.38†	19.15†
S.D.		0.79	0.70		0.55	0.16		0.13	0.08		1.85	1.00

Table 3 (continued)

	$FeAsO_3 \cdot 1/2H_2O$			$FeAsO_4 \cdot Fe(OH)_3$			$Fe(H_2AsO_4)_2OH \cdot 3H_2O$			$Fe_2(HAsO_4)_3 \cdot H_2O$		
Initial pH	Final pH	pFe + 3pOH	pFe + $pAsO_4$	Final pH	pFe + 3pOH	pFe + $pAsO_4$	Final pH	pFe + 3pOH	pFe + $pAsO_4$	Final pH	pFe + 3pOH	pFe + $pAsO_4$
2	2.40	39.22	20.55	5.36	33.09	17.26	5.42	33.39	17.52	2.08	41.57	22.71
3	2.35	39.23	20.38									
4	2.31	39.44	20.84	5.42	32.44	16.47	5.15	33.70	17.68	4.61	34.78	18.05
5	2.31	39.35	20.62									
6	2.25	39.55	20.69	5.64	32.98	17.12	5.15	33.80	17.77	5.41	33.11	17.25
7	2.22	39.38	20.78									
8	2.18	40.03	21.23	6.59	32.26	17.47	5.30	33.87	18.13	5.80	33.51	17.87
Mean		39.46	20.73		32.69	17.08		33.69	17.78		$33.80^{\dagger}$	$17.72^{\dagger}$
S.D.		0.28	0.27		0.40	0.43		0.21	0.26		0.87	0.42

*Eh, total As, Fe and Al, and specific conductance are in Appendix 1, Tables XXIII and XXIV.

†Value at initial pH 2 not used in calculating mean.

Table 4. Standard cell potentials and free energies of formation of Mn_3O_4, Mn_2O_3, and MnO_4 formed by the reaction of $Mn_3(AsO_4)_2$ with dilute HCl and NaOH.*

Preparation	Initial pH	Final pH	Eh	E°†	E°‡	E°§	ΔF°_f Mn_3O_4	ΔF°_f Mn_2O_3	ΔF°_f MnO_2	3pMn + 2pAsO_4
			mV	mV	mV	mV	kcal/mole	kcal/mole	kcal/mole	
T3	2	3.81	772	1269	1179	1088	-331.70	-224.70	-117.71	41.06
	3	7.01	627	1906	1617	1329	-302.34	-204.46	-106.57	29.99
	4	7.32	613	1908	1620	1333	-302.25	-204.33	-106.41	31.01
	5	7.40	608	1976	1666	1355	-299.09	-202.23	-105.37	28.93
	6	7.44	606	1934	1638	1341	-301.05	-203.53	-106.01	30.36
	7	7.44	601	1932	1635	1337	-301.13	-203.66	-106.19	30.29
	8	7.44	597	1920	1625	1331	-301.70	-204.10	-106.50	30.55
Mean				1929	1634	1338	-301.26	-203.72	-106.18	30.19
S.D.				26	18	10	1.192	0.815	0.445	0.70
T4	2	3.85	752	1281	1181	1080	-331.15	-224.61	-118.06	40.05
	3	5.96	631	1650	1427	1205	-314.16	-213.23	-112.29	34.74
	4	6.69	597	1755	1501	1246	-309.30	-209.85	-110.40	33.66
	5	7.01	582	1816	1543	1269	-306.48	-207.91	-109.34	32.78
	6	6.91	555	1743	1483	1223	-309.87	-210.68	-111.48	33.77
	7	6.91	588	1775	1515	1256	-308.37	-209.17	-109.96	33.79
	8	7.00	572	1780	1515	1250	-308.17	-209.20	-110.22	33.65
Mean				1753	1497	1242	-309.39	-210.01	-110.62	33.73†
S.D.				56	39	23	2.61	1.82	1.08	0.62

Table 4 (continued)

Prepa- ration	Initial pH	Final pH	Eh	E°†	E°‡	E°§	ΔF°_f			$3pMn + 2pAsO_4$
							Mn_3O_4	Mn_2O_3	MnO_2	
			mV				kcal/mole			
T5	2	3.83	735	1260	1160	1060	-332.15	-225.56	-118.96	40.13
	3	5.81	646	1640	1423	1206	-312.60	-213.43	-112.25	34.83
	4	5.33	609	1668	1486	1205	-312.55	-211.73	-111.91	33.69
	5	6.61	588	1742	1487	1233	-309.90	-210.46	-111.02	33.18
	6	6.56	580	1711	1463	1215	-311.34	-211.59	-111.83	33.68
	7	6.60	582	1722	1472	1222	-310.81	-211.17	-111.52	33.63
	8	6.58	585	1717	1469	1221	-311.06	-211.31	-111.55	33.87
Mean				1700	1467	1217	-311.38	-211.62	-111.68	33.59
S.D.				38	23	11	1.05	0.99	0.42	0.29

*The values obtained at initial pH 2 were not used in determining the mean.

†Computed for the reaction: $3Mn^{2+} + 4H_2O = Mn_3O_4 + 8H^+ + 2e^-$.

‡Computed for the reaction: $2Mn^{2+} + 3H_2O = Mn_2O_3 + 6H^+ + 2e^-$.

§Computed for the reaction: $Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$.

Table 5. Ion products of synthesized calcium and lead arsenates.*

	$Ca_3(AsO_4)_2 \cdot 14H_2O$		$Pb_3(AsO_4)_2 \cdot 4H_2O$	
Initial pH	Final pH	$3pCa + 2pAsO_4$	Final pH	$3pPb + 2pAsO_4$
2	12.45	16.91	1.82	53.11
3	12.41	18.06	2.90	48.41
4	12.33	18.82	3.64	47.46
5	12.15	17.95	6.23	39.30
6	12.33	18.74	6.40	38.42
7	12.42	18.56	5.46	40.88
8	12.31	19.31	4.20	46.51
Mean		18.57†		44.87
S.D.		0.51		5.45

*Eh, total As, Pb and Ca, and specific conductance are in Appendix 1, Table XXIII.

†$3pCa + 2pAsO_4$ at initial pH 2 not used in calculating mean.

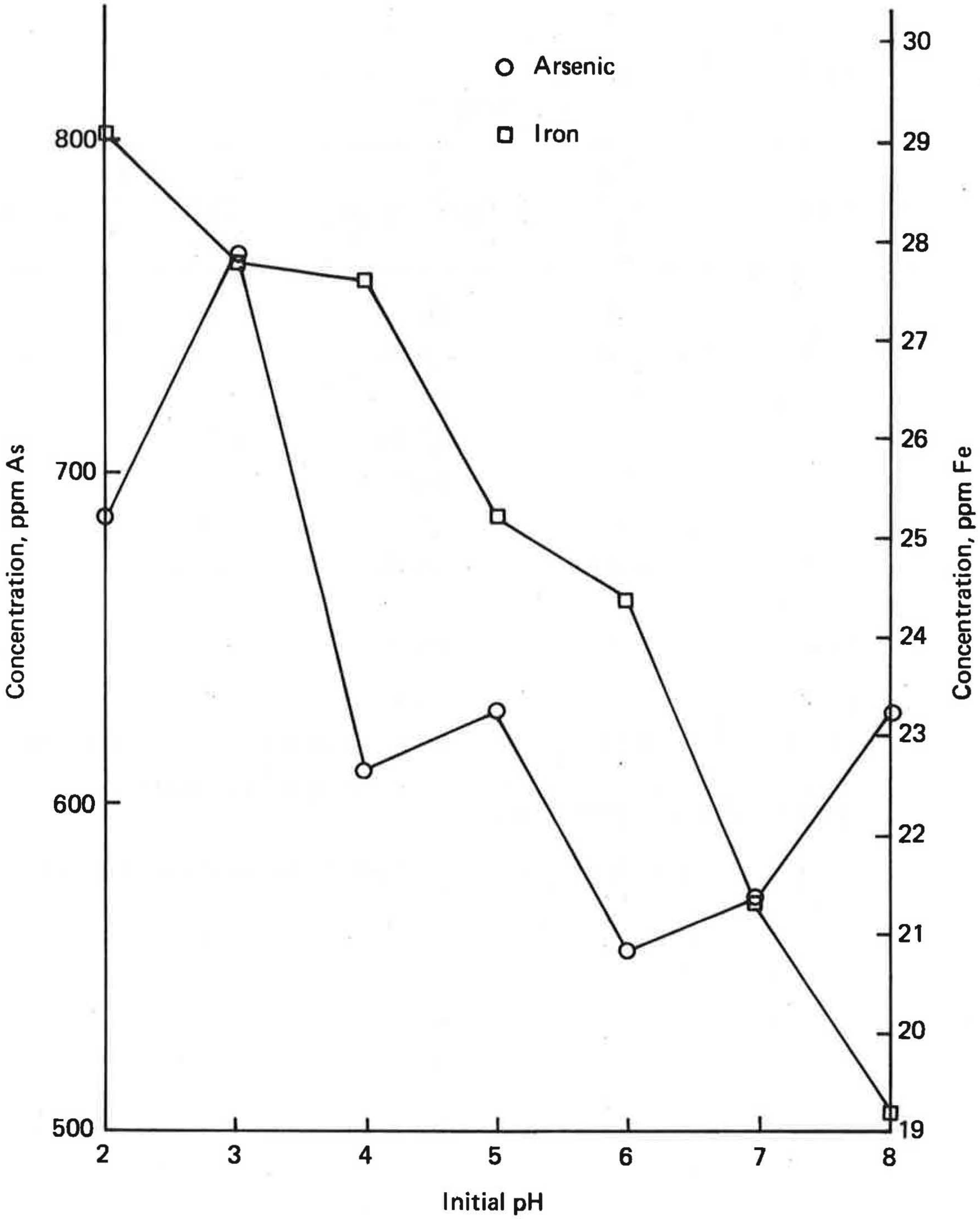

Figure 1. Arsenic and iron concentration in solution after 7 days of shaking $FeAsO_4 \cdot 2H_2O$ with dilute HCl and NaOH at 25° C.

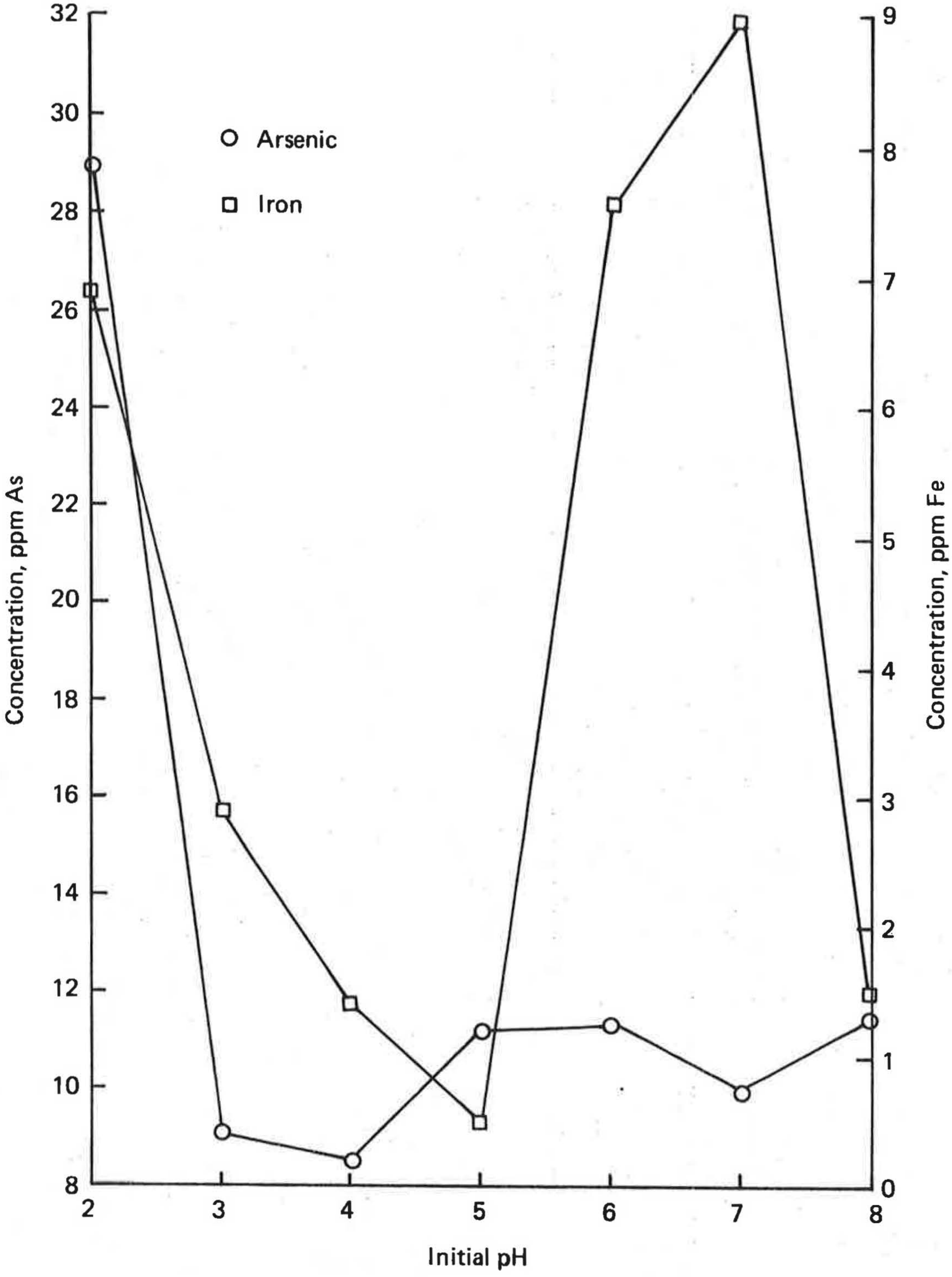

Figure 2. Arsenic and iron concentration in solution after 7 days of shaking $FeAsO_4 \cdot 1/5Fe(OH)_3 \cdot 2H_2O$ with dilute HCl and NaOH at 25° C.

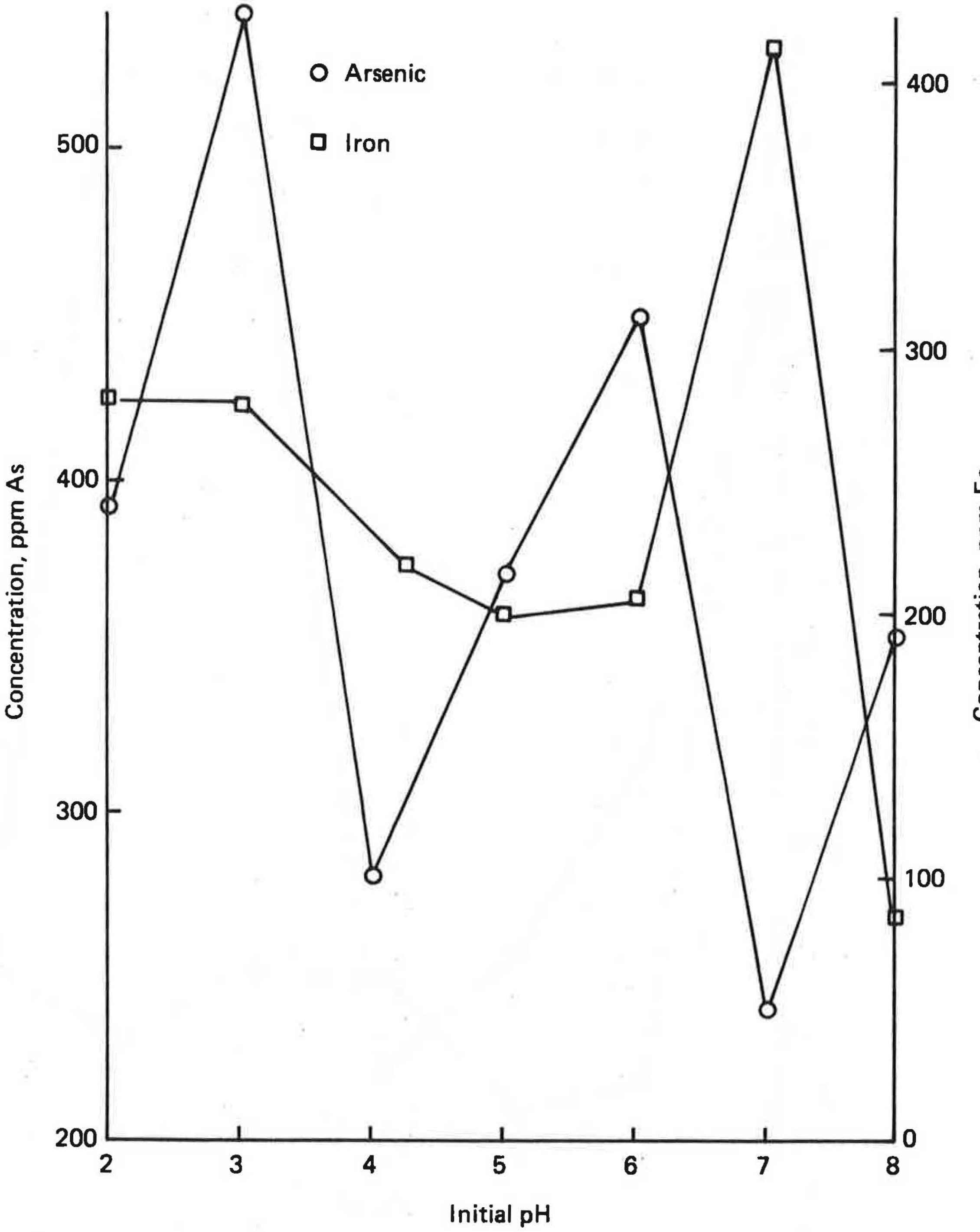

Figure 3. Arsenic and iron concentration in solution after 7 days of shaking $FeAsO_3 \cdot 1/2H_2O$ with dilute HCl and NaOH at 25° C.

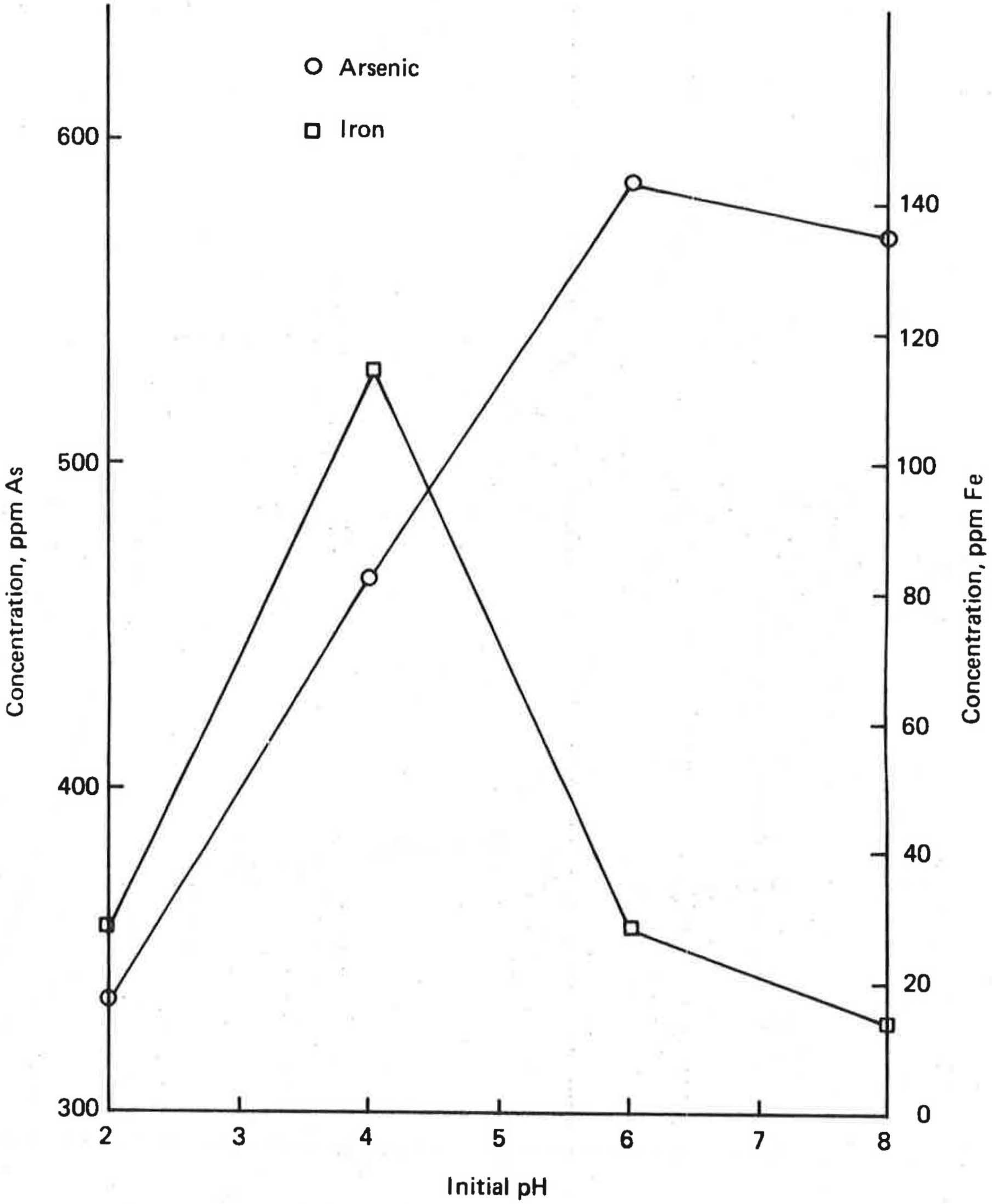

Figure 4. Arsenic and iron concentration in solution after 7 days of shaking $FeAsO_4 \cdot Fe(OH)_3$ with dilute HCl and NaOH at 25° C.

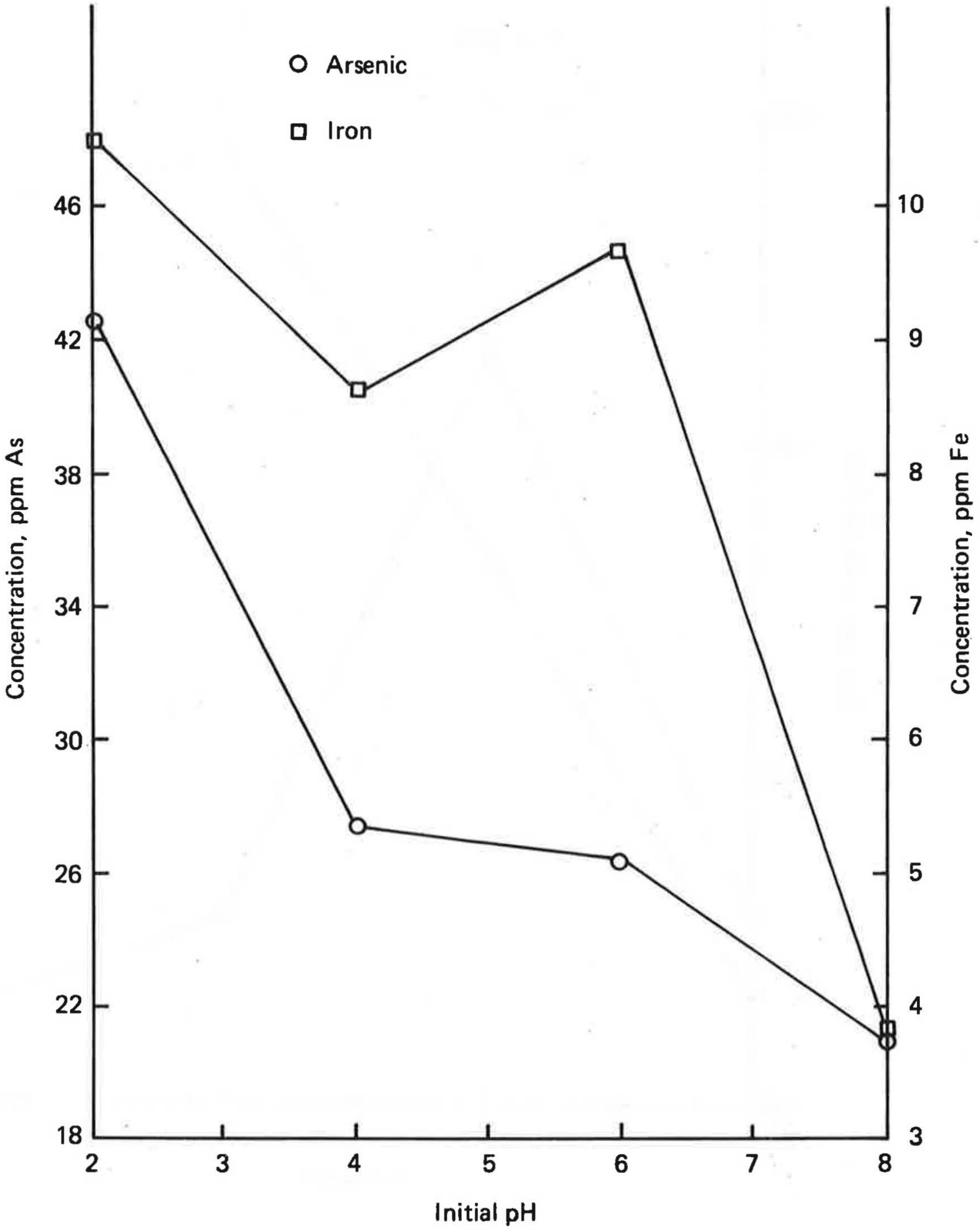

Figure 5. Arsenic and iron concentration in solution after 7 days of shaking $Fe(H_2AsO_4)_2OH \cdot 3H_2O$ with dilute HCl and NaOH at 25° C.

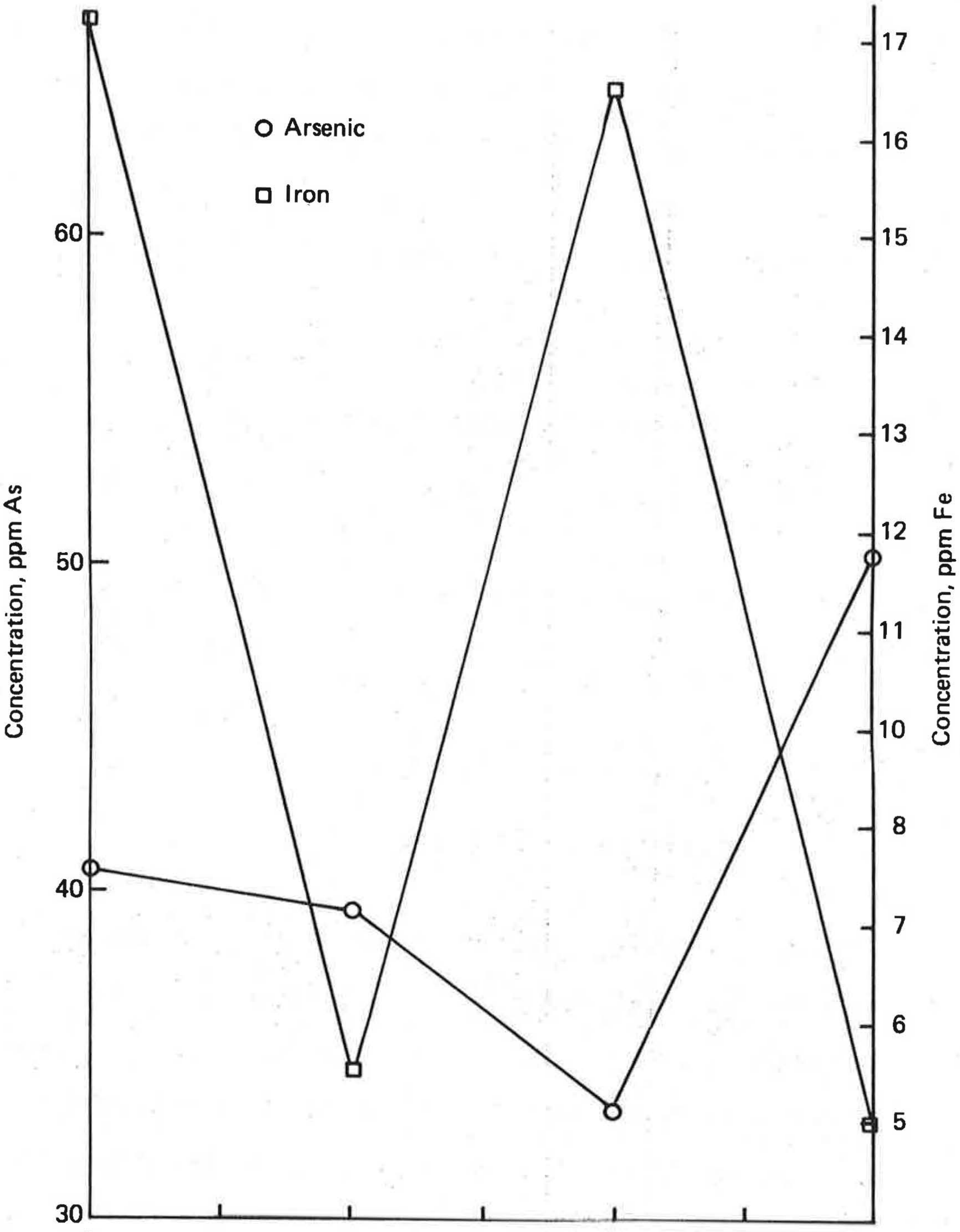

Figure 6. Arsenic and iron concentration in solution after 7 days of shaking $Fe_2(HAsO_4)_3 \cdot H_2O$ in dilute HCl and NaOH at 25° C.

In the case of ferric arsenite the ratio of As to Fe was that predicted from the Stoiciometric composition of the compound. The following reactions depict the dissolution of ferric arsenate, the solution species and the overall reaction to form a solid phase of ferric hydroxide:

$$FeAsO_4 \rightleftarrows Fe^{3+} + AsO_4^{3+} \qquad [8]$$

$$Fe^{3+}\ H_2O \rightleftarrows Fe(OH)^{2+} + H^+ \qquad [9a]$$

$$Fe(OH)^{2+} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+ \qquad [9b]$$

$$Fe(OH)_2^{2+} + H_2O \rightleftarrows Fe(OH)_3 + H^+ \qquad [9c]$$

$$AsO_4^{3-} + H^+ \rightleftarrows HAsO_4^{2-} \qquad [10a]$$

$$HAsO_4^{2-} + H^+ \rightleftarrows H_2AsO_4^- \qquad [10b]$$

$$H_2AsO_4^- + H^+ \rightleftarrows H_3AsO_4 \qquad [10c]$$

Reactions [9a-c] leading to the precipitation of ferric hydroxide would tend to make the solution more acid, while reactions [10a-c] leading to the formation of arsenic acid would tend to neutralize the acid produced in the formation of ferric hydroxide. An overall reaction may be expressed as follows:

$$FeAsO_4 + H_2O \rightleftarrows Fe(OH)_3 + H_2AsO_4^- + H^+ + H_2O \qquad [11]$$

The data presented in Figures 1, 2, 4, 5, and 6, the equilibrium constants in Table 1, and the observed pH values of 3 to 6 in Table 3 tends to support this postulate.

Sergeyeva and Khodakovskiy (18) have determined the stabilities for arsenates and arsenites in geological samples and have shown that $H_2AsO_4^-$ is the predominant form in the pH range of 2.2 to 7.0. The ferric arsenates attain equilibrium in this range, therefore, it would be expected that the addition of ferric arsenate to a solution would tend to increase the pH about 5 to 6.

The incongruency of ferric arsenate dissolution was not consistent for the ferric arsenates synthesized. Two samples, $FeAsO_4 \cdot 2H_2O$, and $FeAsO_4 \cdot Fe(OH)_3$ brought over ten times as many moles of As into solution as they did Fe. $FeAsO_4 \cdot 1/5Fe(OH)_3 \cdot H_2O$, $Fe(H_2AsO_4)_2OH \cdot 3H_2O$, and $Fe_2(H_2AsO_4)_3 \cdot H_2O$ all brought in about three times as many moles As into solution as Fe. For the last two samples, this can be explained by the fact that some $HAsO_4^{2-}$ and $H_2AsO_4^-$ were already present in solution, therefore, there was not as much force in the system to push the equilibration further in that direction. This would also explain why the first two samples have much more As in solution than they do Fe.

The ion products of 32.69 to 35.38 for pFe + 3pOH, where a value of 36-37 is expected, indicate that a complex ion of some sort not accounted for in our computations is reducing the activity of the ferric ion in respect to the total iron in solution (Perhaps the $FeHAsO_4^+$ specie?). The values of $pFe + pAsO_4$ would also be expected to be low by the same value. The equation below can be used to extend our findings presented in Table 3 to the soil system.

$$pAsO_4 + 3pH - 42 = (pFe + pAsO_4) - (pFe + 3pOH) \qquad [12]$$

$$pAsO_4 = 26.07 - 3pH \qquad [13]$$

This relationship is only valid in the presence of freshly precipitated ferric hydroxide. If more stable forms of iron oxide such as Goethite, $pK = 41$ instead of freshly precipitated ferric hydroxide $pK = 36$ control the ferric ion activity the level of arsenate would be predicted to increase proportionally.

The final pH for the dissolution of ferric arsenite was about 2.3, perhaps this was because the arsenite ion does not react with water to take up hydrogen ions the way the arsenate ion does. This may be the reason why ferric arsenite exhibited congruent dissolution and the ferric arsenates did not.

Data showing the amounts of Al and As in solution when $AlAsO_4 \cdot 4H_2O$ or $AlAsO_4 \cdot 2H_2O$ are equilibrated with various solutions are given in Figures 7 and 8. In both cases there was a greater quantity of As in solution than Al. It is probable that a solid phase of $Al(OH)_3$ formed

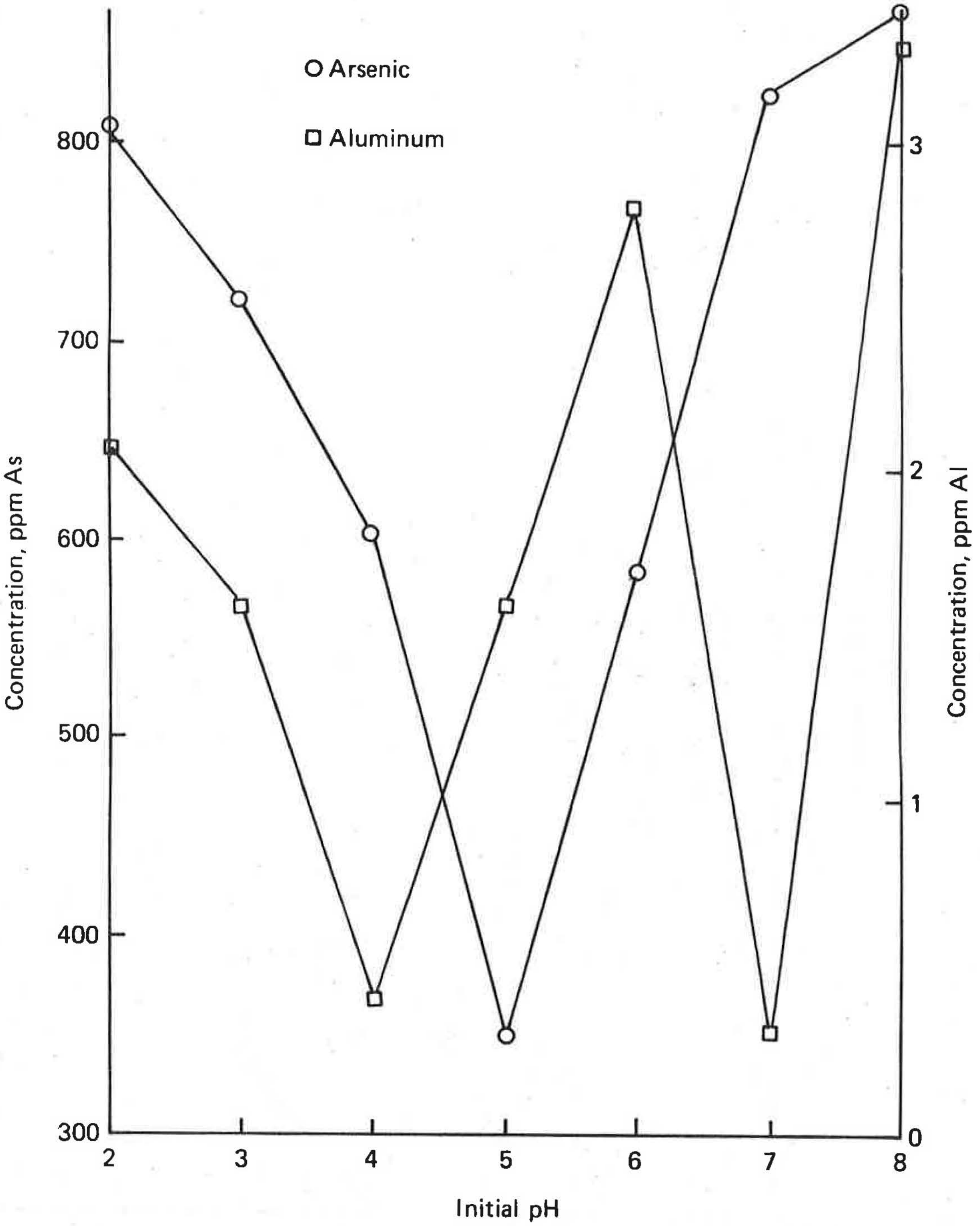

Figure 7. Arsenic and aluminum concentration in solution after 7 days of shaking $AlAsO_4 \cdot 4H_2O$ with dilute HCl and NaOH at 25° C.

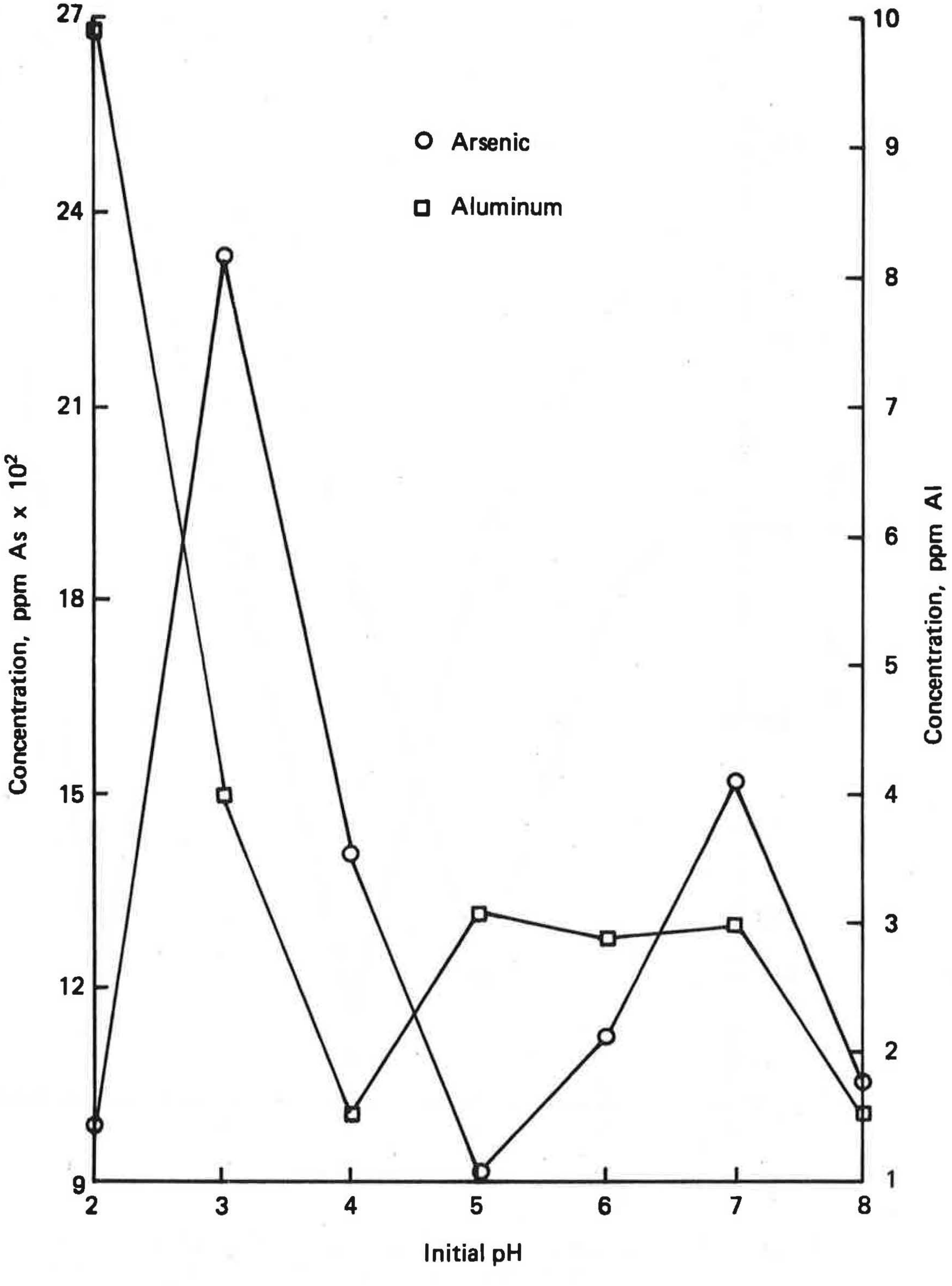

Figure 8. Arsenic and aluminum concentration in solution after 7 days of shaking $AlAsO_4 \cdot 2H_2O$ in dilute HCl and NaOH at 25° C.

during the equilibration as illustrated in Equation [14].

$$AlAsO_4 + 3H_2O \rightleftarrows Al(OH)_3 + H_2AsO_4^- + H^+ \qquad [14]$$

The equilibrium pH of the dissolution of aluminum arsenate is much lower than that of the ferric arsenate, at 3.3, but the species $H_2AsO_4^-$ is still the dominate form of As in solution. According to Misra et al. (12) and Blanchar and Scrivner (2), the ion product of aluminum hydroxide in soils at a pH of about 3 should be about 36, which is the value calculated for aluminum hydroxide in the dissolution of aluminum arsenate. Based on this, it appears that a stable aluminum hydroxide is formed, and this explains the large amount of As in solution shown in Figures 9 and 10.

The factors which affect the ion product of $pAl + 3pOH$ have been investigated as a function of pH but not explained adequately. The values comparing $pAl + 3pOH$ to $pAl + pAsO_4$ cannot be used with a great deal of confidence. Values in Table 3 were used to predict the level of $pAsO_4$ from the measured solubility of aluminum oxide and arsenate as shown in the following equations:

$$pAl + 3pOH = 36.92 \qquad [15]$$

$$+\ 19.43 = pAsO_4 + pAl \qquad [16]$$

$$\underline{42 - 3pH = 3pOH} \qquad [17]$$

$$24.51 - 3pH = pAsO_4 \qquad [18]$$

The manganese arsenates did not undergo congruent dissolution (Figures 9 and 10). Examination of Figure 10 shows that about 1.5 times as many moles As is in solution as is Mn. For the dissolution to be congruent, there would have to be 1.5 moles of Mn for every mole of As in solution. Comparison of the free energies of formation of the manganese oxides listed in the National Bureau of Standards Technical Note 270-4 (17) suggests that stable manganese oxides may form on the dissolution of manganese arsenates. Note 270-4 lists values of -306.7, -210.6, and -111.18 kcal/mole for the formation of Mn_3O_4, Mn_2O_3, and MnO_2, respectively. The calculated free energies of formation for these oxides from manganese arsenate dissolution for preparation: T4 was -311.81, -211.62, and -110.68; and for T5 was -309.39, -210.01, and -110.62, respectively. Based on the free energies of formation, it is highly possible that MnO_2 and Mn_2O_3 would form upon dissolution of manganese arsenate for both preparations T4 and T5 as shown in Equation [19].

$$Mn_3(AsO_4)_2 + H_2O \rightleftarrows Mn_2O_3 + MnO_2 + 2HAsO_2 \qquad [19]$$

Manganese arsenate preparation T3 behaves quite differently than does either of the other manganese arsenates. There are approximately 50 moles of As in solution for every mole of Mn. This may be attributable to the mode of synthesis rather than the actual dissolution.

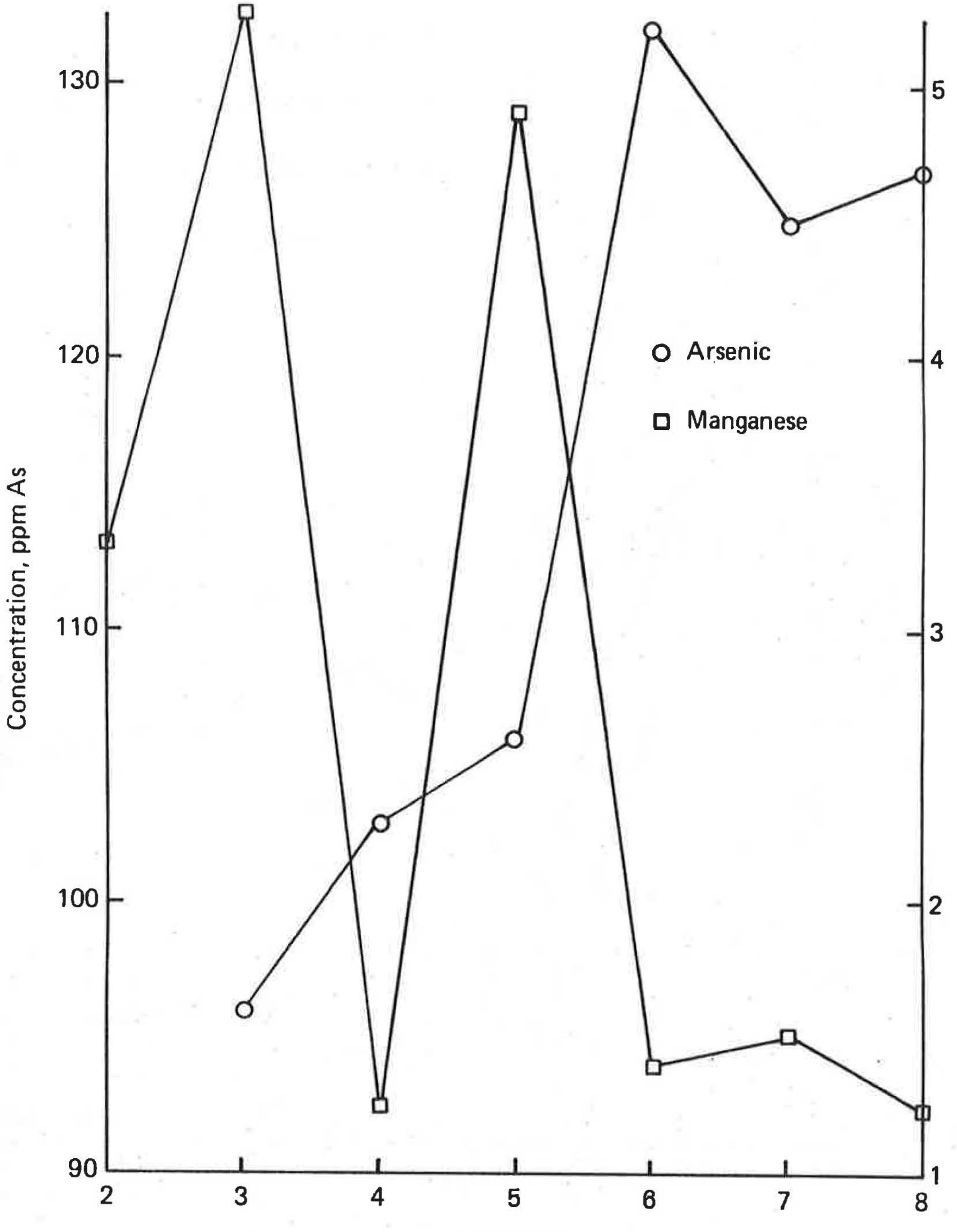

Figure 9. Arsenic and manganese concentration in solution after 7 days of shaking $Mn_3(AsO_4)_2$ (preparation T3) in dilute HCl and NaOH at 25° C.

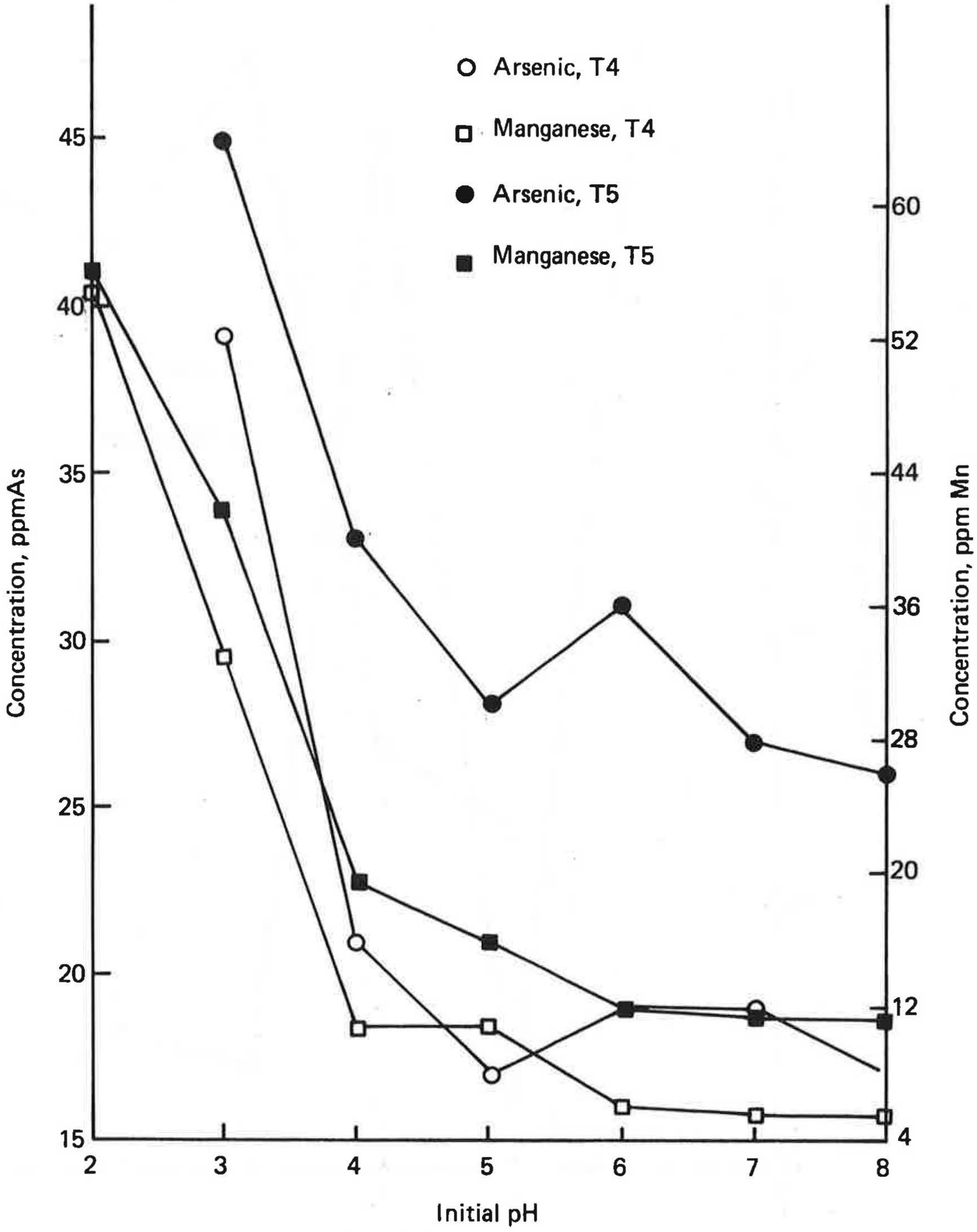

Figure 10. Arsenic and manganese concentration in solution after 7 days of shaking $Mn_3(AsO_4)_2$ (preparations T4 and T5) in dilute HCl and NaOH at 25° C.

The brownish violet color of the compound indicated that MnOOH may have formed. Yamane (21) indicates that MnOOH upon dehydration proceeds toward Mn_2O_3, which is quite insoluble. This would then explain why more As was in solution than Mn.

An analyses of data presented in Table 4 shows that when $18Eh + pH = 16.7$ Mn_2O_3 is as stable as MnO_2. The relationship between $pAsO_4$ was computed for the reaction of $Mn_3(AsO_4)_2$ with Mn_2O_3 below these pH-Eh values and with MnO_2 above these values and shown in Equations [20] and [21], respectively.

$$pAsO_4 = 35.6 - 12.8Eh - 2.3pH \qquad [20]$$

$$pAsO_4 = 47.3 - 25.4Eh - 3pH \qquad [21]$$

The dissolution of calcium arsenate radically departs from the dissolution of the other arsenates. Figure 11 shows that the calcium level of the solution is elevated and Table 6 shows the equilibrium pH to be much higher than the values obtained in the dissolution of the other arsenates. Greater calcium content in the solution can only be explained by a reversion of $Ca_3(AsO_4)_2$ to a compound richer in As. The following reaction is suggested.

$$Ca_3(AsO_4)_2 + 2H_2O \rightleftarrows 2CaHAsO_4 + 2OH^- + Ca^{2+} \qquad [22]$$

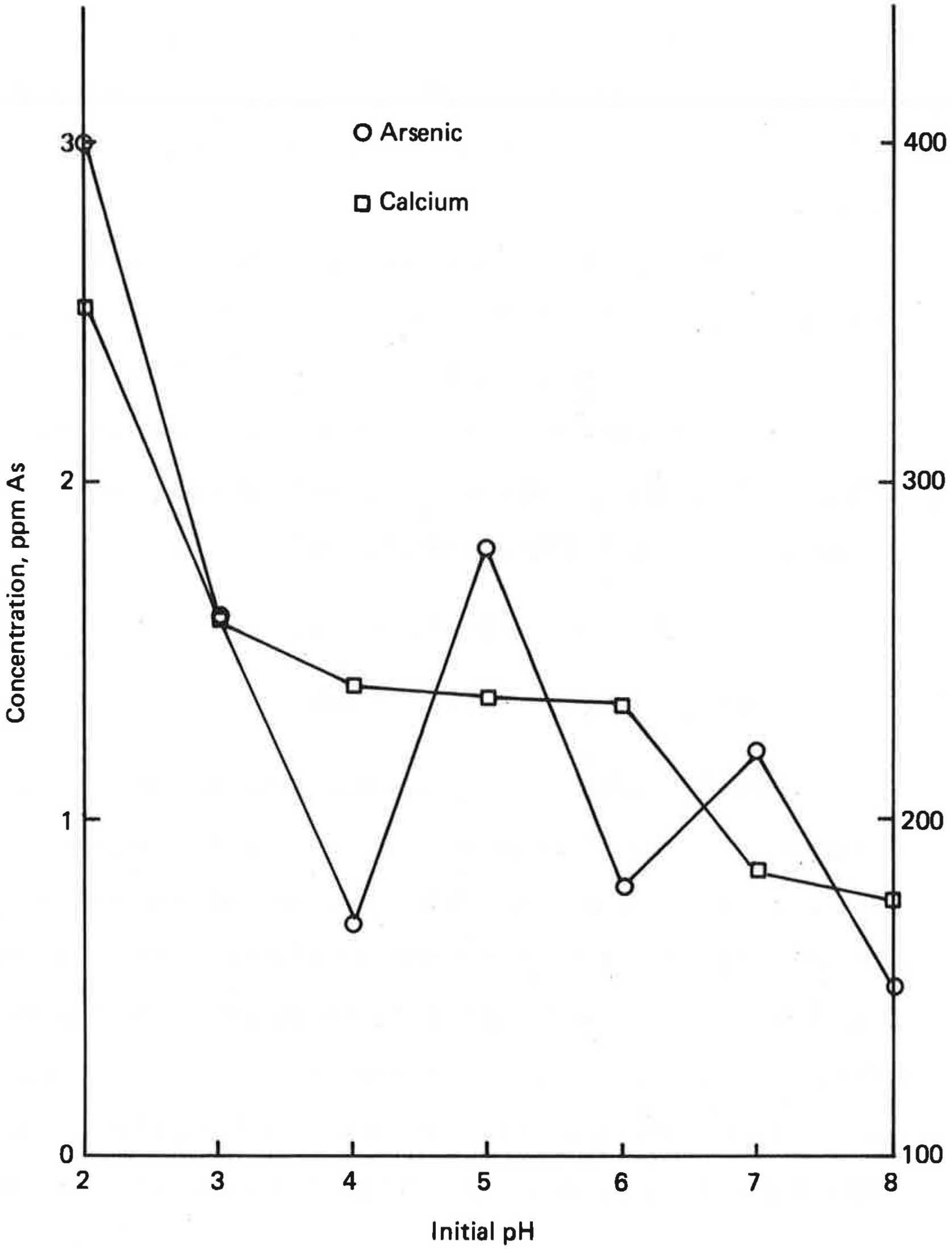

Figure 11. Arsenic and calcium concentration in solution after 7 days of shaking $Ca_3(AsO_4)_2 \cdot 14H_2O$ in dilute HCl and NaOH at 25° C.

It is postulated that the final pH is that where both phases have equal stability. Carbon dioxide was not flushed from the system before equilibration and from the free energies of formation presented in Garrels and Christ (6) with calcium solutions above pH 8, calcium carbonate would be predicted to form. The average value for $3pCa + 2pAsO_4$ of 18.57 is presented in Table 5.

In the dissolution of lead arsenate, about 200 moles of As came into solution for every mole of Pb. The ion products listed in Table 6 change with changing pH, reaching a minimum at final pH of 6.40 (initial pH 6.0), and increasing in both directions. The low ion product value was also the high final pH value. Some naturally occurring minerals may explain the situation with lead arsenate. These are synadelphite ($Pb_4AsO_4(OH)_5$), bayldonite (Pb_2AsO_4OH), georgiadesite ($Pb_3AsO_4Cl_3$), mimetite ($Pb_5(AsO_4)_3Cl$, and lead arsenate chloride ($Pb_3AsO_4Cl_2$). Synadelphite and bayldonite may form and cause the increase in the ion product above an initial pH of 6. Georgiadesite, mimetite, and lead arsenate chloride may form below pH 6, since the equilibration was carried out in dilute HCl. Figure 12 shows the results of the lead arsenate dissolution with changing pH.

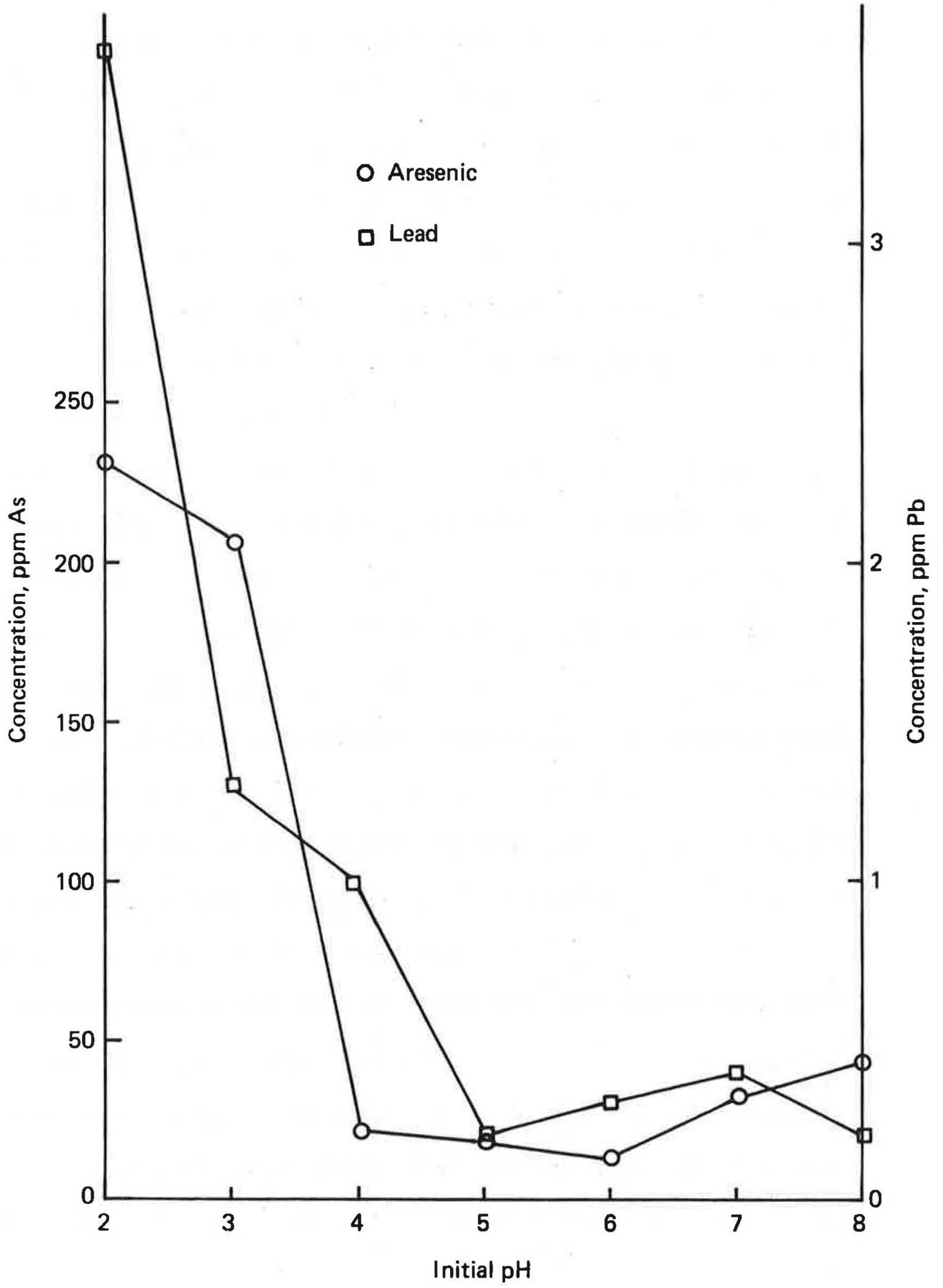

Figure 12. Arsenic and lead concentration in solution after 7 days of shaking $Pb_3(AsO_4)_2 \cdot 4H_2O$ in dilute HCl and NaOH at 25° C.

The values for $3pPb + 2pAsO_4$ presented in Table 5 were extremely variable. However, the values obtained at a final pH near 6, (39.5), are compared with the value of 35.39 reported by Chukhlantsev (3).

Arsenate Sorption on Freshly Precipitated Aluminum, Iron and Manganese Hydroxides

Arsenate was reacted with freshly precipitated manganese, ferric and aluminum hydroxides and the data expressed according to the Langmuir adsorption isotherm. Many studies on the sorption of phosphate in the soil show that phosphate sorption follows the Langmuir adsorption isotherm (4,8,9,13,20), and since arsenate has frequently been compared to phosphate, it was treated in the same manner.

The reaction of arsenate with freshly precipitated manganese hydroxide followed the Langmuir adsorption isotherm (Figure 13). Yamane (21) has pointed out that when sodium hydroxide is added to a solution of Mn^{2+} in the absence of air, that a white precipitate, $Mn(OH)_2$ is formed, and that when this is exposed to the air, the $Mn(OH)_2$ is oxidized to MnOOH, which is brown in color. Since the formation of manganese hydroxide occurred in the presence of air, the reaction of arsenate was with freshly precipitated MnOOH. MnOOH is readily converted to Mn_2O_3 with heat.

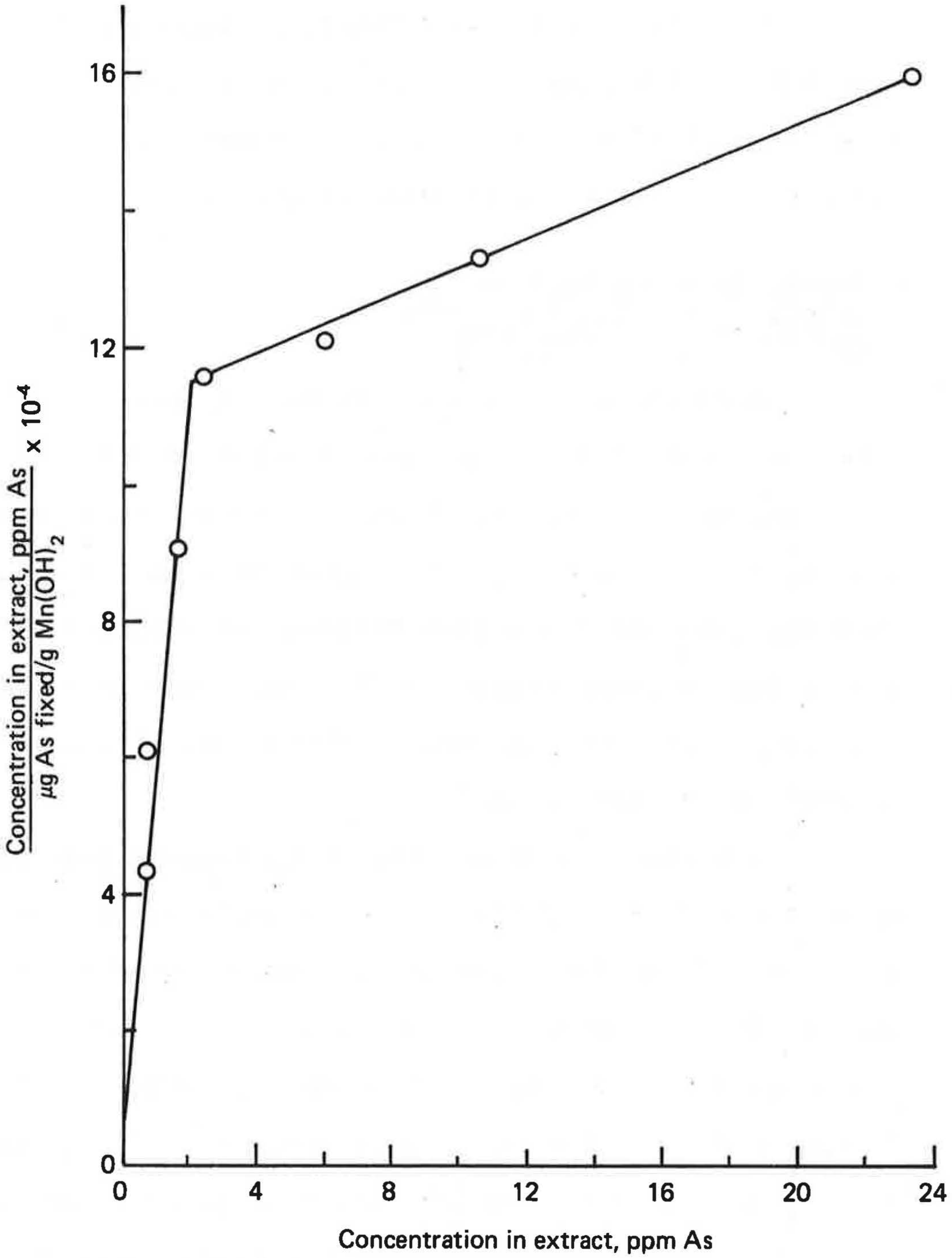

Figure 13. Langmuir adsorption isotherm for the reaction of arsenate with freshly precipitated $Mn(OH)_2$.

When arsenate was reacted with freshly precipitated ferric hydroxide, the ratio of the amount of As in the solution phase to the amount fixed per gram of ferric hydroxide was a constant. The procedure used by Deuel and Swoboda (5) for the synthesis of ferric arsenate may offer an explanation for the reaction of arsenate with freshly precipitated ferric hydroxide. When the pH of ferric chloride in solution is brought to 5.5, as it was in the procedure of Deuel and Swoboda, then freshly precipitated ferric hydroxide forms. The arsenate added must then react with the ferric hydroxide, and since chemical analysis of the precipitate yielded 1 mole of As for every 2 moles of Fe, it was concluded that the formula was $FeAsO_4 \cdot Fe(OH)_3$, or one molecule consisted of both ferric arsenate and ferric hydroxide. Figure 14 suggests that the amount of ferric arsenate formed is a function of the amount of arsenate added, i.e., as more arsenate is added, more ferric arsenate-ferric hydroxide is formed, and if the formation is one ferric arsenate per ferric hydroxide and the Fe^{3+} activity in solution is proportionally reduced when AsO_4^{3-} is increased, then the ratio of As in solution phase to the amount fixed should remain a constant.

With the reaction of arsenate on freshly precipitated aluminum hydroxide, a new pattern of fixation was observed. Rather than the amount in solution per the amount fixed increasing as the amount in solution increased,

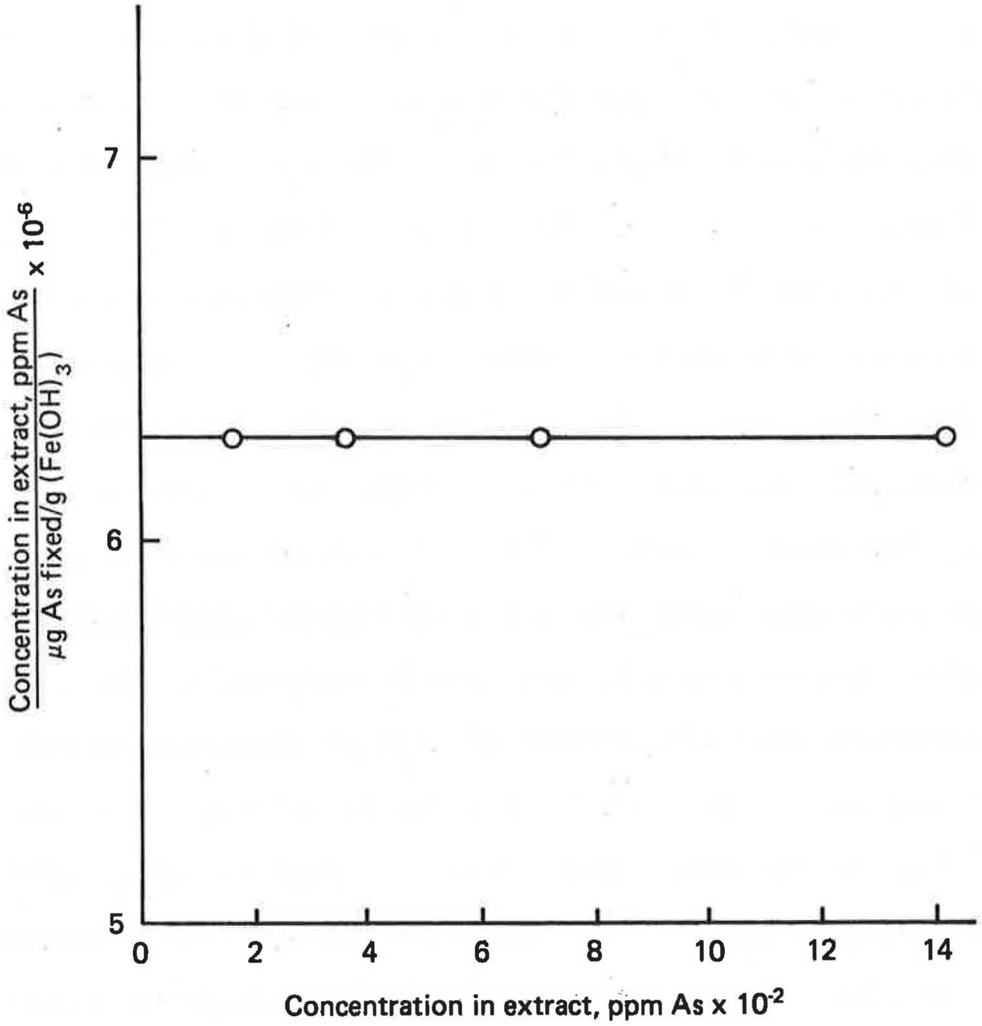

Figure 14. Langmuir adsorption isotherm for the reaction of arsenate with freshly precipitated $Fe(OH)_3$.

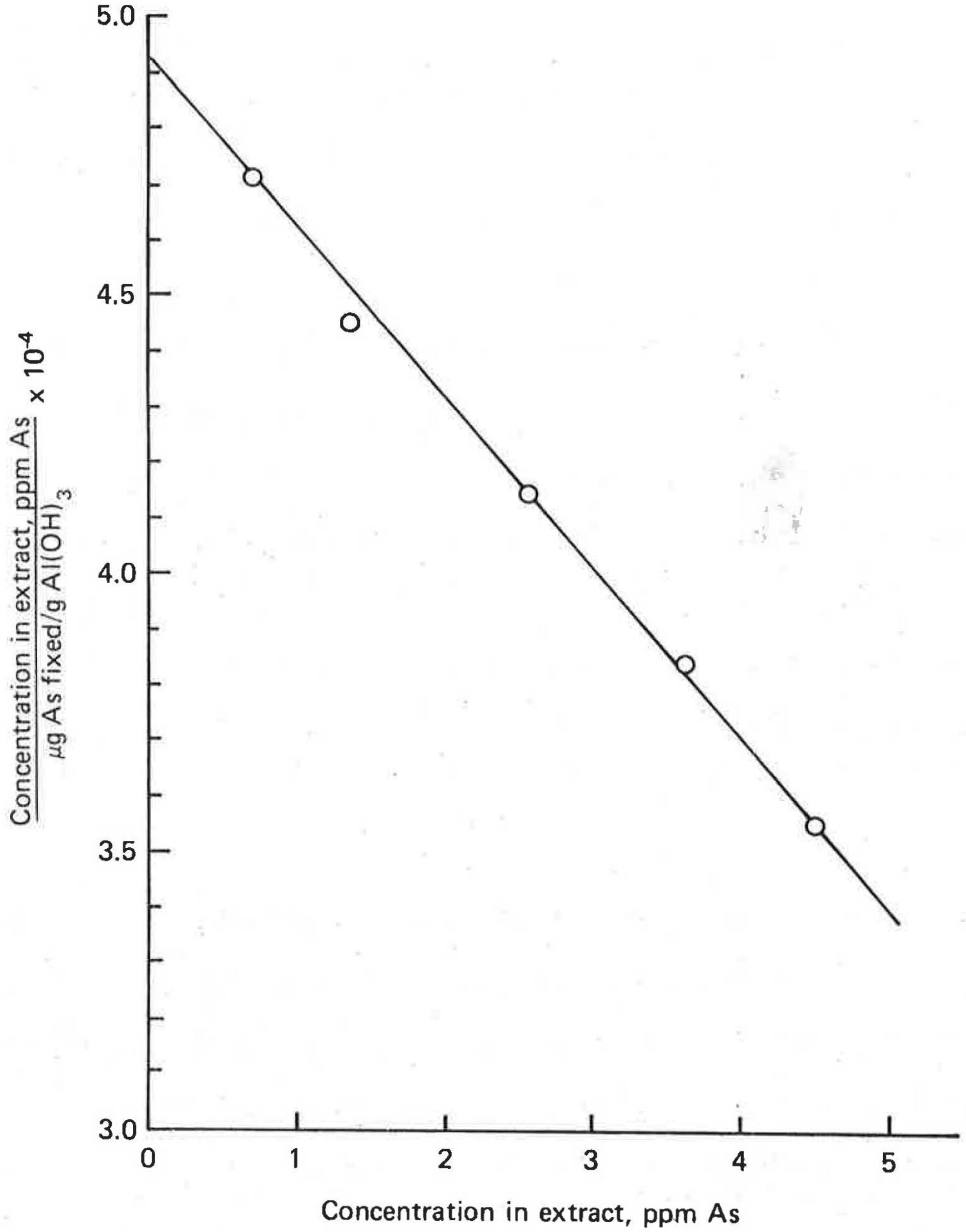

Figure 15. Langmuir adsorption isotherm for the reaction of arsenate with freshly precipitated $Al(OH)_3$.

it decreased. After the aluminum arsenate (T2) had been synthesized and analyzed for As and Al, the mole ratio of Al to As was 1:1, indicating that all of the Al had reacted with all of the As added. This could indicate what happens when arsenate is reacted with freshly precipitated aluminum hydroxide and the pH maintained constant. Rather than maintaining a ratio of one aluminum hydroxide for every aluminum arsenate formed, as did the ferric hydroxide-ferric arsenate, the Al completely reacted with the added arsenate, and therefore, when an excess of arsenate is added, all of the aluminum hydroxide will be converted to aluminum arsenate. The ratio of the As in solution to the amount fixed should decrease as the As in solution increases.

CONCLUSION

A comparison of arsenate sorption on aluminum, iron and manganese oxides indicated that monolayer sorption as predicted by the Langmuir equation occurred on the manganese oxide, but not on the aluminum or iron oxide. The observations tend to support the concept that arsenate solubility in these systems may be better predicted in terms of precipitate formation, rather than monolayer sorption.

The value of $pAl + pAsO_4$ found in this study was 19.43, which is higher than the value of 14.8 reported by

Chukhlantsev (3). It is likely that Chukhlantsev (3) did his study in the presence of a solid phase of gibbsite which has a pAl + 3pOH value of 34.2 at pH 4, but close to 37 at pH 3. Had a value of 34.2 been assumed for pAl + 3pOH in our study a value of 16.6 would have been computed which is closer to Chukhlantsev's (3) value. The relationship which incorporates the pH dependents into the pAl term and then eliminates it gives a means to interpret the mineral stability in soils ($pAsO_4 = 24.51 - 3pH$).

The $pFe + pAsO_4$ values found in this study averaged 17.73 and are lower than those of Chukhlantsev (3) 20.24. It was postulated that a ferric dihydrogen arsenate ion was formed which we did not account for in our computations. If the pFe + 3pOH values are subtracted from its $pFe + pAsO_4$ values a very constant relationship was found for the 5 ferric arsenates ($pAsO_4 = 26.07 - 3pH$) which is only valid in the presence of freshly precipitated ferric hydroxide. This value is comparable to the value one would obtain using Chukhlantsev's (3) value for ferric arsenate and a pK of 37 for freshly precipitated ferric hydroxide. Samples in this study where the pH was near 3, our values were very close to Chukhlantsev's (3).

The ion product of $Ca_3(AsO_4)_2$ reported in Table 5 was 18.57 and compares well with Chukhlantsev's (3) value of 18.17.

Our values of $3pMn + 2pAsO_4$ were 30.19, 33.73, and 33.59 for 3 different preparations. The value for the particular compound evaluated by Chukhlantsev (3) was 28.72. The free energies of formation of Mn_2O_3 and MnO_2 which were thought to form during the Mn_2AsO_4 equilibration were computed and compared very closely to those in the NBS Handbook (16).

Values of $3pPb + 2pAsO_4$ for $Pb_3(AsO_4)_2$ reported in Table 5 are very eratic and do not agree with previously published values of 35.39, (3), but are closest when the final equilibrium pH was between 5.46 and 6.40 with a mean of 39.5. It was assumed that this value would be useful in this range.

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CHAPTER 6

ARSENIC SOLUBILITY IN MENFRO AND SHARPSBURG SOILS

SYNOPSIS

Fifteen g samples of Sharpsburg and Menfro soils containing 320 and 160 μg As, respectively were equilibrated for 21 days with 30 ml of distilled water or 1% dextrose. Eh and pH were measured daily. Arsenic was measured daily for 10 days and on even numbered days thereafter. Fe, Al, Mn, Ca, and Pb in solution were determined at 4 day intervals, beginning with day 0. The reduction potential reached a minimum of -150 mV after the first day for both soils in 1% dextrose, and the pH reached a minimum of 4.6 after 8 days in the Sharpsburg soil, and 4.2 after 10 days in the Menfro soil. The Eh remained constant in the Sharpsburg soil during equilibration with water, but gradually decreased in the Menfro. The pH increased in both soils during water equilibration. After the initial drop in the reduction potential in the 1% dextrose equilibration, the As in solution increased rapidly in both soils, but was constant after 12 days. The As in solution increased more slowly in the water equilibration, but also remained constant after 12 days.

After 21 days, the remaining samples were freeze dried and divided into 2 groups. One sample was air dry and the other was brought to 26.7% moisture. Both groups remained in contact with the atmosphere. At intervals of 4, 8, 12, 24, and 48 days from the time of freeze drying, the pH, Eh, As, Al, Ca, Fe, Mn, and Pb concentrations of 1 to 2 soil to water extracts were measured and found to be steady, except for the pH of the 26.7% moisture, dextrose sample of the Menfro, which increased to 7.9 over 24 days and remained steady thereafter.

Both soils were equilibrated with dilute HCl and NaOH for 7 days at 25° C, and the above parameters were measured.

The values of pAl + 3pOH, pAl + $pAsO_4$, pFe + 3pOH, pFe + $pAsO_4$, 3pMn + $2pAsO_4$, 3pCa + $2AsO_4$, and 3pPb + $2pAsO_4$ were computed for each soil equilibration solution. The standard cell potential and the free energies of formation of Mn_3O_4, Mn_2O_3, and MnO_2 were also determined for each equilibration solution. These were compared to the mineral values. The Menfro soil was undersaturated with respect to aluminum, ferric, and calcium arsenate, but was oversaturated with respect to manganese and lead arsenates. The Sharpsburg soil was undersaturated with aluminum, calcium, ferric arsenates, supersaturated with lead and manganese arsenates.

Arsenate was reached with each soil according to the Langmuir adsorption isotherm, and found to deviate.

An experiment was designed to observe and measure biological reduction of arsenic in the soil system to volatile arsenicals. Within 4-7 days, it was possible to measure the evolution of volatile arsenicals.

INTRODUCTION

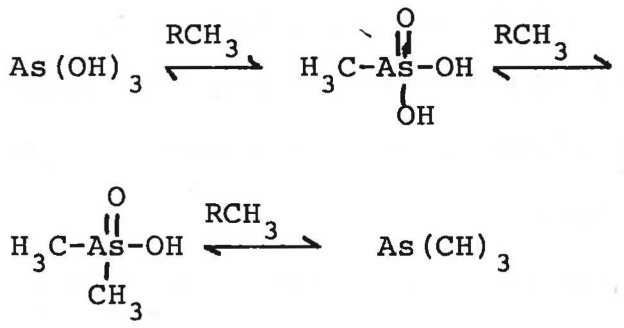
Many orchards in Missouri have been treated with lead arsenate for 20 to 80 years, causing the As concentration in the soil to increase from normal to levels in excess of 300 ppm As. Arsenates have been assumed to react in the soil in the same manner as phosphates, forming insoluble compounds with aluminum, iron, and calcium. Johnson and Hiltbold (13) showed that the arsenates in soils were more soluble than phosphates. They also showed in the soil they worked with that phosphate was present as organic and iron compounds, whereas As was associated with aluminum. Deuel and Swoboda (9) indicated that in the soil they worked with that As was precipitated as iron compounds.

Deuel and Swoboda (9) also added sugar and water to soil samples in an oxygen free environment. They measured Eh levels between 25 and 100 mV and found that the more reduced the environment, the higher the level of soluble As. It was concluded that under the conditions of their experiment soluble As increased due to the reduction of Fe from Fe^{3+} to Fe^{2+} and the subsequent dissolution of ferric arsenate (9). They also stated that arsenate was not reduced to arsenite under the conditions of their experiment (9). They did not find As levels high enough to be toxic to plants.

Phytotoxicity studies have shown that 1 ppm soluble As caused injury to cowpeas (1), barley 2ppm As (27), rice 7 ppm As (11), and 9 ppm As for peas, beans and barley (4). Yields of cotton and soybeans were reduced when As content of the tissue reached 4.4 and 1.0 ppm As respectively (10).

Reduction potentials reported by Bass Becking et al. (3) show that reducing conditions more extreme than those reported by Deuel and Swoboda (9) occur in natural soil systems. Reduction potentials as low as -300 mV are reported by Bass Becking et al. (3). The present study represents an attempt to study As in the soil after subjecting it to extreme reducing conditions.

Reed and Sturgis (23) suggested as early as 1936 that As was reduced to arsine in the soil, or to some other volatile organic arsenical. The reduction of arsenite has been shown to be biological, but the experimental evidence has resulted in the rejection of the early concept that the final product is arsine (2). Perotti and Verona (20) and Vinogradov (28) have shown that soil microorganisms produce gaseous arsenicals, which can be released from soils treated with salts of arsenic. Deuel and Swoboda (9) attempted to measure gaseous arsenic production from the soil they worked with, however the oxidation-reduction potential they reported may not have been low enough to activate the microoganisms. Challenger (6) proposed the following mechanism for the reduction of arsenious acid to trimethyl arsine:



$$\mathrm{As(OH)_3} \xleftrightarrow{\mathrm{RCH_3}} \mathrm{H_3C{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}{-}OH} \xleftrightarrow{\mathrm{RCH_3}}$$

$$\mathrm{H_3C{-}\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{As}}{-}OH} \xleftrightarrow{\mathrm{RCH_3}} \mathrm{As(CH)_3} \qquad [1]$$

Methyl arsonic acid and cacodylic acid are the two suggested intermediate products, but they have not been isolated. They both yield trimethylyarsine when present in bread cultures of <u>Scopulariopsis</u> <u>brevicaulis</u> (6). Biological oxidation of arsenite to arsenate in the soil has also been studied and found to be reversible and rapid (22,26).

MATERIALS AND METHODS

Description of the Sites

Two orchard sites, Unity Village near Independence and Valley View near McBaine, were selected on the basis of a past history of lead arsenate treatment and As levels exceeding 150 ppm As in the 0-5 cm horizon. The Unity Village orchard is on a Sharpsburg soil, which is classified as a fine, montmorillonitic, mesic family of the Typic Argiudolls. Valley View is a former orchard that has been converted to pasture without plowing and is on a Menfro soil, classified as a member of the fine-silty, mixed, mesic family of Typic Hapludalfs. Mechanical analysis (Table 1) showed the Sharpsburg soil to be a silty clay loam, and the Menfro to be a silt loam. The Sharpsburg has 5.69% and the Menfro 4.47% organic matter.

Table 1. Mechanical analysis of a Sharpsburg and a Menfro soil.

Particle size	Sharpsburg	Menfro
microns	% composition	
20-200	10.92	21.39
5- 20	46.38	56.95
2- 5	8.30	4.81
less than 2	34.40	16.85

Sampling Procedure

Using the sampling pattern for obtaining samples around orchard trees, samples were taken from 2 trees at each site. A portion of soil 12 inches in diameter was taken to a depth of 6 inches with a shovel. Twelve such portions from around each tree were combined, resulting in 2 bulk samples from each orchard.

Dissolution Study

Anaerobic. Solution soil equilibrations were prepared by placing 30 ml of distilled water or 1% dextrose plus urea, 100 ppm N, solution and 15 g of soil in 50 ml centrifuge tubes. Enough samples for the entire experiment were prepared and allowed to stand without shaking at 25 ± 2° C. Each day, for 21 days, Eh and pH of duplicate samples were measured using an Orion model 801/digital pH ionalyzer with an Orion model 855 automatic electrode switch. Soluble As was determined daily for 10 days, and every other day thereafter. At 4 day intervals, Fe, Al, Mn, Ca, and Pb were determined.

Aerobic. The remaining anaerobic samples were freeze dried after 21 days of anaerobic incubation, and divided into 2 groups. One set of samples was kept dry and the other adjusted to 26.7% soil moisture. Both groups remained in contact with the atmosphere. The 15 g samples were shaken with 30 ml of water for 2 hours 4, 8, 12, 24, and 48 days from the day of freeze drying. Eh, pH, As, Fe, Al, Mn, Ca, and Pb contents of the solution phase were measured. The conductivity of the solution from the samples at 26.7% moisture was measured.

Acid-base equilibration. Dilute solutions of HCl and NaOH were prepared with final pH values of 2.00, 3.00, 4.00, 5.00, 6.00, 7.00 and 8.00. Fifteen g soil and 30 ml of each of these solutions were equilibrated for 7 days at 25° C in a constant temperature water bath-shaker. After equilibration, Eh, pH, specific conductance, As, Fe, Al, Mn, and Ca and Pb were determined on the solution phase.

Chemical Analysis

Soluble As, Fe, Al, Mn, Ca, and Pb were determined on the equilibrated solutions. Arsenic was determined by transferring a 15 ml aliquot of the equilibrium solution to an arsine generator, collecting the As in 15 ml of 0.004 M iodine solution, developing the blue arseno-molybdenum complex and measuring the color intensity at a wavelength at 840 nm as detailed in Chapter 3. The remaining solution was diluted 1 to 20 for the determination of Fe, Al, Mn, and Ca. All solutions were adjusted to 0.5% lanthanum chloride and 0.05% potassium chloride to compensate for interference in the determination of Ca and Al. Aluminum was determined by flame emission using nitrous oxide-acetylene flame at a wavelength of 395.3 nm. Iron, lead, calcium and manganese were determined by atomic absorption at wavelengths of 248.3 nm, 217.0 nm, 422.8 nm, and 279.4 nm respectively.

Determination of Ion Products

Specific conductivity was measured using a Yellow Springs Instrument Co. Model 31 conductivity bridge and Model 3403 conductivity cell with a cell constant of 1.0. Specific conductivity was estimated for the anaerobic and the dry aerobic samples by dividing the specific conductivity of the measured aerobic and acid-base equilibration samples by the sum of the concentration of the measured cations in solution in ppm, and obtaining a constant. The sum of the measured cations in solution in the anaerobic and the dry aerobic samples was then multiplied by this constant. Ionic strength was estimated using the empirical relationship of Ponnamperuma et al. (21), in which the specific conductivity in μ mhos is multiplied by 1.59×10^{-5}. Activity coefficients were estimated using the extended form of the Debye-Huckel Equation [2],

$$\text{Log } 1/\gamma = 0.509Z^2\sqrt{I}/(1 + aB\sqrt{I}) \qquad [2]$$

in which Z is the charge on the ion species, I is the ionic strength of the solution, a is effective radius, B is a constant which accounts for variation in electrical properties of water, and γ is the activity coefficient.

Total As, Fe, Al, Mn, Ca, and Pb were considered to be composed of the following:

$$As_t = [AsO_4^{3-}]_c + [HAsO_4^{2-}]_c + [H_2AsO_4^-]_c + [H_3AsO_4]_c + [AsO_2^-]_c + [HAsO_2]_c \quad [3]$$

$$Fe_t = [Fe^{3+}]_c + [FeOH^{2+}]_c + [Fe(OH)_2^+]_c + [Fe(OH)_{3collodial}]_c + [Fe^{2+}]_c \quad [4]$$

$$Al_t = [Al^{3+}]_c + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_4^-] + [Al_6(OH)_{15}^{3+}] \quad [5]$$

$$Mn_t = [Mn^{2+}] + [MnOH^+] \quad [6]$$

$$Ca_t = [Ca^{2+}] + [CaOH^+] \quad [7]$$

$$Pb_t = [Pb^{2+}] + [PbOH^+] \quad [8]$$

Activities for various species were solved for by expressing terms in Equation [3] to [8] in measureable parameters. The computation was done on an IBM 370/168 computer.

Sources and values for constants used to solve the equation derived are presented in Chapter 5 Table 1, and in Table 2 of Chapter 6.

Table 2. Constants used in computations of ion products.

Constant	Form of equation	K	Source
K11	$(H^+)(AsO_2^-)$	5.89×10^{-10}	(17)
K12	$(Al(OH)_2^+)(H^+)^2/(Al^{3+})$	1.59×10^{-10}	(24)
K13	$(Al(OH)_4^-)(H^+)^4/Al^{3+}$	8.71×10^{-23}	(25)
K14	$(Al_6(OH)_{15}^{3+})\cdot(H^+)^{15}/(Al^{3+})^6$	1.00×10^{-36}	(24)

Arsenate Sorption Study

Solutions, 30 ml, containing 1, 2, 4, 8, and 16 ppm As as arsenate were transferred to 50 ml centrifuge tubes containing 3 g of either the Sharpsburg or the Menfro soil. The samples were equilibrated for 96 hours at 25° C in a constant temperature water bath-shaker, after which the As in solution was measured, and the amount fixed by the soil was calculated.

Biological Reduction of Arsenic to Trimethylarsine

One hundred g samples of each soil were placed in 500 ml erlenmeyer flasks, and 200 ml of 1% dextrose containing 100 ppm N as urea were added. Each flask was connected to an 18 x 150 mm test tube through rubber stoppers, creating a closed system. The test tube contained 15 ml of 0.004 M iodine solution. Samples were allowed to incubate for 7 and 10 days at 25° C and 34° C. The carbon dioxide evolved by microbial action was the carrier for gaseous arsenicals produced. A second group of samples was purged continuously with nitrogen at a rate of 10 bubbles per minute at 25° C for 4 days. At the end of each time period, the As in solution was determined.

RESULTS AND DISCUSSION

Dissolution Study

Figures 1 and 2 show the change in the oxidation-reduction potential for the Sharpsburg and the Menfro soils with time under various anaerobic and aerobic conditions. The plotted points are the means of duplicate determinations of the field replicates (Appendix Tables I, III, V, and VII). Figure 1 indicates that in the Sharpsburg soil under anaerobic conditions with 1% dextrose that a minimum reduction potential of about -150 mV was attained after one day of incubation. This was also the case for the Menfro soil as shown in Figure 2. The oxidation reduction potential in both soils gradually increased after the first day, and appeared to become steady after 15 or 16 days, at about 350 mV for the Sharpsburg and 300 mV for the Menfro soil. When equilibrated with water under anaerobic correlations the Eh of the Sharpsburg remained steady between 400 and 500 mV throughout the 21 days, while the Eh of the Menfro gradually decreased from a high of about 600 mV to about 200 mV, and it appeared constant after 15 days. After the samples were freeze dried, the Eh was approximately equal to the original Eh before the anaerobic dissolution began, except for the aerobic equilibration at 26.7% moisture. It decreased and then with time became nearly equal to the other aerobic samples (Figures 1 and 2).

Legend for Figures 1 through 12

○ 15 g of soil was equilibrated with 30 ml of water.

□ 15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried and maintained in contact with air.

△ 15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried, the water adjusted to 26.7%, and maintained in contact with air.

● 15 g of soil was equilibrated with 30 ml of 1% dextrose.

■ 15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried and maintained in contact with air.

▲ 15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried, the water adjusted to 26.7%, and maintained in contact with air.

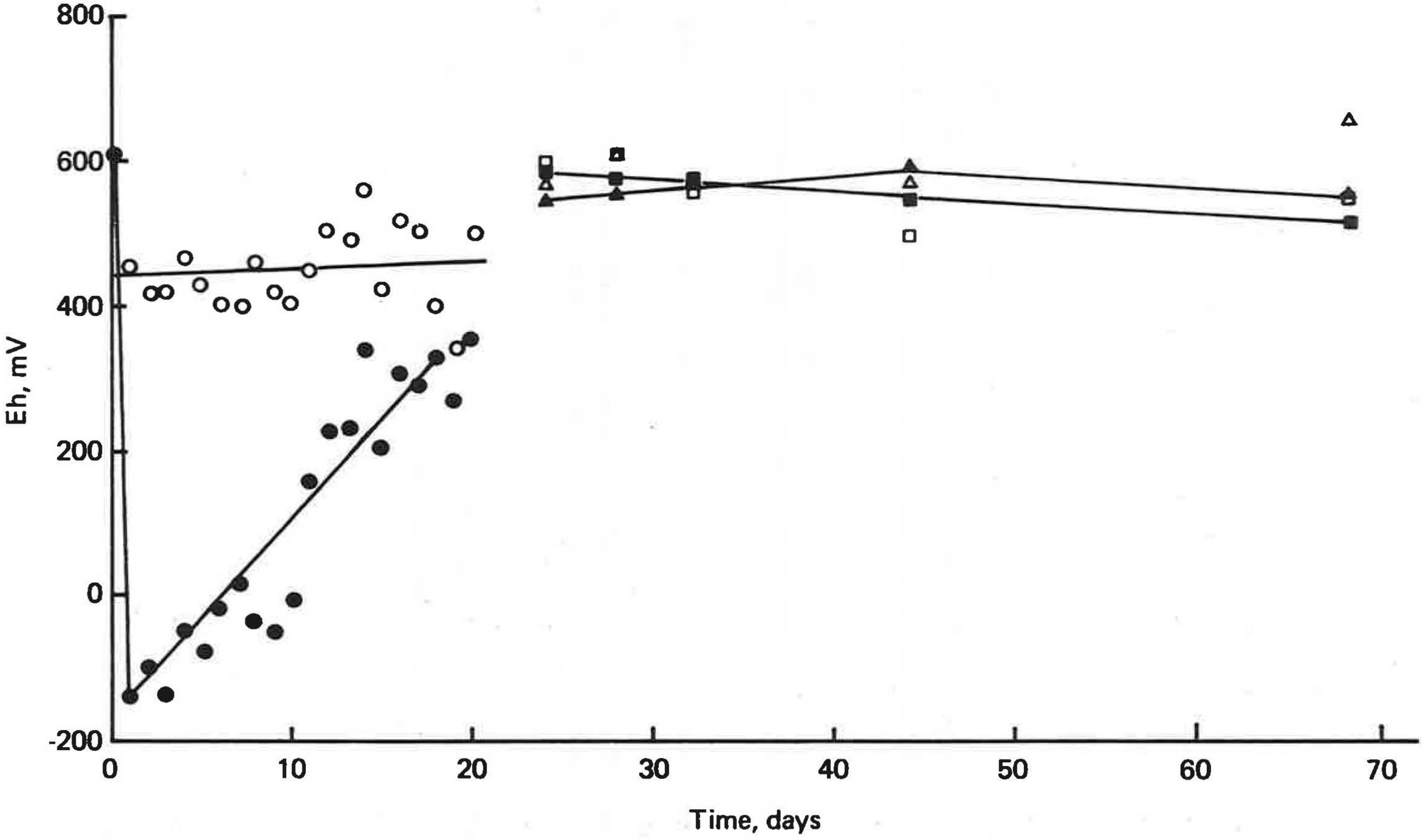


Figure 1. Change of oxidation-reduction potential with time in a Sharpsburg soil under anaerobic and oxidizing conditions.

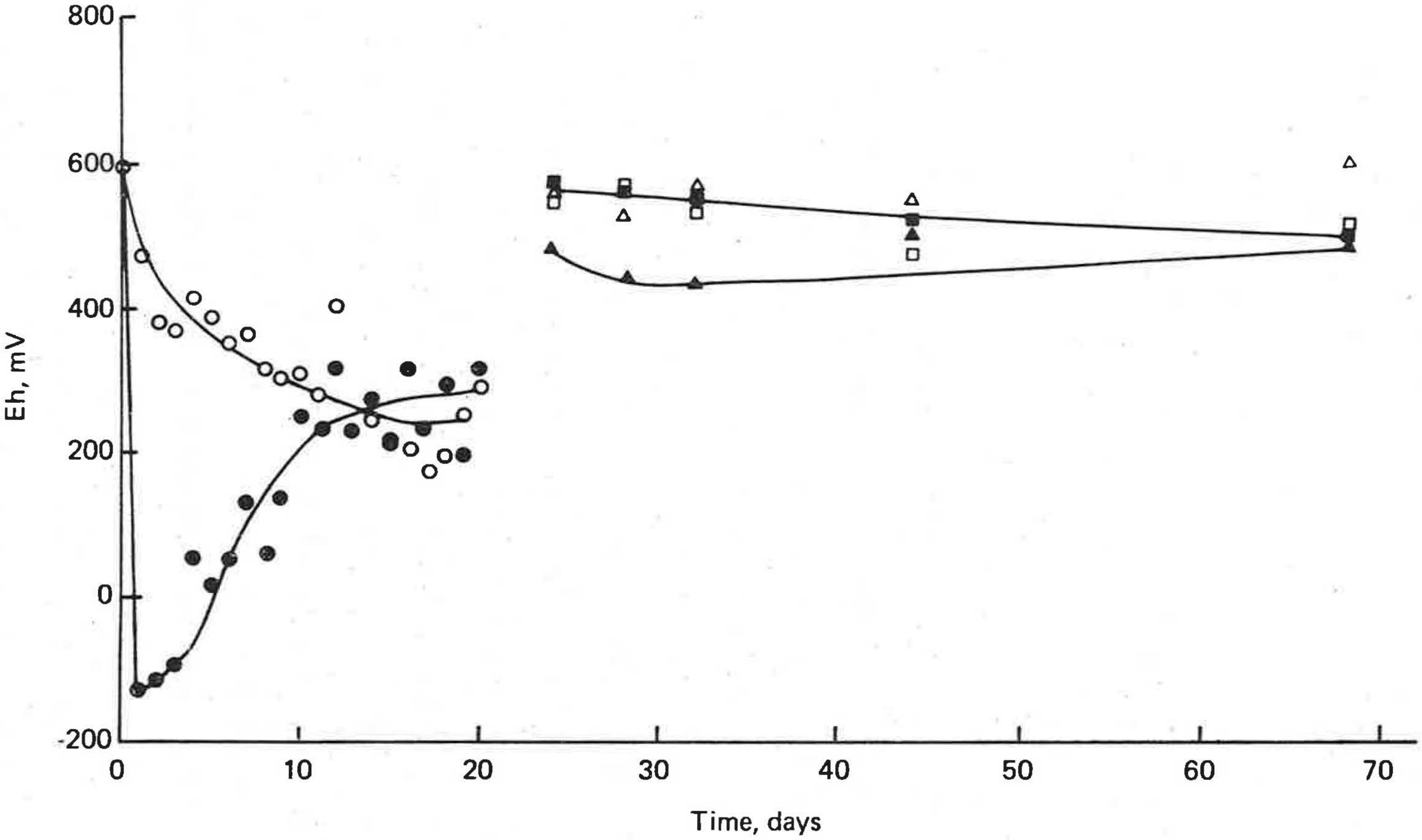


Figure 2. Change of oxidation-reduction potential with time in a Menfro soil under anaerobic and oxidizing conditions.

Figures 3 and 4 show the change in pH with time under various anaerobic and aerobic conditions. The Sharpsburg soil under 1% dextrose anaerobic reached a minimum pH of 4.55 at 8 days incubation and the Menfro reached a minimum pH of 4.2 at 10 days incubation. In both soils, the decrease in the pH was rapid until the minimum was reached, then a rapid increase followed for 4 days in the Menfro, and for about 6 to 7 days in the Sharpsburg. At 14 days in both soils under 1% dextrose solution, a steady pH was observed. The pH in both soils under anaerobic water increased for about 15 days, and then remained steady at about 6.4 for the Sharpsburg, and 7.0 for the Menfro.

After freeze drying, the pH of the aerobic water samples of the Sharpsburg soil showed a rapid decrease, followed by a more gradual decrease to a pH of about 6. The pH of the Menfro soil showed a steady decrease to about 6.6. The pH of the aerobic dextrose samples for the Sharpsburg soil was constant and near 5.2 the final pH under the anaerobic conditions. The pH of the Menfro soil responded quite differently. The pH of the aerobic dry samples increased from the end of the anaerobic experiment to the fourth day of aerobic from about 4.5 to 5.7, and remained steady thereafter. The pH of the aerobic 26.7% moisture samples gradually increased from the fourth day after freeze drying to a high of 7.9,

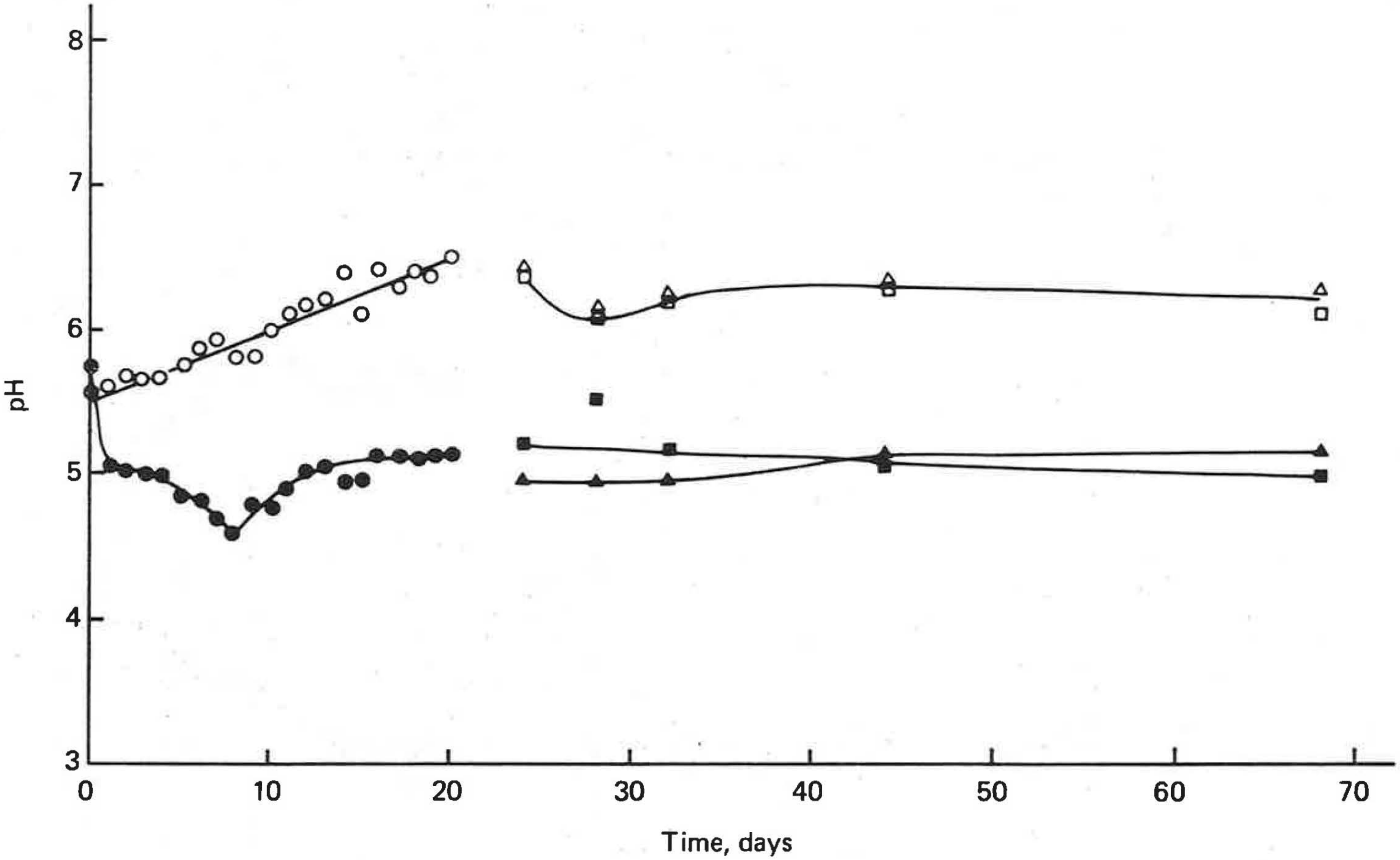


Figure 3. Change of pH with time in a Sharpsburg soil under anaerobic and oxidizing conditions.

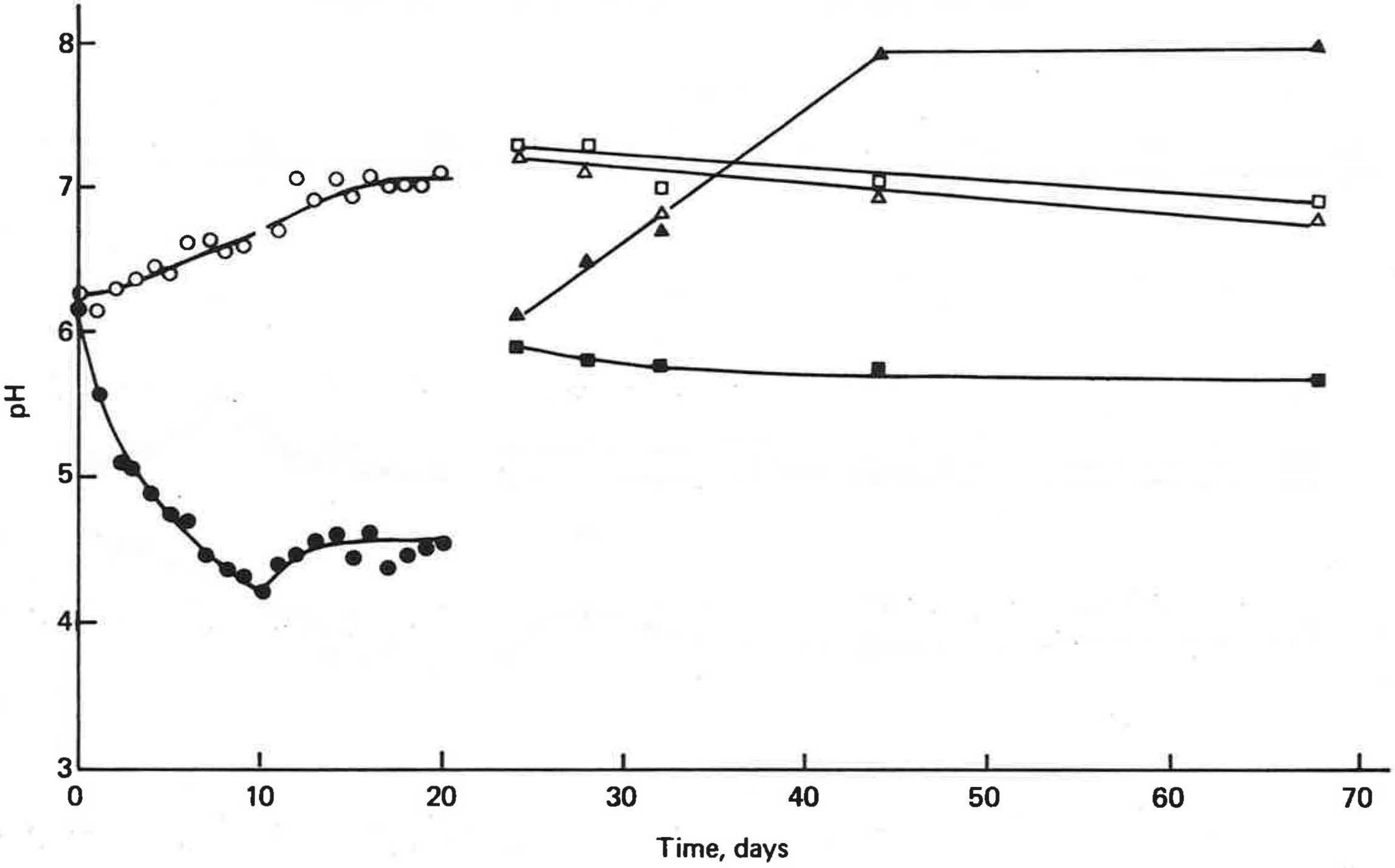


Figure 4. Change of pH with time in a Menfro soil under anaerobic and oxidizing conditions.

which was attained after 24 days of contact with the atmosphere. This pH value then remained constant.

Figures 5 and 6 show the dissolution of As with time as a function of various anaerobic and aerobic conditions. In the Sharpsburg soil reacted with dextrose As in solution gradually increased to about 14 ppm, approximately 10% dissolution, and was level after about 14 days. The As in solution in the Menfro soil was constant at about 14 days, but at a concentration close to 32 ppm approximately 30% dissolution. The anaerobic water samples equilibrated with water show the same pattern with lower amounts of As in solution, about 3 ppm for the Sharpsburg and 7.5 ppm for the Menfro. Immediately after freeze drying and beginning aerobic conditions, the amount of As in solution decreased. The drop was large and rapid in both the Sharpsburg and the Menfro soils. The concentration of As in solution remained constant under the aerobic equilibration conditions except for the case of the dry Sharpsburg soil. This soil had about the same soluble As content 4 days after freeze drying as it did at the end of the anaerobic period, but then decreased for the next 4 days, after which it remained fairly constant.

Figures 7 and 8 show the change in As concentration with pH under the various anaerobic and aerobic conditions.

○ 15 g of soil was equilibrated with 30 ml of water.

□ 15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried and maintained in contact with air.

△ 15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried, the water adjusted to 26.7%, and maintained in contact with air.

● 15 g of soil was equilibrated with 30 ml of 1% dextrose.

■ 15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried and maintained in contact with air.

▲ 15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried, the water adjusted to 26.7% and maintained in contact with air.

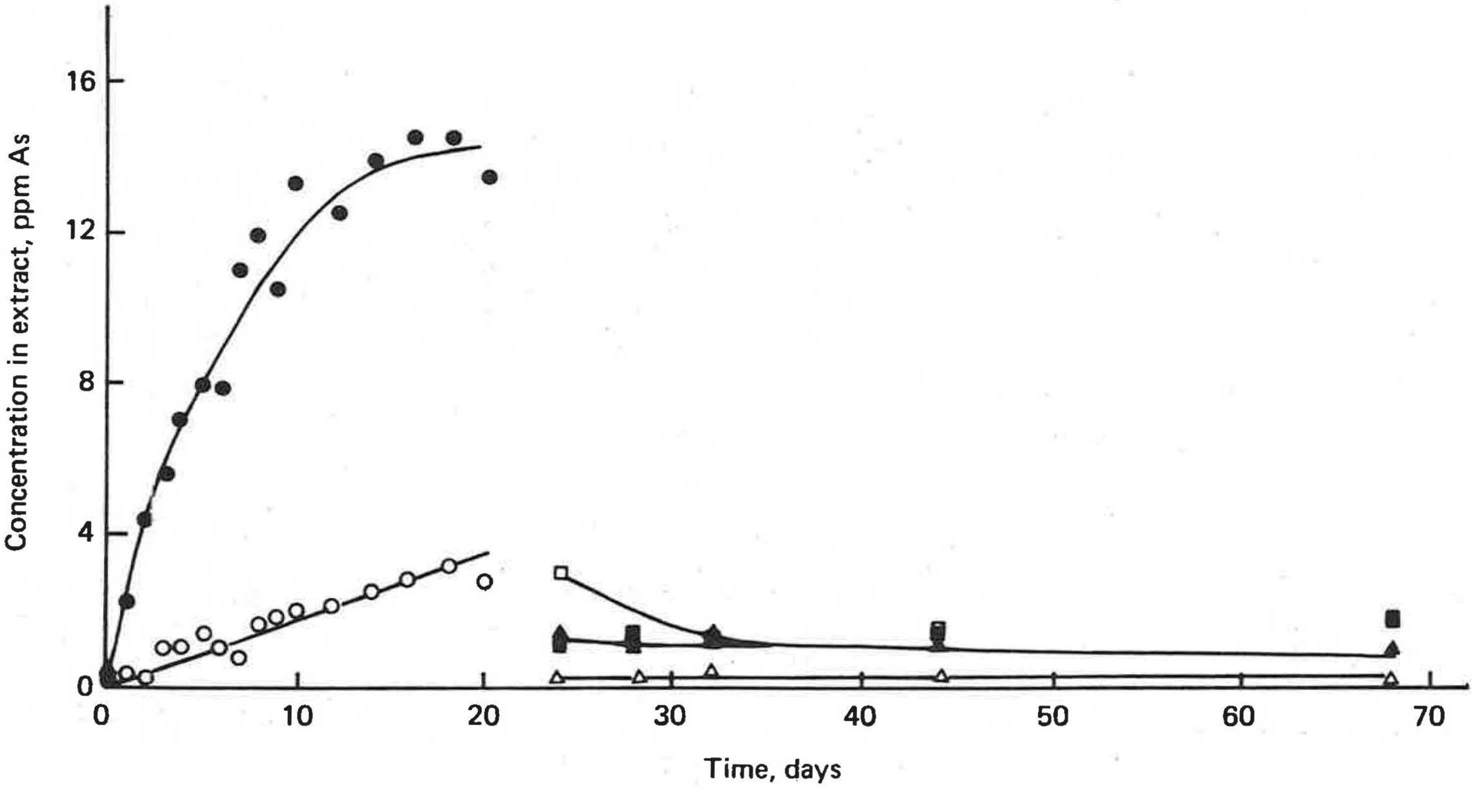


Figure 5. Change of soluble arsenic with time from a Sharpsburg soil under anaerobic and oxidizing conditions.

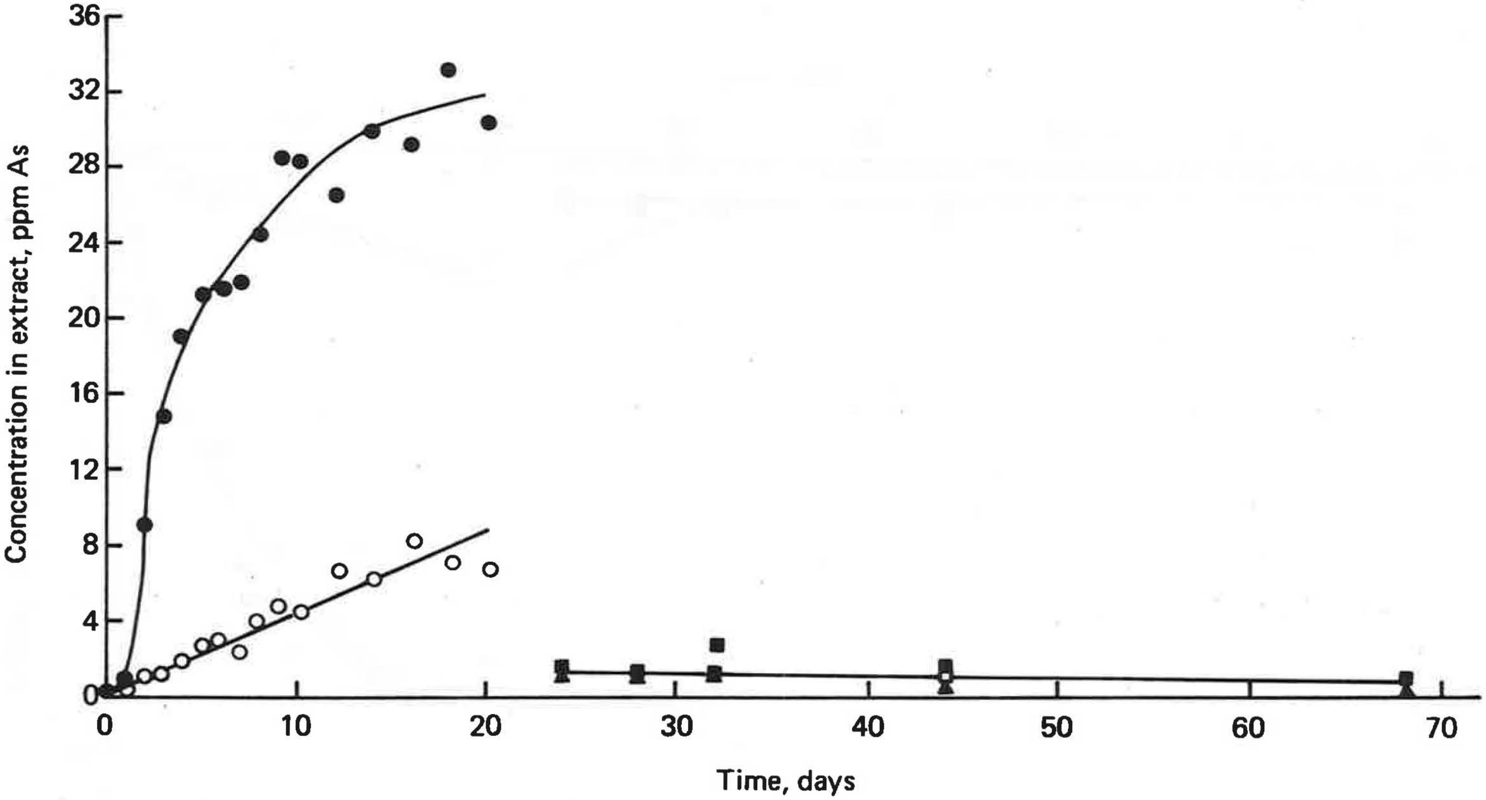


Figure 6. Change of soluble arsenic with time from a Menfro soil under anaerobic and oxidizing conditions.

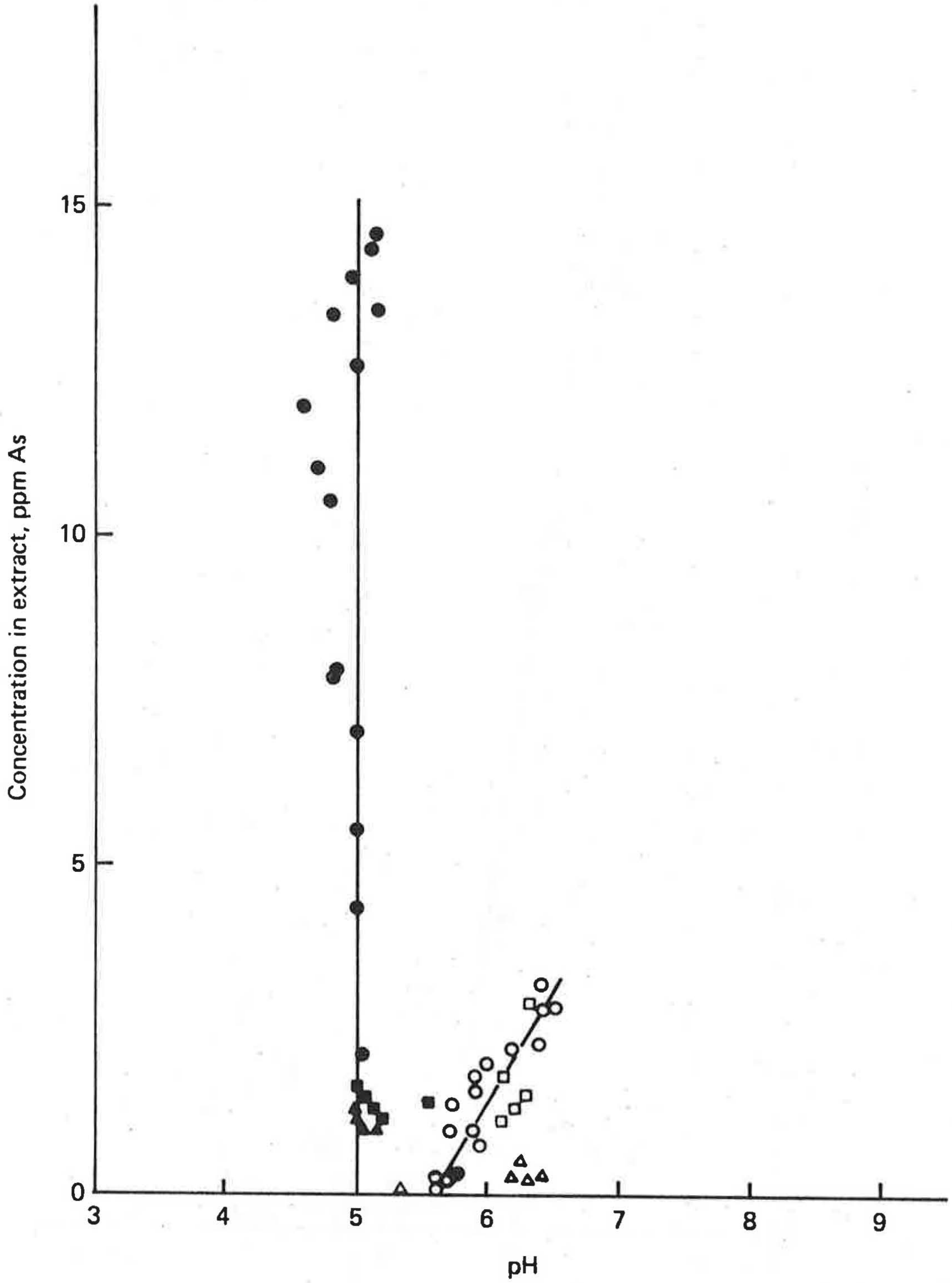


Figure 7. Relationship between soluble arsenic and pH in a Sharpsburg soil under anaerobic and oxidizing conditions.

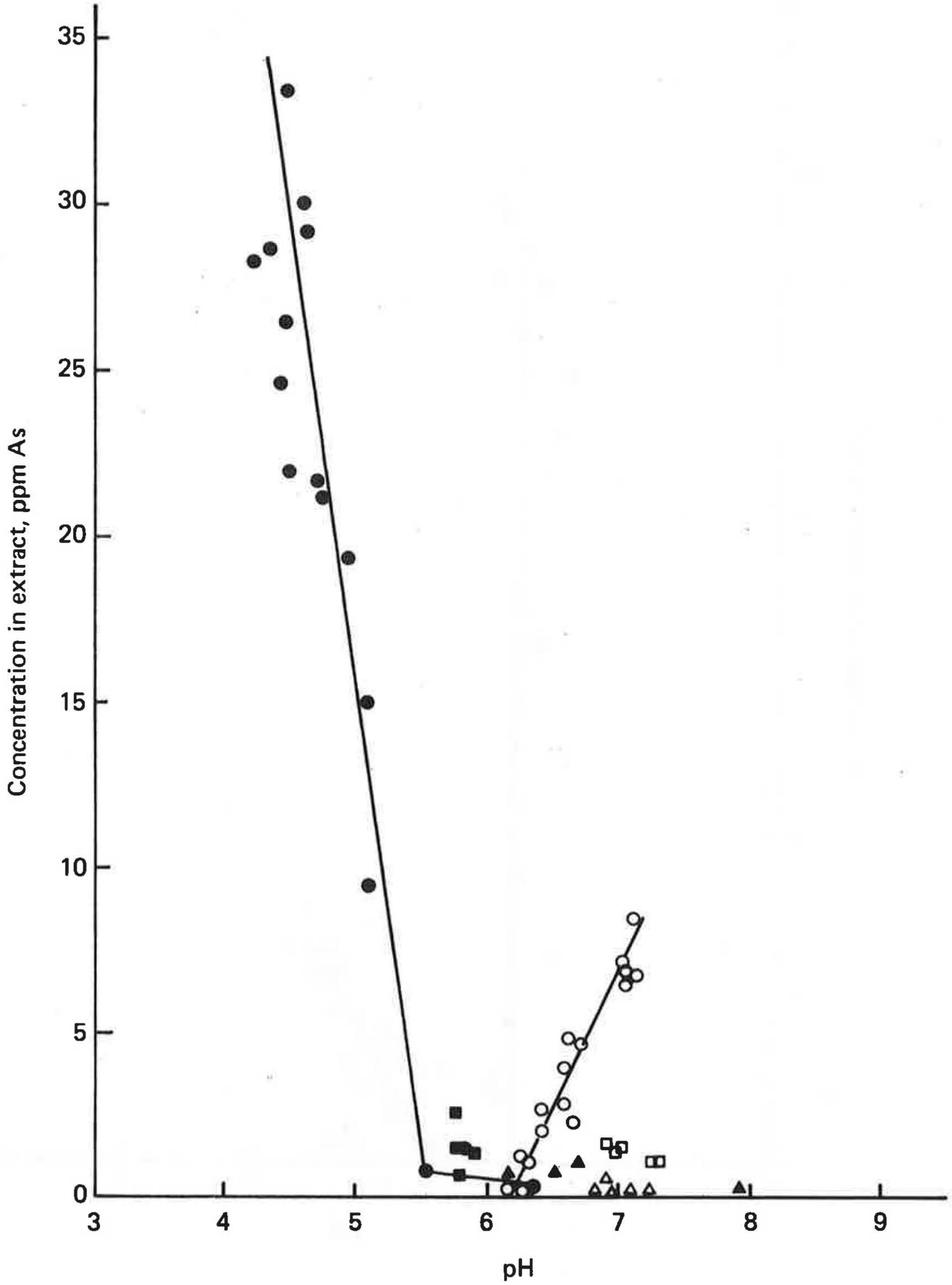


Figure 8. Relationship between soluble arsenic and pH in a Menfro soil under anaerobic and oxidizing conditions.

In the Sharpsburg soil with dextrose under anaerobic conditions, the amount of As in solution does not appear to be a function of pH, while in the Menfro soil, it appears to increase as the pH decreases. In both soils equilibrated with water under anaerobic conditions the amount of As in solution appears to increase as the pH does, but once the conditions in the soils become aerobic, then the As in solution and the pH appear to be independent of each other.

Figures 9 and 10 show the relationship between As in solution and the change in the oxidation-reduction potential under various anaerobic and aerobic conditions. In both the Sharpsburg and the Menfro soils, the amount of As in the dextrose solution with anaerobic conditions begins to increase after the initial decrease in the reduction potential. The increased level of As in solution for both soils was accompanied by an increase in Eh. This relationship is interpreted as resulting from the dissolution of arsenic with time in a non equilibrium system, which happened to coincide with the increase in Eh due to decreasing anaerobic activity. The other Sharpsburg samples, whether aerobic or anaerobic, appear to be independent of Eh.

During the anaerobic and aerobic experiments on the dissolution of As from the Sharpsburg and Menfro soils, the ion products of aluminum hydroxide, aluminum arsenate,

○	15 g of soil was equilibrated with 30 ml of water.
□	15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried and maintained in contact with air.
△	15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried, the water adjusted to 26.7%, and maintained in contact with air.
●	15 g of soil was equilibrated with 30 ml of 1% dextrose.
■	15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried and maintained in contact with air.
▲	15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried, the water adjusted to 26.7% and maintained in contact with air.

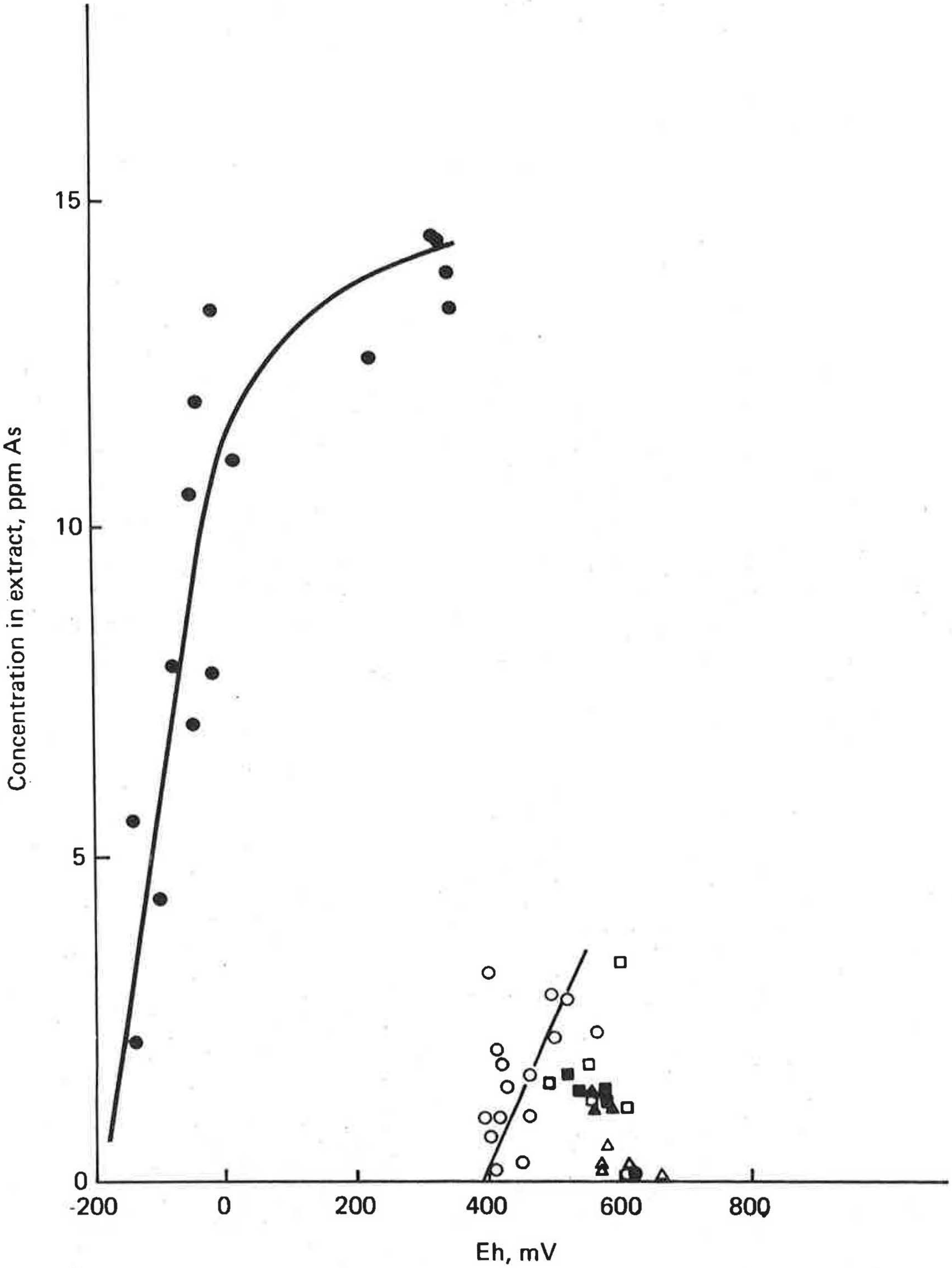


Figure 9. Relationship between soluble arsenic and oxidation-reduction potential in a Sharpsburg soil under anaerobic and oxidizing conditions.

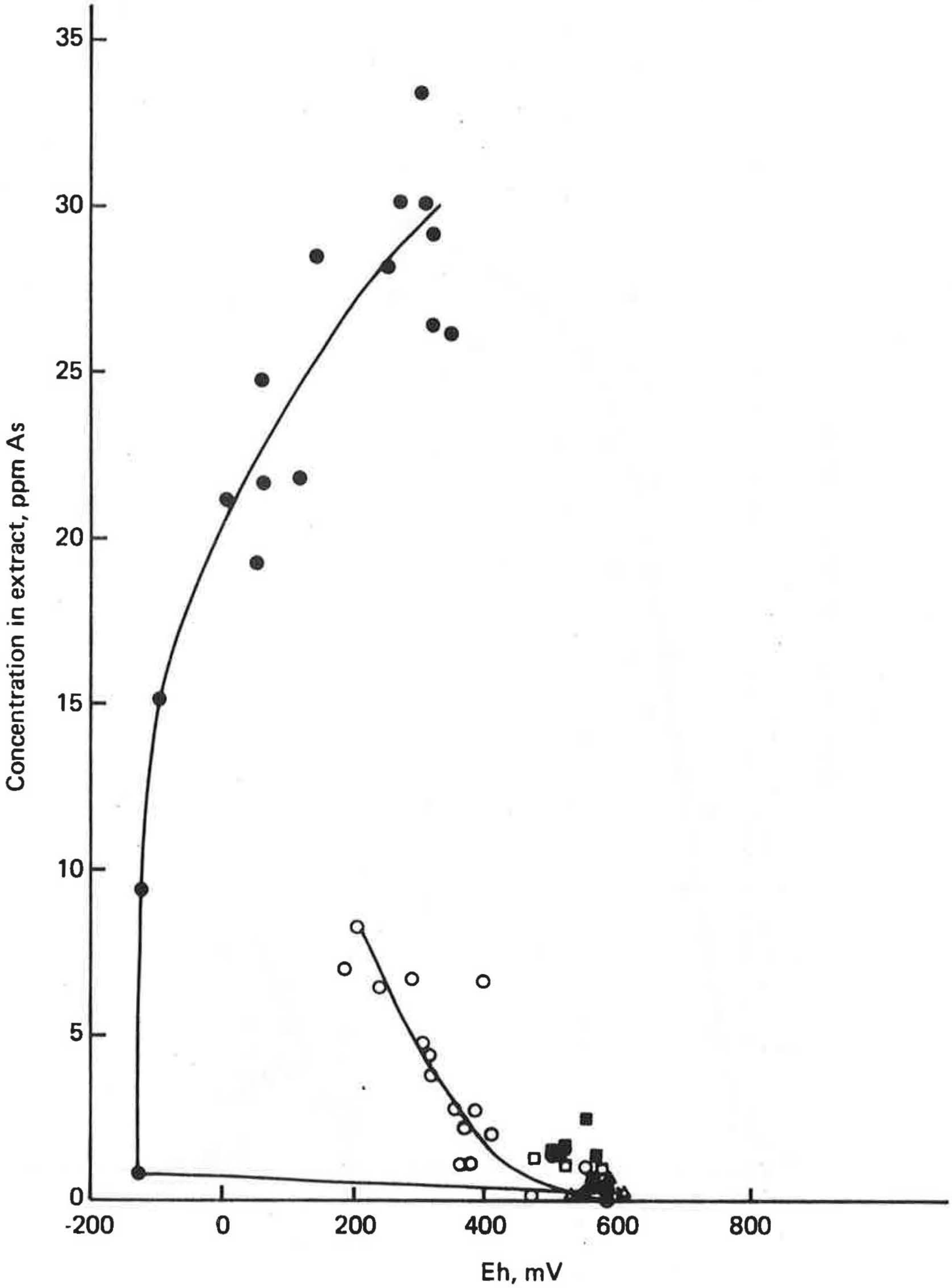


Figure 10. Relationship between soluble arsenic and oxidation-reduction potential in a Menfro soil under anaerobic and oxidizing conditions.

ferric hydroxide, ferric arsenate, manganese arsenate, calcium arsenate, and lead arsenate were determined for the solution phases. The free energies of formation and the standard cell potential of Mn_3O_4, Mn_2O_3, and MnO_2 were calculated for the manganese species in solution, based on the reaction of Mn^{2+} with water.

Table 3 lists the ion products for aluminum hydroxide, aluminum arsenate, ferric hydroxide, and ferric arsenate determined for the Sharpsburg soil. The ion product pAl + 2pOH is constant throughout, regardless of whether the measurement was taken during an anaerobic stage or an aerobic one, with a mean value of 33.81. This is comparable to the values predicted by Misra et al. (16), and Blanchar and Scrivner (5) for the pH values of the soil. The values of the ion product was slightly higher for all samples that were equilibrated with dextrose, but the standard deviation on all samples was 0.32. There is a degree of variation in the values of the ion product of $pAl + pAsO_4$, with mean values of 19.95 and 22.31 for the anaerobic and aerobic equilibrations in the absence of dextrose.

A value of $pAl + pAsO_4$ of 19.43 was reported for $AlAsO_4$ (Table 3 Chapter 5), at a pH of near 3. A functional relationship developed showed that $pAsO_4 = 24.51 - 3pH$ for the $AlAsO_4$. Under the present study the $pAsO_4$ values for both the Menfro and Sharpsburg soil are

Table 3. The effect of time on the ion products of iron and aluminum oxides and arsenates in a Sharpsburg soil under anaerobic and aerobic conditions.

	water						1% dextrose					
Time	pH	Eh	pAl + 3pOH	pAl + $pAsO_4$	pFe + 3pOH	pFe + $pAsO_4$	pH	Eh	pAl + 3pOH	pAl + $pAsO_4$	pFe + 3pOH	pFe + $pAsO_4$
days		mV						mV				
						Anaerobic						
0	5.57	606	33.81	21.86	33.79	21.63	5.73	602	33.74	21.86	33.69	21.25
4	5.68	467	33.76	19.76	34.48	21.44	4.98	-54	34.10	29.14	44.18	29.64
8	5.81	460	33.64	19.18	33.54	20.44	4.59	-40	34.25	28.88	44.34	29.22
12	6.17	499	33.49	19.68	32.36	19.52	5.00	227	34.12	19.62	38.45	23.73
16	6.41	516	33.35	19.65	32.30	19.63	5.12	307	34.03	19.65	36.75	22.09
20	6.48	501	33.35	19.65	32.15	19.57	5.14	347	34.04	19.69	36.06	21.45
Mean			33.57	19.95	33.10	20.37			34.05	23.14	38.91	24.56
S.D.			0.20	0.96	0.97	0.96			0.17	4.63	4.42	3.87
	after anaerobic, water						after anaerobic, 1% dextrose					
						Aerobic, 26.7% moisture						
4*	6.39	577	33.30	22.56	33.23	20.49	4.97	556	34.08	20.43	36.47	21.60
8	6.17	612	33.51	22.31	33.23	20.23	4.94	559	34.13	20.47	36.35	21.51
12	6.23	585	33.40	22.15	33.43	20.28	4.94	572	34.15	20.43	36.33	21.45
24	6.30	571	33.37	22.63	33.72	21.04	5.09	591	34.07	20.70	36.08	21.48
48	5.30	662	33.93	21.88	34.78	21.36	5.15	558	34.11	20.75	36.25	21.70
Mean			33.50	22.31	33.68	20.69			34.11	20.56	36.30	21.55
S.D.			0.25	0.31	0.65	0.51			0.03	0.15	0.14	0.10

*Day 0 = day 21 of anaerobic.

several orders of magnitude lower than would be predicted for $AlAsO_4$. It is concluded that $AlAsO_4$ would not be stable under these conditions.

The reasons why the $pAl + pAsO_4$ ion product may not be used as a reliable index of $AlAsO_4$ stability are interrelated to the uncertainty as to the $pAl + 3pOH$ value at various pH levels. If variation of $pAl + 3pOH$ occurs because Al ion species in solution are not accounted for, then a function relationship $pAsO_4 = 24.51 - 3pH$ is a valid predictor, because Al^{3+} activity cancels from the equation. If $pAl + 3pOH$ varies due to a change in the solid phase as suggested (5,16) then the solid phase of $AlAsO_4$ must be assumed to change in approximately the same manner. No data is currently available to resolve this question.

The ion product $pFe + 3pOH$ for the non dextrose samples of the Sharpsburg equilibration averages 33.5, indicating that the Sharpsburg soil is supersaturated with respect to ferric hydroxide. For the anaerobic dextrose sample, the mean is 38.91, with a standard deviation of 4.42, showing that the system is not an equilibrium system. After the dextrose samples had been converted to aerobic in the Sharpsburg soil, the $pFe + 3pOH$ product indicated that freshly precipitated ferric hydroxide may have formed.

With the low levels of total iron in solution and the possible existence of chelates of iron in solution an accurate estimate of Fe^{3+} ion activity cannot be made. However, the functional relationship developed in Chapter 5 ($pAsO_4 = 26.07 - 3pH$), indicates that $FeAsO_4$ is unstable in both Menfro and Sharpsburg soils.

The ion product $pFe + pAsO_4$ for the Sharpsburg soil is 24.56 ± 3.87 for the anaerobic dextrose and 21.55 ± 0.10 for the aerobic following dextrose.

Examination of the ion products $pAl + 3pOH$, $pAl + pAsO_4$, $pFe + 3pOH$, and $pFe + pAsO_4$ listed in Table 4 for the Menfro soil under anaerobic and aerobic conditions indicate that the Menfro soil has values similar to the Sharpsburg. The aluminum hydroxide ion product is what is predicted from the data of Misra et al. (16), and Blanchar and Scrivner (5). The ferric hydroxide ion product for the dextrose anaerobic is high, but the other values indicate that the Menfro soil is supersaturated with respect to ferric hydroxide. The ion products for $pAl + pAsO_4$ and $pFe + pAsO_4$ show that the Menfro soil is undersaturated in respect to aluminum and ferric arsenate, with ion product values of 22.83 and 21.42. The dextrose anaerobic equilibration data for the Menfro soil indicate that the system is not an equilibrium system in agreement with the Sharpsburg soil.

Table 5 lists ion products for the Sharpsburg and the Menfro soil equilibrated with acid-base solutions.

Table 4. The effect of time on the ion products of iron and aluminum oxides and arsenates in a Menfro soil under anaerobic and aerobic conditions.

Time	water						1% dextrose					
	pH	Eh	pAl + 3pOH	pAl + pAsO$_4$	pFe + 3pOH	pFe + pAsO$_4$	pH	Eh	pAl + 3pOH	pAl + pAsO$_4$	pFe + 3pOH	pFe + pAsO$_4$
days		mV						mV				
						Anaerobic						
0	6.24	581	33.49	22.87	33.26	21.83	6.33	581	33.49	22.53	33.20	21.43
4	6.42	409	33.33	21.79	32.85	20.34	4.89	55	34.14	24.72	42.22	27.17
8	6.56	314	33.33	21.71	33.84	21.25	4.38	61	34.34	25.20	43.38	27.74
12	7.07	398	33.08	22.22	32.11	20.03	4.45	315	34.36	18.70	38.80	23.20
16	7.07	205	33.07	22.13	34.01	21.84	4.62	315	34.23	18.82	38.43	22.96
20	7.11	293	33.04	22.32	32.66	20.68	4.53	307	34.29	18.71	38.76	23.17
Mean			33.22	22.17	33.12	21.00			34.14	21.45	39.13	24.28
S.D.			0.19	0.43	0.73	0.77			0.33	3.09	3.56	2.55
	after anaerobic, water						after anaerobic, 1% dextrose					
						Aerobic, 26.7% moisture						
4*	7.22	547	32.96	23.72	33.40	21.82	6.13	481	33.53	21.91	34.04	20.65
8	7.12	534	33.00	23.74	33.48	21.92	6.50	439	33.37	22.36	33.95	21.01
12	6.89	575	33.15	22.92	33.83	21.45	6.68	434	33.29	22.49	34.17	21.36
24	6.92	555	33.13	23.44	33.70	21.84	7.91	498	32.68	24.97	33.71	23.38
48	6.82	604	33.20	23.62	33.86	22.18	7.91	493	32.67	25.45	33.71	23.87
Mean			33.09	23.49	33.61	21.84			33.11	23.44	33.92	22.05
S.D.			0.10	0.34	0.21	0.26			0.40	1.64	0.20	1.47

*Day 0 = day 21 of anaerobic.

Table 5. Ion products of aluminum and iron oxides and arsenates in a Sharpsburg and a Menfro soil after equilibration with dilute HCl and NaOH for 7 days at 25° C.

	Sharpsburg						Menfro					
Initial pH	Final pH	Eh	pAl + 3pOH	pAl + $pAsO_4$	pFe + 3pOH	pFe + $pAsO_4$	Final pH	Eh	pAl + 3pOH	pAl + $pAsO_4$	pFe + 3pOH	pFe + $pAsO_4$
		mV						mV				
2	3.61	685	35.22	19.61	37.01	22.32	6.84	523	33.23	22.15	32.69	20.54
3	4.89	642	34.13	20.04	34.10	19.84	7.42	485	32.93	22.85	32.54	21.09
4	5.55	600	33.67	20.47	32.83	19.00	7.35	486	32.98	22.86	32.65	21.21
5	6.43	564	33.34	21.64	32.32	19.65	7.17	491	33.06	22.53	32.62	20.85
6	6.38	573	33.34	21.70	32.27	19.67	7.35	486	32.98	22.80	32.47	20.97
7	6.42	555	33.31	21.51	31.87	19.09	7.32	482	33.00	22.72	32.45	20.87
8	6.39	550	33.31	21.42	32.12	19.24	7.26	482	33.03	22.65	32.53	20.88
Mean			33.51*	21.13*	32.28†	19.42‡			33.03	22.65	32.59	20.92
S.D.			0.33	0.70	0.35	0.35			0.10	0.25	0.09	0.21

*Values at initial pH 2, 3, and 4 were not used in determining the mean.

†Values at initial pH 2 and 3 were not used in determining the mean.

‡Value at initial pH 2 was not used in determining the mean.

The ion products of pAl + 3pOH, pAl + $pAsO_4$, pFe + 3pOH, and pFe + $pAsO_4$ for the Menfro and the Sharpsburg soil suggests that they are undersaturated and that these forms of arsenic are not stable in these soil systems.

Examination of Table 6 shows that the ion product 3pMn + $2pAsO_4$ varies under the conditions of the experiment. For the anaerobic water, the value is 34.54, which is comparable with the values of 33.66 determined on the manganese arsenate synthesized the laboratory. However, no comparison can be made between the two values because of the high value of the standard deviation of 3.69. The value of the ion product for the anaerobic dextrose is not an equilibrium value, with a standard deviation of 10.45, and a mean of 40.72. The mean value is high due to the ion product values obtained at pH 4.98 and 4.59, where the Eh value is negative. At these values of oxidation-reduction potential, the form of As in solution would be expected to be $HAsO_2$, and this would account for the increase in the value of the ion product. Both the water and the dextrose aerobic samples show the Sharpsburg soil to be undersaturated with respect to manganese arsenate, with values of 37.07 and 36.71. The free energies of formation of the manganese oxides, Mn_3O_4,

Table 6. Standard cell potentials and free energies of formation for Mn_3O_4, Mn_2O_3, and MnO_2, and the ion product of $Mn_3(AsO_4)_2$ calculated for a Sharpsburg soil at various times after anaerobic and aerobic treatment.

Time	pH	Eh	E°*	E°†	E°‡	ΔF°_f			3pMn + 2pAsO$_4$
						Mn_3O_4	Mn_2O_3	MnO_2	
days		mV				kcal/mole			
					Anaerobic water				
0	5.57	606	1486	1302	1118	-321.72	-219.00	-116.29	40.99
4	5.68	467	1440	1227	1015	-323.83	-222.45	-121.07	36.30
8	5.81	467	1492	1262	1032	-321.45	-220.85	-120.25	34.45
12	6.17	499	1619	1367	1115	-315.58	-216.01	-116.45	32.70
16	6.41	516	1683	1420	1157	-312.62	-213.56	-114.50	31.91
20	6.48	501	1707	1433	1158	-311.50	-212.98	-114.46	30.90
Mean			1571	1335	1099	-318.22	-217.48	-117.14	34.54
S.D.			113	85	62	5.72	3.90	2.81	3.69

Table 6 (continued)

Time	pH	Eh	E°*	E°†	E°‡	F_f°			3pMn + 2pAsO$_4$
						Mn$_3$O$_4$	Mn$_2$O$_3$	MnO$_2$	
days		mV				kcal/mole			
					Anaerobic, 1% dextrose				
0	5.73	602	1559	1353	1146	-318.33	-216.66	-114.99	38.12
4	4.98	-54	833	636	438	-351.81	-249.75	-147.69	53.55
8	4.59	-40	787	602	416	-353.95	-251.31	-148.68	54.31
12	5.00	227	1151	941	732	-337.16	-235.64	-134.13	33.23
16	5.12	307	1265	1046	828	-331.92	-230.81	-129.70	32.47
20	5.14	347	1303	1086	868	-330.13	-228.98	-127.84	32.64
Mean			1500	944	738	-337.23	-235.53	-133.84	40.72
S.D.			295	286	278	13.62	13.21	12.81	10.45
			Aerobic, 26.7% moisture, following anaerobic, water						
4	6.39	577	1694	1447	1201	-312.13	-212.32	-112.50	35.45
8	6.17	612	1671	1439	1208	-313.20	-212.69	-112.17	36.47
12	6.23	585	1650	1418	1185	-314.14	-213.67	-112.21	36.06
24	6.30	571	1634	1403	1173	-314.89	-214.33	-112.76	37.23
48	5.30	662	1536	1349	1162	-319.41	-216.85	-114.99	40.14
Mean			1637	1411	1186	-314.75	-213.97	-112.93	37.07
S.D.			61	39	19	2.80	1.79	1.18	1.83

Table 6 (continued)

						F°_f			
Time	pH	Eh	E°*	E°†	E°‡	Mn_3O_4	Mn_2O_3	MnO_2	3pMn + 2pAsO_4
days		mV				kcal/mole			
			Aerobic, 26.7% moisture, following anaerobic, 1% dextrose						
4	4.97	556	1442	1244	1047	-323.75	-221.67	-119.59	36.17
8	4.94	559	1432	1238	1044	-324.20	-221.95	-119.71	36.62
12	4.94	572	1444	1251	1057	-323.64	-221.38	-119.12	36.47
24	5.09	591	1444	1251	1071	-324.26	-221.37	-118.47	38.52
48	5.15	558	1488	1279	1071	-321.60	-220.50	-118.49	35.67
Mean			1450	1253	1058	-323.49	-221.37	-119.08	36.71
S.D.			22	16	13	1.09	0.54	0.58	1.08

*Computed for the reaction: $3Mn^{2+} + 4H_2O = Mn_3O_4 + 8H^+ + 2e^-$.

†Computed for the reaction: $2Mn^{2+} + 3H_2O = Mn_2O_3 + 6H^+ + 2e^-$.

‡Computed for the reaction: $Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$.

Mn_2O_3, and MnO_2 indicate that the soil is undersaturated with these oxides, except for the free energy of formation of MnO_2 in the aerobic water determination where the value is -112.93, which is comparable to the reported value of -111.18 (18), showing only a slight undersaturation.

Table 7 shows the values of the ion product $3pMn + 2pAsO_4$ and the free energies of formation of the manganese oxides for the Sharpsburg soil equilibration with dilute HCl and NaOH. The ion product value of 33.56 agrees very well with that of the mineral (33.66), suggesting that the Sharpsburg soil may have a solid phase of manganese arsenate present. The values for the free energies of formation of the oxides also indicate that they are not as undersaturated as the values obtained in the anaerobic and the aerobic experiment, but that for MnO_2 and Mn_2O_3, they are only slightly undersaturated, with values of -113.60 and -213.92 compared to -111.18 and -210.6.

Table 8 lists the values of the ion product $3pMn + 2pAsO_4$ and the free energies of formation of the manganese oxides for the Menfro soil. The ion product, $3pMn + 2pAsO_4$, for the anaerobic studies is not an equilibrium product, with values of 31.15 ± 3.92 for the water anaerobic, and 37.91 ± 5.83 for the dextrose anaerobic. The ion product value of the water anaerobic shows it to be supersaturated, while the value of the dextrose anaerobic shows it to be

Table 7 . Standard cell potentials and free energies of formation for Mn_3O_4, Mn_2O_3, and MnO_2 and the ion product of $Mn_3(AsO_4)_2$ calculated for a Sharpsburg soil after equilibration with dilute HCl and NaOH for 7 days at 25° C.

Initial pH	Final pH	Eh	E°*	E°†	E°‡	ΔF°_f Mn_3O_4	ΔF°_f Mn_2O_3	ΔF°_f MnO_2	$3pMn + 2pAsO_4$
		mV				kcal/mole			
2	3.61	685	1236	1123	1011	-333.24	-227.25	-121.26	43.16
3	4.89	642	1412	1251	1091	-325.14	-221.35	-117.56	39.17
4	5.55	600	1517	1321	1124	-320.20	-218.15	-116.03	36.35
5	6.43	564	1676	1432	1188	-312.92	-213.01	-113.09	33.82
6	6.38	573	1605	1386	1168	-316.23	-215.57	-114.01	33.59
7	6.42	555	1663	1420	1177	-313.54	-213.57	-113.59	33.70
8	6.39	550	1668	1421	1174	-313.30	-213.51	-113.72	33.11
Mean			1653§	1415§	1177§	-313.84§	-213.92§	-113.60§	33.56§
S.D.			32	20	8	1.35	1.13	0.38	0.31

*Computed for the reaction: $3Mn^{2+} + 4H_2O = Mn_3O_4 + 8H^+ + 2e^-$.

†Computed for the reaction: $2Mn^{2+} + 3H_2O = Mn_2O_3 + 6H^+ + 2e^-$.

‡Computed for the reaction: $Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$.

§Values at initial pH 2, 3 and 4 were not used in determining the mean.

Table 8. Standard cell potentials and free energies of formation for Mn_3O_4, Mn_2O_3, and MnO_2, and the ion product of $Mn_3(AsO_4)_2$ calculated for a Menfro soil at various times after anaerobic and aerobic treatment.

						ΔF°_f			
Time	pH	Eh	E°*	$E^{\circ\dagger}$	$E^{\circ\ddagger}$	Mn_3O_4	Mn_2O_3	MnO_2	$3pMn + 2pAsO_4$
days		mV				kcal/mole			
					Anaerobic, water				
0	6.24	581	1637	1408	1178	-314.73	-214.13	-113.52	37.81
4	6.42	409	1534	1285	1037	-319.48	-219.77	-120.06	33.68
8	6.56	314	1530	1254	978	-319.66	-221.22	-122.79	30.70
12	7.07	398	1747	1436	1126	-309.69	-212.82	-115.96	28.26
16	7.07	205	1557	1246	934	-318.42	-221.61	-124.80	27.97
20	7.17	293	1645	1334	1023	-314.39	-217.54	-120.68	28.45
Mean			1608	1327	1046	-316.06	-217.85	-119.64	31.15
S.D.			84	80	91	3.88	3.70	4.21	3.92
					Anaerobic, 1% dextrose				
0	6.33	581	1730	1472	1213	-310.43	-211.18	-111.92	34.15
4	4.89	55	938	740	542	-346.99	-244.94	-142.89	41.97
8	4.38	61	843	669	494	-351.35	-248.22	-145.09	48.04
12	4.45	315	1109	932	755	-339.10	-236.08	-133.07	34.79
16	4.62	315	1149	962	775	-337.23	-234.68	-132.13	34.00
20	4.53	307	1115	935	755	-338.80	-235.94	-133.07	34.49
Mean			1147	952	756	-337.32	-235.17	-133.03	37.91
S.D.			309	282	254	14.27	12.98	11.74	5.83

Table 8 (continued)

Time	pH	Eh	E°*	E°†	E°‡	ΔF_f°			
						Mn_3O_4	Mn_2O_3	MnO_2	$3pMn + 2pAsO_4$
days		mV				kcal/mole			
Aerobic, 26.7% moisture, following anaerobic, water									
4	7.22	547	1855	1561	1267	-304.70	-207.07	-109.44	32.95
8	7.12	534	1832	1539	1247	-305.77	-208.07	-110.38	33.13
12	6.89	575	1823	1543	1262	-306.16	-207.91	-109.66	32.71
24	6.92	555	1811	1529	1246	-306.70	-208.55	-110.40	33.53
48	6.82	604	1859	1575	1291	-304.49	-206.42	-108.34	33.73
Mean			1836	1549	1263	-305.56	-207.60	-109.64	33.21
S.D.			21	18	18	0.95	0.85	0.84	0.42
Aerobic, 26.7% moisture, following anaerobic, 1% dextrose									
4	6.13	481	1643	1376	1109	-314.46	-215.58	-116.70	32.09
8	6.50	439	1671	1388	1105	-313.16	-215.03	-116.89	31.34
12	6.68	434	1696	1407	1117	-312.03	-214.18	-116.34	30.97
24	7.91	498	2041	1682	1324	-296.09	-201.46	-106.83	28.85
48	7.91	493	1988	1645	1302	-298.56	-203.18	-107.80	31.45
Mean			1808	1500	1191	-306.86	-209.89	-112.92	30.94
S.D.			191	151	111	8.79	6.95	5.12	1.24

*Computed for the reaction: $3Mn^{2+} + 4H_2O = Mn_3O_4 + 8H^+ + 2e^-$.

†Computed for the reaction: $2Mn^{2+} + 3H_2O = Mn_2O_3 + 6H^+ + 2e^-$.

‡Computed for the reaction: $Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$.

undersaturated. The dextrose anaerobic also exhibits the phenomonum of a high 3pMn + 2pAsO$_4$ ion product when low oxidation-reduction potentials exists, as did the Sharpsburg soil. Following the anaerobic phase, the water aerobic ion product agrees quite well with the values determined for the mineral, 33.21 to 33.66. However, the dextrose aerobic indicates that the solution is still supersaturated with respect to manganese arsenate. The free energies of formation of the manganese oxides for the anaerobic phase of the experiment show that the system is undersaturated, while the aerobic phase shows that it is supersaturated with respect to Mn_2O_3, and Mn_3O_4, with values of -208.75 kcal/mole and -306.21 kcal/mole, respectively, compared to reported values of -210.5 and -306.7 kcal/mole (18). The free energy of formation for MnO_2, -111.28, agrees very well with the values reported by the National Bureau of Standards Technical Note 270-4 (18). Table 9 lists the ion product values and free energies of formation for the Menfro soil equilibrated for 7 days at 25° C with dilute HCl and NaOH. The average value of the ion product shows that the Menfro soil is supersaturated with respect to manganese arsenate, and that a stable phase of MnO_2 probably exists, based on the value of the free energy of formation of -111.19 kcal/mole. The free energies of formation of Mn_2O_3 and Mn_3O_4 indicate that the system is supersaturated

Table 9 . Standard cell potentials and free energies of formation for Mn_3O_4, Mn_2O_3, and MnO_2, and the ion product of $Mn_3(AsO_4)_2$ calculated for a Menfro soil after equilibration with dilute HCl and NaOH for 7 days at 25° C.

Initial pH	Final pH	Eh	$E°*$	$E°^{\dagger}$	$E°^{\ddagger}$	$\Delta F_f°$			3pMn + 2pAsO$_4$
						Mn_3O_4	Mn_2O_3	MnO_2	
		mV				kcal/mole			
2	6.84	523	1817	1520	1223	-306.43	-208.94	-111.44	29.51
3	7.42	485	1887	1566	1244	-303.21	-206.85	-110.49	28.41
4	7.32	486	1857	1545	1232	-304.57	-207.80	-111.04	29.33
5	7.17	491	1827	1522	1218	-306.00	-208.84	-111.69	29.54
6	7.35	486	1864	1549	1234	-304.28	-207.61	-110.94	28.99
7	7.32	482	1859	1544	1229	-304.48	-207.83	-111.18	28.78
8	7.26	484	1838	1529	1221	-305.48	-208.52	-111.56	29.32
Mean			1850	1539	1229	-304.85	-208.06	-111.19	29.13
S.D.			24	17	9	1.060	0.75	0.41	0.42

*Computed for the reaction: $3Mn^{2+} + 4H_2O = Mn_3O_4 + 8H^+ + 2e^-$.

†Computed for the reaction: $2Mn^{2+} + 3H_2O = Mn_2O_3 + 6H^+ + 2e^-$.

‡Computed for the reaction: $Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$.

with these two oxides, with free energies of formation of -208.06 and -304.85 kcal/mole. The standard deviations indicated that these values can be considered equilibrium values.

The ion products $3pCa + 2pAsO_4$ and $3pPb + 2pAsO_4$ are listed in Tables 10 and 11 for the Sharpsburg and the Menfro soils for anaerobic and aerobic conditions. In both soils the ion product $3pCa + 2pAsO_4$ is much higher than that predicted by the mineral data, showing that in both soils calcium arsenate was not stable. The predicted value of this ion product is 18.57, which is in agreement with the value of Chukhlantsev's 18.17 (7). In the case of the Sharpsburg soil, the values are all greater than 30, and for the Menfro soil greater than 25.

The ion product $3pPb + 2pAsO_4$ for the Sharpsburg soil in the water anaerobic and aerobic agrees with the predicted value of 39.53 from the mineral. The value for the aerobic water is 39.18, and for the anaerobic water it is 36.92, showing that the aerobic water is saturated with respect the lead arsenate. The values of 34.08 and 37.18 for the Menfro anaerobic and aerobic show that it is supersaturated with respect to lead arsenate. The values of the ion product for the dextrose samples show that the ion product decreased at low oxidation-reduction potential, as did the ion products of several of the other arsenates.

Table 10. Ion products of calcium and lead arsenates in a Sharpsburg soil under anaerobic and aerobic conditions.

	water				1% dextrose			
Time	pH	Eh	3pCa + $2pAsO_4$	3pPb + $2pAsO_4$	pH	Eh	3pCa + $2pAsO_4$	3pPb + $2pAsO_4$
days		mV				mV		
				Anaerobic				
0	5.57	606	35.90	40.53	5.73	602	32.75	39.35
4	5.68	467	32.26	37.98	4.98	-54	50.50	58.26
8	5.81	460	30.92	37.50	4.59	-40	51.86	60.24
12	6.17	499	29.27	36.42	5.00	227	30.88	38.97
16	6.41	516	28.63	34.76	5.12	307	30.20	38.40
20	6.48	501	27.91	34.34	5.14	347	30.20	38.20
Mean			30.82	36.92			37.73	45.57
S.D.			2.95	2.28			10.47	10.62
	after anaerobic, water				after anaerobic, 1% dextrose			
				Aerobic				
4*	6.39	577	31.90	38.08	4.97	556	33.80	42.94
8	6.17	612	32.70	39.36	4.94	559	33.91	43.50
12	6.23	585	32.02	38.84	4.94	572	33.91	43.52
24	6.30	571	32.56	39.99	5.09	591	33.90	43.62
48	5.30	662	32.00	39.64	5.15	558	33.78	42.15
Mean			32.24	39.18			33.86	43.15
S.D.			0.37	0.75			0.06	0.62

*Day 0 = day 21 anaerobic.

Table 11. Ion products of calcium and lead arsenates in a Menfro soil under anaerobic and aerobic conditions.

	water				1% dextrose			
Time	pH	Eh	$3pCa + 2pAsO_4$	$3pPb + 2pAsO_4$	pH	Eh	$3pCa + 2pAsO_4$	$3pPb + 2pAsO_4$
days		mV				mV		
				Anaerobic				
0	6.24	581	33.32	38.47	6.33	581	30.22	37.41
4	6.42	409	29.86	34.55	4.89	55	41.97	49.56
8	6.56	314	27.26	35.14	4.38	61	45.60	55.50
12	7.07	398	24.90	32.44	4.45	315	32.19	39.85
16	7.07	205	24.62	31.72	4.62	315	31.41	39.00
20	7.11	293	24.27	32.13	4.53	307	31.92	39.43
Mean			27.37	34.08			35.55	43.46
S.D.			3.60	2.56			6.52	7.32
	after anaerobic, water				after anaerobic, 1% dextrose			
				Aerobic				
4*	7.22	547	29.43	36.11	6.13	481	28.89	39.14
8	7.12	534	29.92	36.59	6.50	439	27.92	38.39
12	6.89	575	29.33	37.41	6.68	434	27.34	37.96
24	6.92	555	29.94	37.23	7.91	498	26.28	35.84
48	6.82	604	29.49	38.60	7.91	493	27.41	35.25
Mean			29.62	37.19			27.57	36.72
S.D.			0.29	0.94			0.95	1.38

*Day 0 = day 21 anaerobic.

Table 12 lists the values of $3pCa + 2pAsO_4$ and $3pPb + 2pAsO_4$ and confirms the above conclusion, that calcium arsenate is unstable and that lead arsenate is stable.

The data from the minerals synthesized in the laboratory were used to construct Eh-pH diagrams to predict the stability of the arsenate compounds in Menfro and Sharpsburg soils. Using the ion product values listed in Tables 3, 4, and 5 in Chapter 5 and the standard cell potentials listed in Table 4, phase diagrams of arsenate stability were constructed according to the methods of Garrels and Christ (12). Stability lines were drawn for the indicated arsenates using the following equations:

MnO_2-Mn_2O_3

$$16.89Eh - pH = 16.42 \quad [9]$$

$AlAsO_4$-$Mn_3(AsO_4)_2$, from MnO_2

$$50.67Eh + 3pH = 54.6 \quad [10]$$

$AlAsO_4$-$Pb_3(AsO_4)_2$

$$pH = 4.08 \quad [11]$$

$FeAsO_4$-$Mn_3(AsO_4)_2$, from MnO_2

$$50.67Eh + 3pH = 53.04 \quad [12]$$

Table 12. Ion products of calcium and lead arsenates in a Sharpsburg and a Menfro soil after equilibration with dilute HCl and NaOH for 7 days at 25° C.

	Sharpsburg				Menfro			
Initial pH	Final pH	Eh	$3pCa + 2pAsO_4$	$3pPb + 2pAsO_4$	Final pH	Eh	$3pCa + 2pAsO_4$	$3pPb + 2pAsO_4$
		mV				mV		
2	3.61	685	39.98	44.82	6.84	523	25.60	38.43
3	4.89	642	35.42	39.23	7.42	485	24.73	36.06
4	5.55	600	32.63	35.83	7.35	486	25.54	36.44
5	6.43	564	29.93	33.15	7.17	491	25.94	36.87
6	6.38	573	30.71	33.53	7.35	486	25.46	36.31
7	6.42	555	29.86	32.40	7.32	482	25.31	36.36
8	6.39	550	29.41	32.84	7.26	484	25.68	36.55
Mean			29.98*	32.98*			25.47	36.43†
S.D.			0.54	0.48			0.38	0.27

*Values at initial pH 2, 3, and 4 were not used in determining the mean.

†Value at initial pH 2 was not used in determining the mean.

$FeAsO_4$-$Pb_3(AsO_4)_2$

$$pH = 4.60 \qquad [13]$$

$Pb_3(AsO_4)_2$-$Mn_3(AsO_4)_2$, from MnO_2

$$50.67Eh + 6pH = 66.84 \qquad [14]$$

$Pb_3(AsO_4)_2$-$Mn_3(AsO_4)_2$, from Mn_2O_3

$$25.47Eh + 4.5pH = 42.21 \qquad [15]$$

$AlAsO_4$-$Ca_3(AsO_4)_2$

$$pH = 6.57 \qquad [16]$$

$Ca_3(AsO_4)_2$-$Mn_3(AsO_4)$, from Mn_2O_3

$$25.47Eh + 4.5pH = 49.69 \qquad [17]$$

Figure 11 is a representation of these equations, including the stability lines for water at 1 atmosphere, and the limits of stability in the natural environment as determined by Bass Becking et al. (3), and the measured values of Eh and pH determined for the Sharpsburg soil under anaerobic and aerobic conditions. Figure 12 shows the measured values of Eh and pH for the Menfro soil under various anaerobic and aerobic conditions. The circled numbers in Figures 11 and 12 indicate the equation from which the line was constructed. Equations 16 and 17 were not included in Figures 11 and 12, but are given to

○	15 g of soil was equilibrated with 30 ml of water.
□	15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried and maintained in contact with air.
△	15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried, the water adjusted to 26.7%, and maintained in contact with air.
●	15 g of soil was equilibrated with 30 ml of 1% dextrose.
■	15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried and maintained in contact with air.
▲	15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried, the water adjusted to 26.7% and maintained in contact with air.

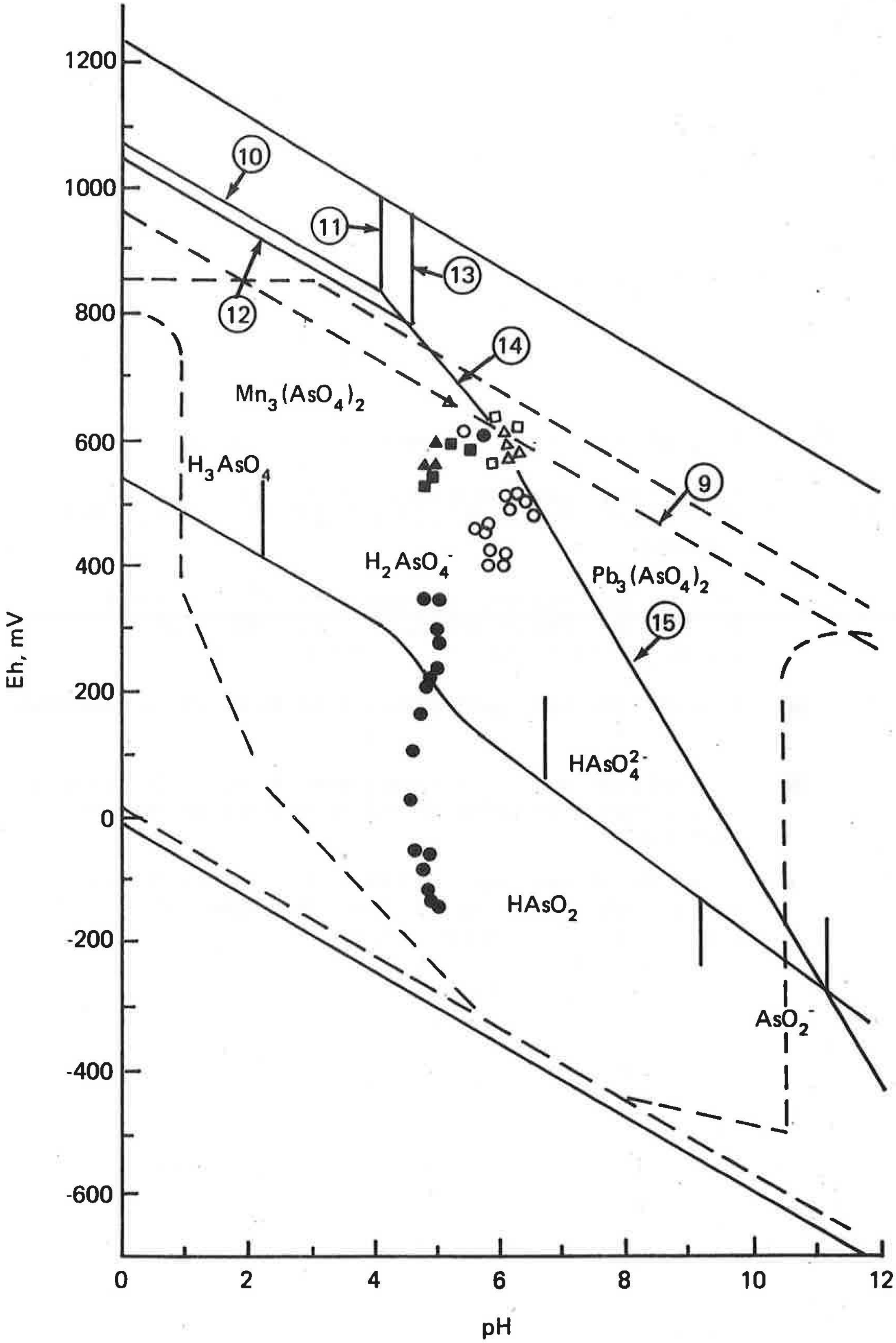


Figure 11. Eh-pH diagram of stable arsenates compared to the measured values in a Sharpsburg soil.

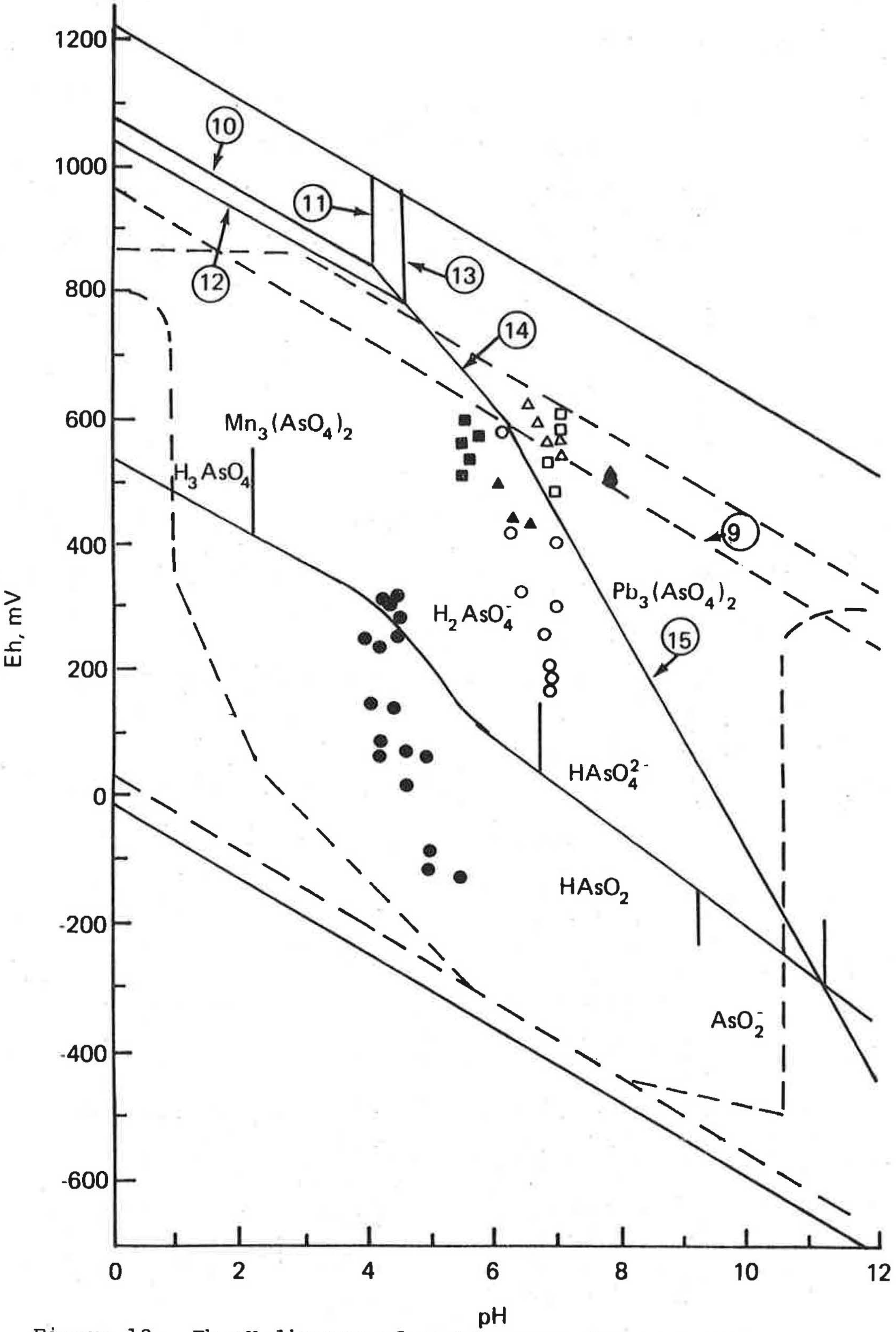


Figure 12. Eh-pH diagram of stable arsenates compared to measured values in a Menfro soil.

show that calcium arsenate is much less stable than is lead arsenate. These soils have higher lead concentrations than would be expected in a non-contaminated soil and may be why lead controls the arsenate solubility in these cases.

Figures 11 and 12 show the stable forms of As that would be expected to be found at various values of Eh and pH. Line 9 is the stability line of MnO_2 and Mn_2O_3 with MnO_2 controlling the formation of manganese arsenate above the line, and Mn_2O_3 below the line. Below line 15, from pH 6 to 12, the stability of manganese arsenate in controlled by Mn_2O_3, and from pH 0 to 6 it is controlled by MnO_2. Manganese arsenate below lines 12 or 10, 14 and 15 is the stable form of As in the system. Above lines 14 and 15, lead arsenate controls the stability of As in the system. Below pH 4.6 ferric arsenate, when the pK of ferric hydroxide is 36, is more stable than lead arsenate. Ferric arsenate is in equilibrium with manganese arsenate on line 12 when ferric hydroxide has a pK of 36, and aluminum arsenate is in equilibrium with manganese arsenate on line 10. Lines 10 and 12 indicated that there is some doubt as to which is controlling the arsenate stability in the pH range of 0 to about 4.5. Freshly precipitated ferric hydroxide would control As in the system over aluminum, but Goethite, pK 41, would not.

It cannot be stated specifically which is in equilibrium with manganese arsenate at low pH values, aluminum or ferric hydroxide. In examining the stability boundaries of the natural environment of Bass Becking et al. (3), the equilibrium of ferric arsenate or aluminum arsenate with manganese arsenate becomes academic. The stability of both do not fall within the range of pH and Eh boundaries observed in nature, and therefore, it may be concluded that at low pH values, manganese arsenate will be the most stable form. It appears that in soils which have been treated with lead arsenate, that above pH 4.75, either manganese or lead arsenate is stable depending on the oxidation-reduction potential, as indicated by line 15 in Figures 11 and 12. These conclusions explain why both the Menfro and the Sharpsburg soils were undersaturated with respect to aluminum and iron arsenate.

The As species considered in Equation [3] were predicted as a function of Eh and pH, based on an assumed total As concentration of 1 ppm. These computations were done with the IBM 370/168 computer, and are indicated in Figures 11 and 12. The calculations were applied to the Sharpsburg and Menfro soils, showing that the species $HAsO_2$ and AsO_2^- existed only at low reduction potentials, those of the anaerobic dextrose equilibration. These species dominated in the Menfro soil at pH 4.89 and Eh 55 mV, when the total As in solution was $10^{-3.59}$.

Only at low oxidation-reduction potential and low pH values were any arsenite species present, other wise, the dominant species were H_2AsO_4 and $HAsO_4^{2-}$, which usually comprised of 85-90% of the arsenic present. Since arsenite is considered to be a more toxic form of arsenic, then it would be an important factor at low Eh-pH values in the soil system, conditions that would only be expected to exist when the soil is flooded.

The dissolution data indicate that the As in solution is not at equilibrium, but rather is transient. This may be the manner in which the lead arsenate dissociates once it has been applied to the soil. During wet seasons, when the potential is low, the lead arsenate would dissociate and if the system has sufficient manganese oxides present, the arsenate will form stable manganese arsenates (Figures 11 and 12).

Arsenate Sorption

Soil samples were equilibrated with solution containing 1, 2, 4, 8, and 16 ppm As in a 10 to 1 solution to soil ratio for 96 hours at 25° C with constant shaking. Arsenate sorption in soil as predicted by the Langmuir equation was compared to phosphate sorption (8,14,15,19,28). Figure 13 shows the results with the Sharpsburg soil. The concentration of As in the extract was plotted against the concentration in the extract per amount fixed by the soil.

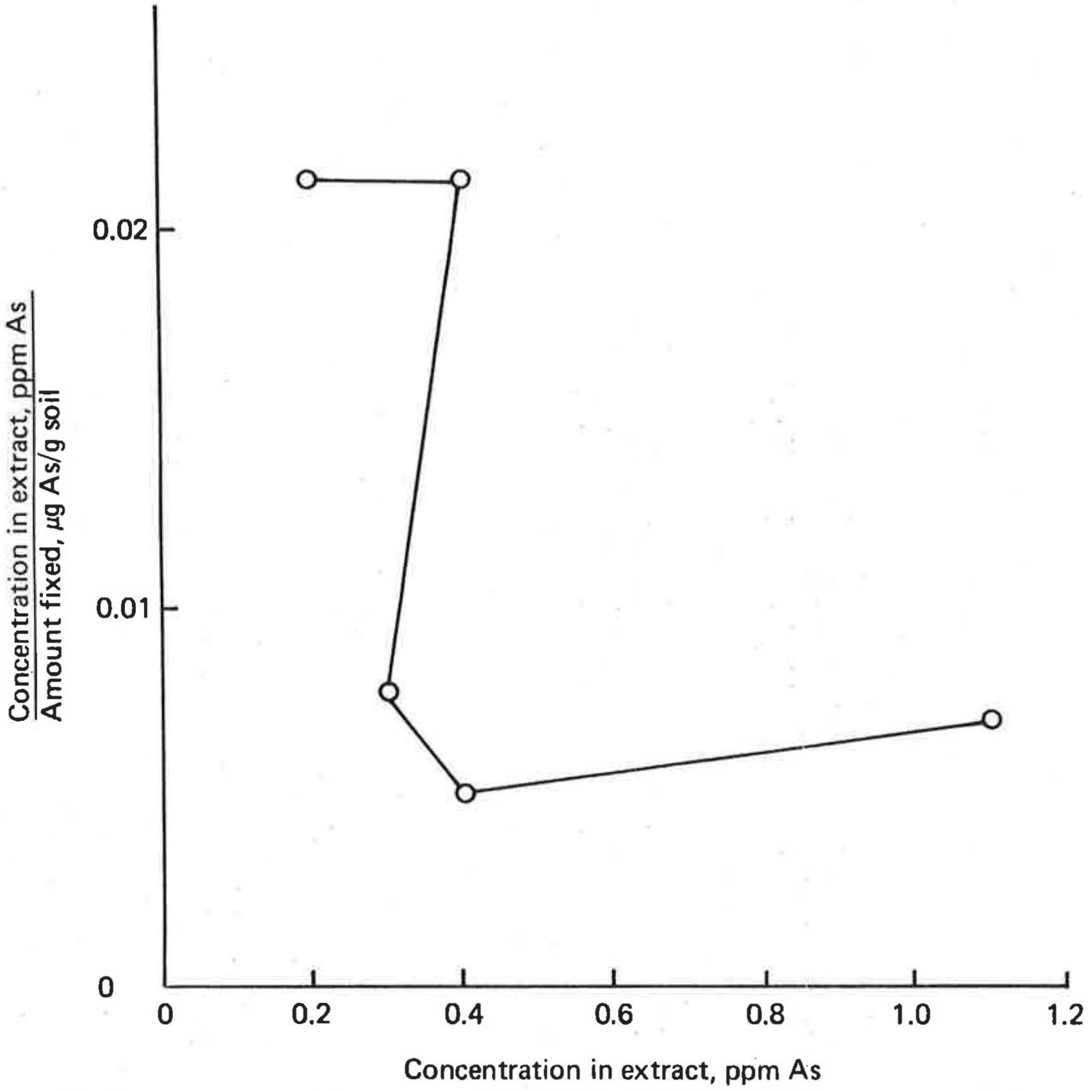


Figure 13. Langmuir adsorption isotherm for the reaction of arsenate with a Sharpsburg soil.

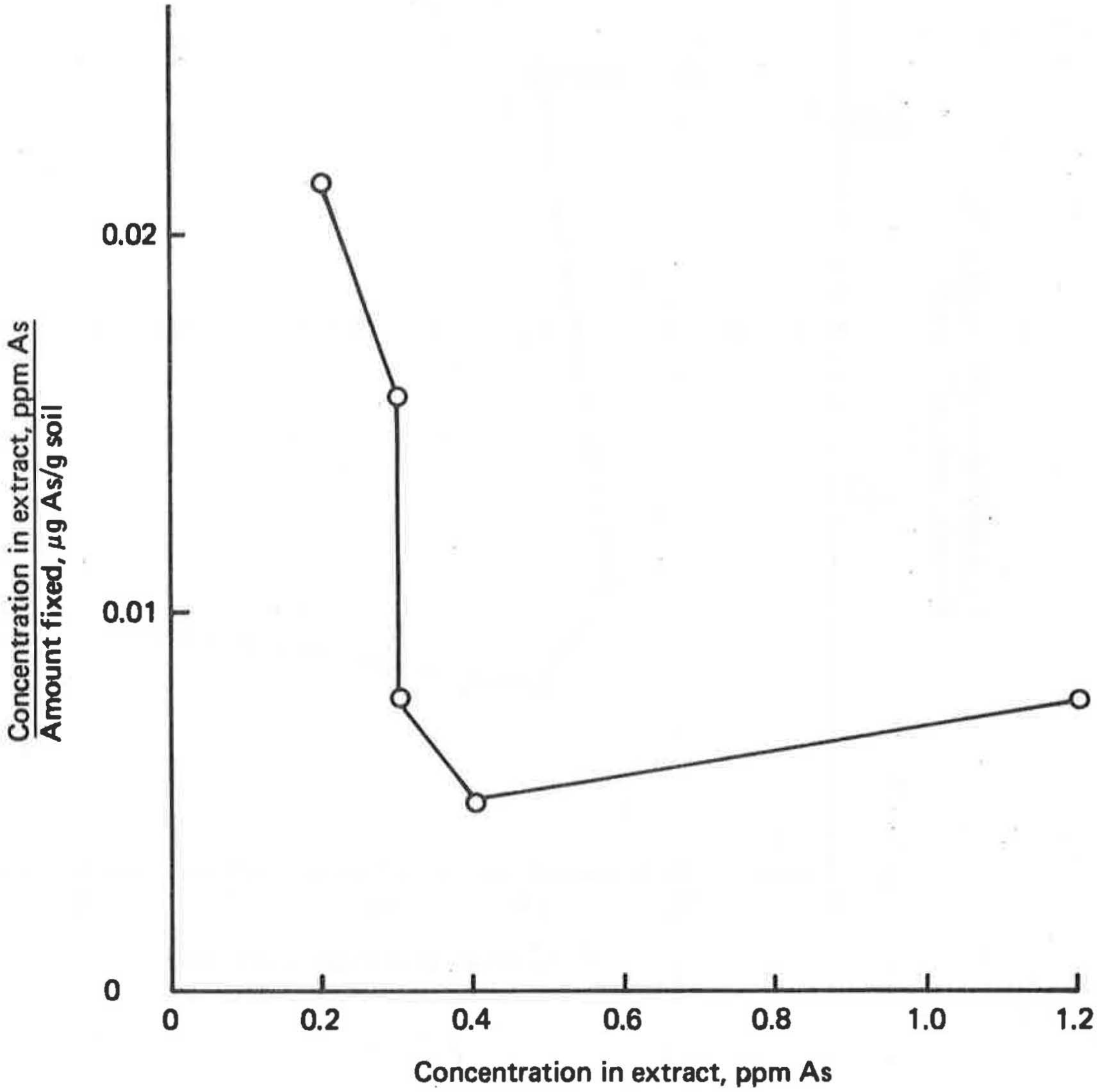


Figure 14. Langmuir adsorption isotherm for the reaction of arsenate with a Menfro soil.

The results show that arsenate sorption by the soil does not follow the predicted relationship for monolayer sorption. The reaction of arsenate with freshly precipitated ferric, aluminum, and manganese hydroxides indicated that arsenate would not be expected to react with the soil as predicted by the Langmuir equation.

The Langmuir equation was developed to predict the sorption of gases on an ideal surface. It apparently does not fit the observed pattern for arsenic interaction with soil. The results of this study indicate that arsenic solubility in the Menfro and Sharpsburg soil can best be predicted from a precipitation mechanism.

Arsenite in solution was also reacted with the soil to discover if it would behave in a similar manner. The arsenite was found to behave similarily, but longer time was needed for equilibrium to occur, indicating that the arsenite had to be first converted to arsenate. This tends to support the hypothosis that arsenate is the stable form of As in the soil.

Biological Reduction of Arsenic to Trimethylarsine

Reed and Sturgis (23) determined that most of the arsenic added to soils that were flooded was lost. They stated that the As levels in the soil returned to levels near that of the naturally occurring As in the soil. They concluded that As loss was due to the biological reduction of arsenate to arsine. It has since been shown that the reduction is not to arsine, but to trimethylarsine (2), and a mechanism for the formation has been proposed (6). No reported methods for measuring the arsenate reduced to trimethylarsine have been found, however, Deuel and Swoboda (9) attempted to show that gaseous loss of As does occur, and to measure the loss. Figures 11 and 12 show that at a partial pressure of 10^{-6} atmospheres, the equilibrium line of arsine coincides with the boundary line of Bass Becking et al. (3) for the most reduced systems which have been observed between pH 6 and 8. Since many soil systems fall into this pH range, it may be that when the potential becomes low enough, some gaseous As would be produced in the soil.

The Sharpsburg and the Menfro soils were tested for the production of gaseous As, by incubating the soil with 1% dextrose and 100 ppm N as urea in a 2 to 1 solution to soil mixture. Table 13 lists the results for the Sharpsburg soil, the Menfro soil, and a uncontaminated Mexico soil, without and with 0.153 g As_2O_5, or 0.132 g As_2O_3 added. The Mexico soil alone showed no As loss throughout the experiment, and with added arsenate and arsenite showed less loss without nitrogen purging than did the contaminated Sharpsburg and Menfro soils. The amount of As lost at 7 and 10 days at 25° C did not change, but when the temperature was increased to 34° C for 7 days, then the

Table 13. Gaseous loss of arsenic from the soil under anaerobic conditions.

	Sharpsburg	Menfro	Mexico	Mexico + AsO_4^{3-}	Mexico + AsO_2^-
	ng As lost/g soil				
	7 days at 25° C				
Mean	12	14	0.0	4	5
S.D.	0.6	3.3		1	0
	7 days at 34° C				
Mean	23	25	0.0	8	9
S.D.	4	1		0.7	0.7
	10 days at 25° C				
Mean	10	14	0.0	7	7
S.D.	0.5	0		1	1
	Continuous nitrogen purging, 4 days at 25° C				
Mean	44.5	64.5	0.0	96	89
S.D.	2.1	5		1.4	1.4

amount of As lost also increased. With continuous nitrogen purging, the amount of As lost as gaseous As increased in many fold.

In the soils where nitrogen was not used as a purging agent, the carrier was the evolved carbon dioxide from the microbial action in the soil. Since gaseous As is more dense than carbon dioxide, and since the evolution of carbon dioxide is not as rapid as the purging with nitrogen, then less As would be lost from the soil. When the oxidation-reduction potential in the soil increased after the initial rapid decrease the gaseous As that had evolved may be reoxidized to arsenite and arsenate. Soil microorganisms have been found that oxidize arsenite to arsenate, then it may be assumed that the gaseous As which was not carried over into the iodine solution would be reoxidized to arsenate. In a natural system, with varying air turbulence the gaseous As may be rapidly removed. Perhaps Reed and Sturgis's conclusion that most of the arsenate added to the soil in flooded areas would be converted to gas and lost is correct.

CONCLUSION

Sharpsburg and Menfro soils contaminated with lead arsenate were subjected to a series of anaerobic and aerobic conditions, and were equilibrated with dilute HCl and NaOH to determine the stable arsenate in the soils. Stability diagrams based on the free energies of formation of ferric, aluminum, manganese, calcium, and lead arsenates were constructed as a model to predict the most stable form of arsenate in the soil. Based on the stability diagram, it was concluded that in a soil that had been treated with lead arsenate, and was saturated with respect the manganese oxides MnO_2 and Mn_2O_3 that manganese and lead arsenate would control the solubility of the arsenate in the soil. The data for both the Menfro and the Sharpsburg soils showed these two soils to be supersaturated with respect to both manganese arsenate and lead arsenate, and therefore, it was concluded that they did control the solubility of arsenate in both of these soils.

It was shown that, as predicted by the reaction of arsenate with freshly precipitated ferric, aluminum, and manganese hydroxides, arsenate did not react with the soil as predicted from the Langmuir equation.

It was shown that the evolution of gaseous As from the soil can be measured, and that in determining the amount converted to a gaseous form, the system needs to be actively purged, otherwise, the gaseous As evolved may be reoxidized to arsenate.

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CHAPTER 7

VARIATIONS IN Eh, pH, AND THE MOBILITY OF ARSENIC IN A MEXICO SOIL

SYNOPSIS

Platinum electrodes were buried at depths of 7.5, 15, 30, and 60 cm in a Mexico soil that had been treated with 100 ppm As and various amounts of sugar sewage sludge, nitrogen, and water. Reed's canary grass was planted after the treatments had been added. One half of the plots were treated with 7.5 cm water per week, while the other half did not receive any added water. The Eh and pH were measured weekly throughout the growing season, and periodically during the rest of the year. The Reed's canary grass was harvested 6 times during the growing season and the yield increased with increased nitrogen application. The amount of arsenic in the plant tissue was measured, and found to decrease toward later stages of the growing season. The amount of As in the plant tissue was independent of the treatment and quite low.

INTRODUCTION

The results of several studies (1,3,4,7,8,12) have been summarized by Woolsen et al. (19), indicating that the soil contains from 0.5 to 14.0 ppm As naturally, and ranges as high as 830 ppm As in contaminated soils. It has been shown that 1 ppm soluble As caused injury to cowpeas (1), 2 ppm As to barley (17), 7 ppm As for rice (6), 9 ppm As for peas, beans, and barley (4), and 4.4 and 1.0 ppm As for soybeans and cotton (5). Soils used to grow cotton that had been treated with calcium arsenate were less productive in the following year when the crop was changed to rice (15).

Jones and Hatch (11) have concluded that the use of arsenical sprays in orchards have made the soil unproductive for future sensitive crops. The As content of soil and ground water was not affected by the treatment of soil with litter, from poultry that had been fed As (13). Only 39-67% of the As added to soils as monosodium methanearsonate was reported recovered (9). Cotton that has not flowered can be treated with monosodium methanearsonate and disodium methanearsonate without increasing the amount of As in the cottonseed or reducing the yield (18). Soil As levels higher than 69.5 ppm As have been found to significantly reduce the growth of lowbush blueberry (2).

The purpose of this study was to examine the conditions that exist in the field in a soil that has been treated with As. Also to determine the mobility and availability of As to canary grass under normal rainfall conditions and under heavy watering.

MATERIALS AND METHODS

The Agronomy Research Farm of the University of Missouri-Columbia was used as the location of this experiment. The experiment was carried out on the Mexico soil type, a fine montmorillonitic mesic Udollic Ochraqualf. The experimental design was a 4 x 4 latin square consisting of sixteen 3 x 3 m plots centered in a 30 x 30 m area, with 1.8 m boundaries between each plot. On all plots 100 ppm As as $(NaH_2AsO_3)_2 \cdot HAsO_2$ was incorporated to a depth of 15 cm. The 4 treatments were:

1. An initial treatment of 11 kg of sugar, 290 kg N/ha as urea, and an additional 7.5 cm water per week during the growing season.
2. An initial treatment of 145 kg N/ha as urea, and 7.5 cm of water per week during the growing season.
3. An initial treatment of 11 kg sugar and 290 kg N/ha as urea.
4. An initial treatment of 145 kg N/ha as urea.

These treatments were applied in August 1973, and were tilled in to a depth of 15 cm with a roto-till. Next platinum electrodes were carefully set in place in a hole made with a 7.5 cm diameter Gideon core sampler. The electrode was placed in the soil so that the platinum wires went gently into the wall of the hole without upsetting the soil at depths of 7.5, 15, 30, and 60 cm. Soil from the core was replaced in the hole by breaking it up according to depth and replacing it with occasional tamping. A second hole was made within 7.5 cm of the electrode and a 40 x 2 cm plastic water pipe with its ends plugged with paraffin was inserted. The purpose of this hole was to insure that the reference electrode reached a point where the soil would be moist throughout most of the season, to provide electrical contact between the two electrodes. After the electrodes were in place, Reed's canary grass was planted. In April 1974, 1 cm of sewage sludge was added to plots with treatments 1 and 3.

The electrode (Figure 1) consisted of a plastic water pipe 1.3 cm in diameter and insulated copper wires with 22 guage platinum wire soldered on one end and a female jack into the other. The wires were placed in the tube so that 2 cm of the platinum would be exposed, and the tube was filled with paraffin to insulate the wires inside the tube against water. The top end of the

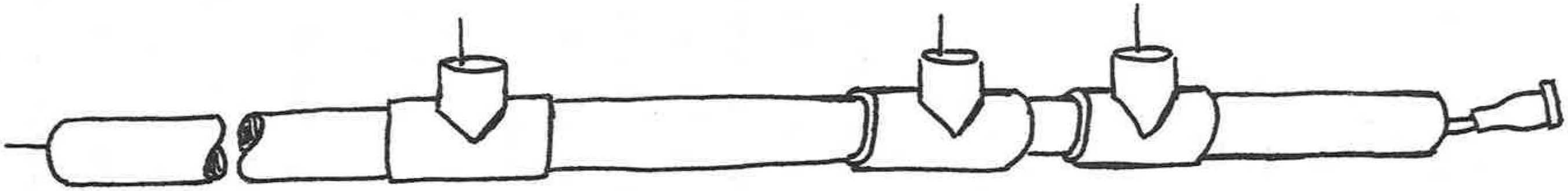

Figure 1. The electrode used to measure the oxidation-reduction potential.

electrode had one female jack for each platinum wire. The 4 electrodes were placed at depths of 7.5, 15, 30 and 60 cm below the soil surface.

Oxidation-reduction potential and pH measurements were made using a portable Orion Research Ionalyzer, Model 404, the platinum electrodes, an Orion sleeve type calomel reference electrode, and a Corning glass electrode. Samples for pH measurements were obtained at the proper depths for the measurement using a Hoffer tube. The soil sampled was placed in a plastic beaker, an equilivalent amount of water added, and the pH measured. The Reed's canary grass was harvested periodically, oven dried for 1 week at 60° C, weighed, and then analyzed for As. Aluminum, iron, calcium manganese and lead were determined on a composite of all the harvests for each treatment, and presented in Appendix Table LXVI.

Soil samples were taken before the As was applied and analyzed for the natural level of As. At the end of the experiment, the plots were again sampled and the soil was analyzed for As to determine As movement in the soil.

RESULTS AND DISCUSSION

Data from Appendix Tables XXV through LV were used to construct Figures 2 through 7. Figures 2 and 3 show the change in pH with depth and time according to the treatment applied. The pattern in all treatments appears

Legend for Figures 2 through 7

* Measurements at a 7.5 cm depth

o Measurements at a 15 cm depth

□ Measurements at a 30 cm depth

Δ Measurements at a 60 cm depth

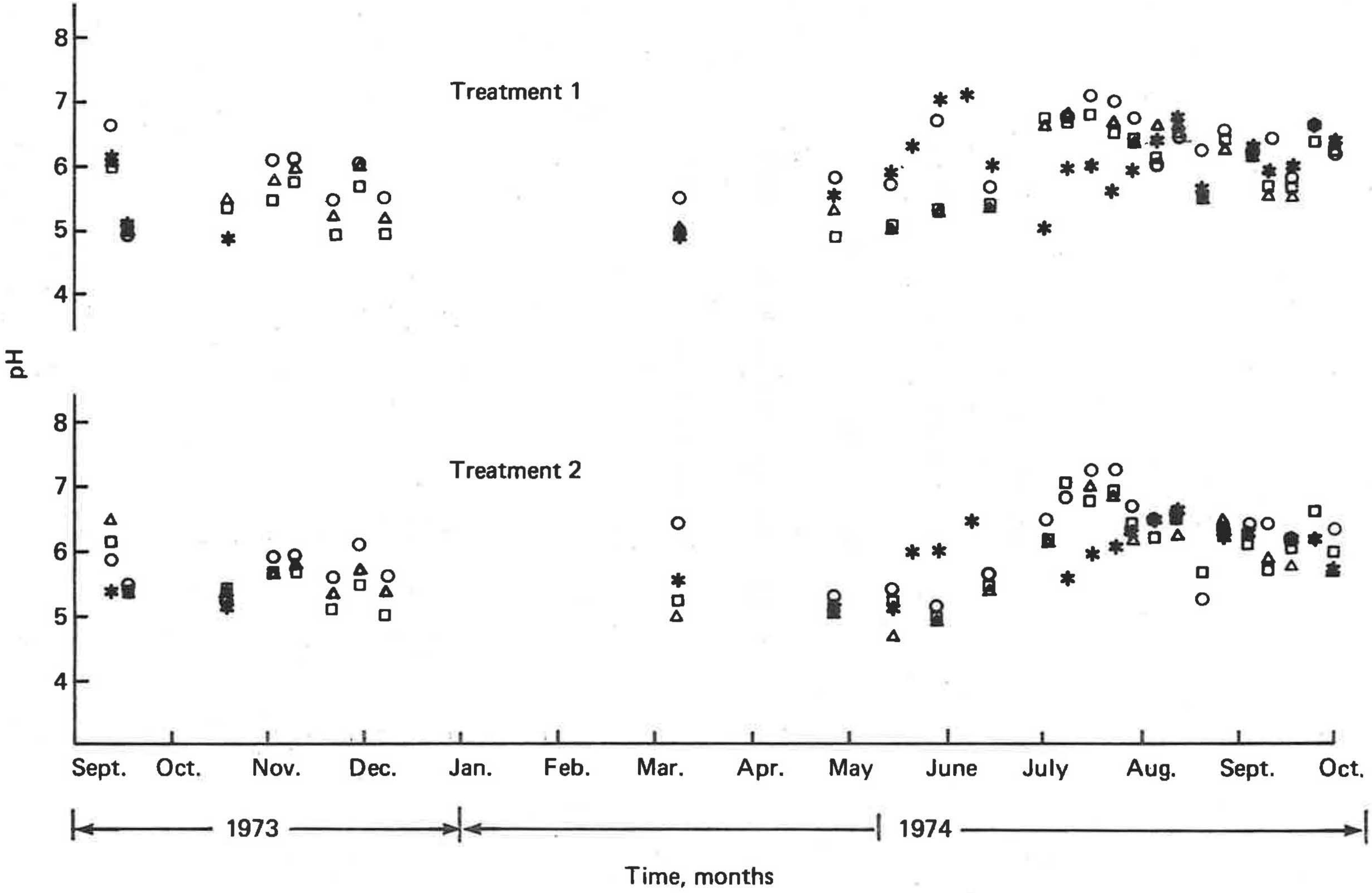

Figure 2. Yearly pH changes in a Mexico soil with depth and excess watering: Treatment 1, sewage sludge + 290 kg N/ha; Treatment 2, 145 kg N/ha.

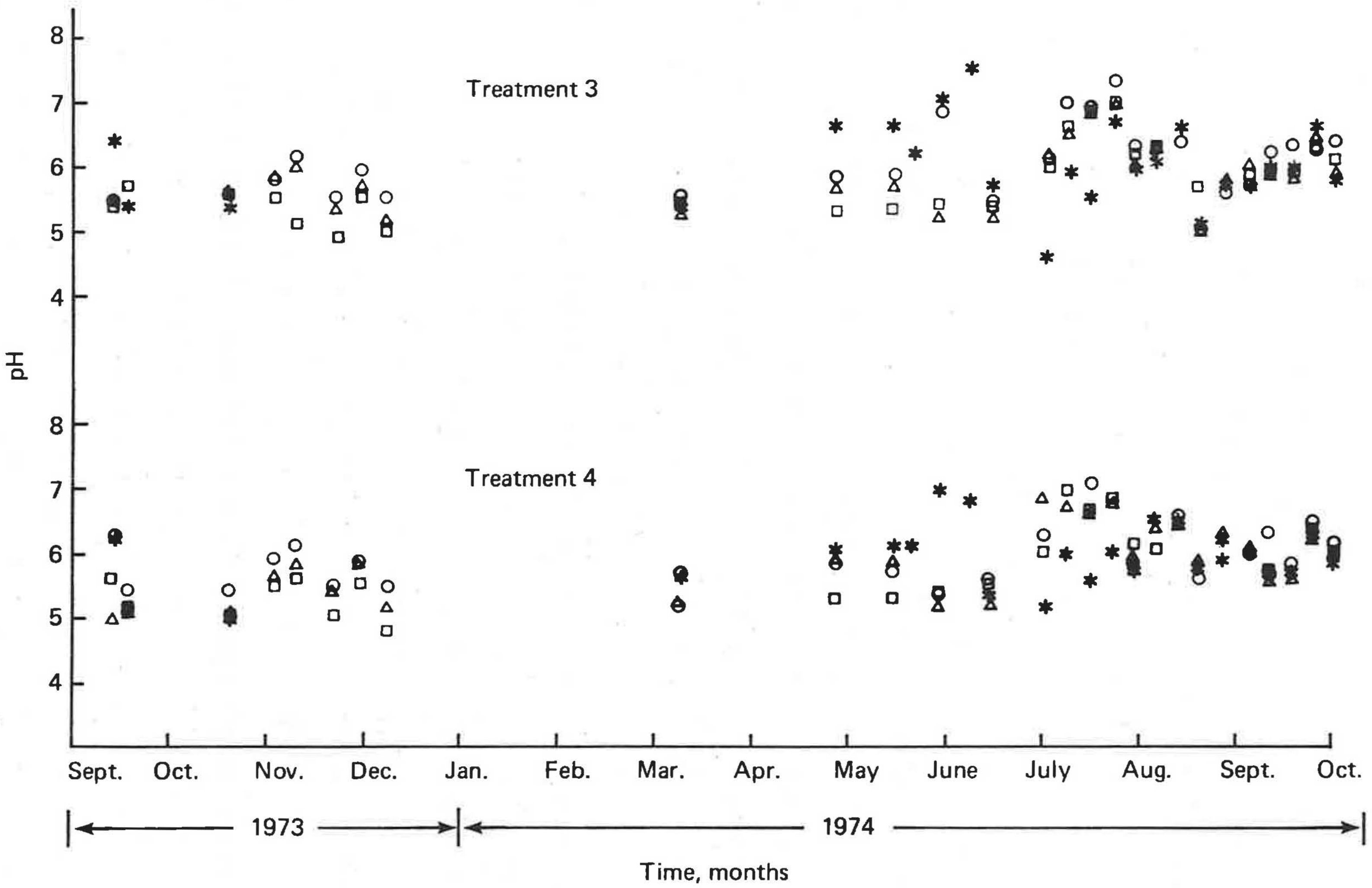

Figure 3. Yearly pH changes in a Mexico soil with depth: Treatment 3, 290 kg N/ha; Treatment 4, 145 kg N/ha.

to be about the same, with the surface pH being the most variable. At 30 and 60 cm below the surface the pH varied less within plots than at 7.5 cm, however there was variation from week to week. Some of the variation may be due to the method of obtaining the soil sample for the measurement. Samples were taken randomly to a depth of 60 cm in each plot for pH measurements. Since the soil is a heterogenous system, it is possible that pH variation was due to sample variation. This would not be expected to account for all of the variation observed in this experiment. Some, perhaps most of it would have to be due to seasonal variation of rainfall, evaporation, and temperature. The pH of the soil was lower in the winter and spring months than it is in the summer and early autumn months. Also, during the winter, spring and late autumn, the soil has a higher percentage of water than it does during the summer and early fall. The highest surface pH was observed in late May, after the sewage sludge had been on the plots for about 1 month and an overnight heavy rainfall of about 2 inches.

Figures 4 and 5 show the variation in the oxidation-reduction potential with depth and time in the plots that had received 7.5 cm of water per week throughout the summer. Treatment 1, with added sugar and 290 kg N/ha showed an increase in Eh at the 60 cm level during mid to late June, and then it dropped to a low of -210 mV in

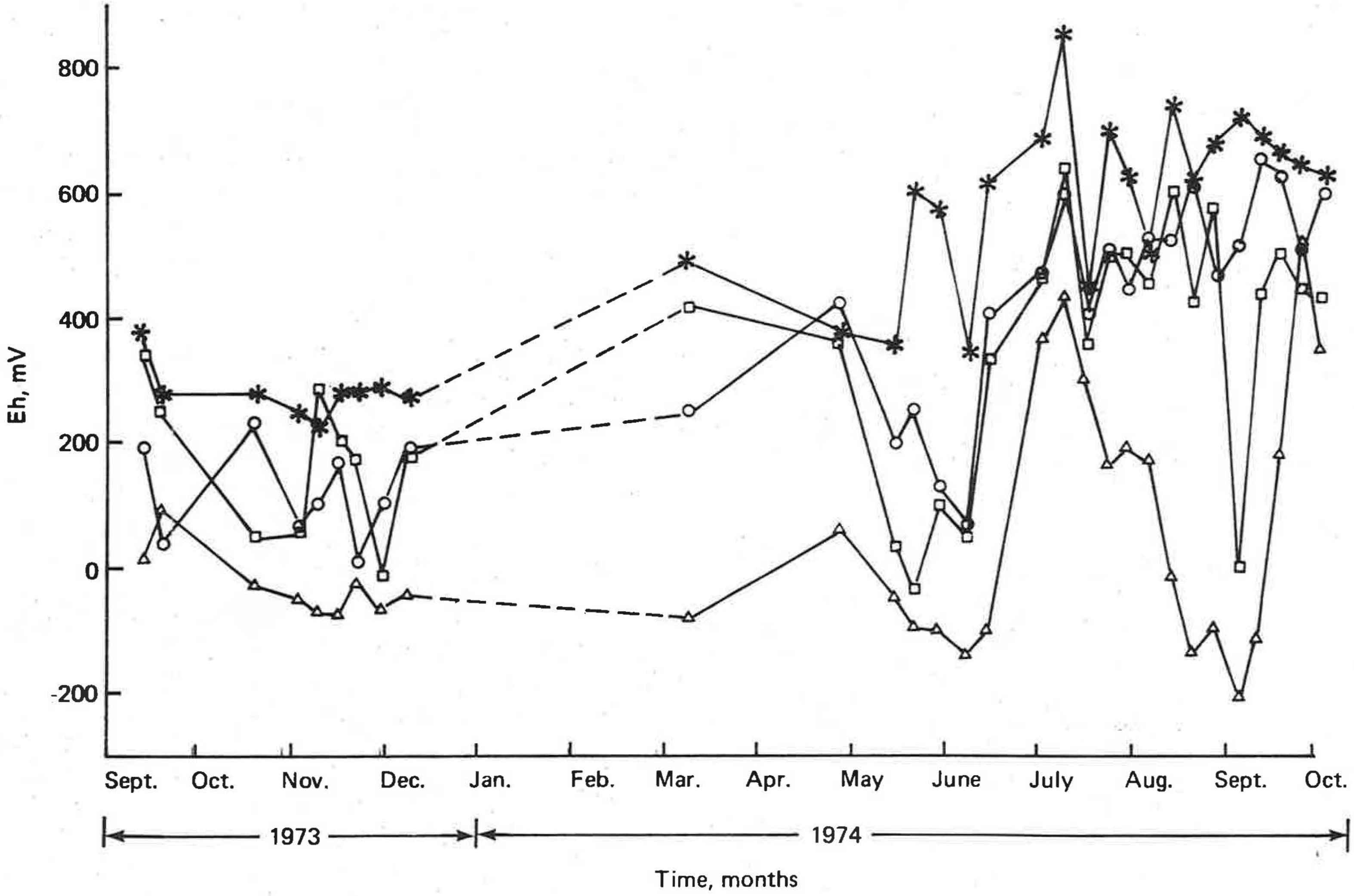

Figure 4. Yearly Eh changes in a Mexico soil with 290 kg N/ha + sewage sludge + excess water.

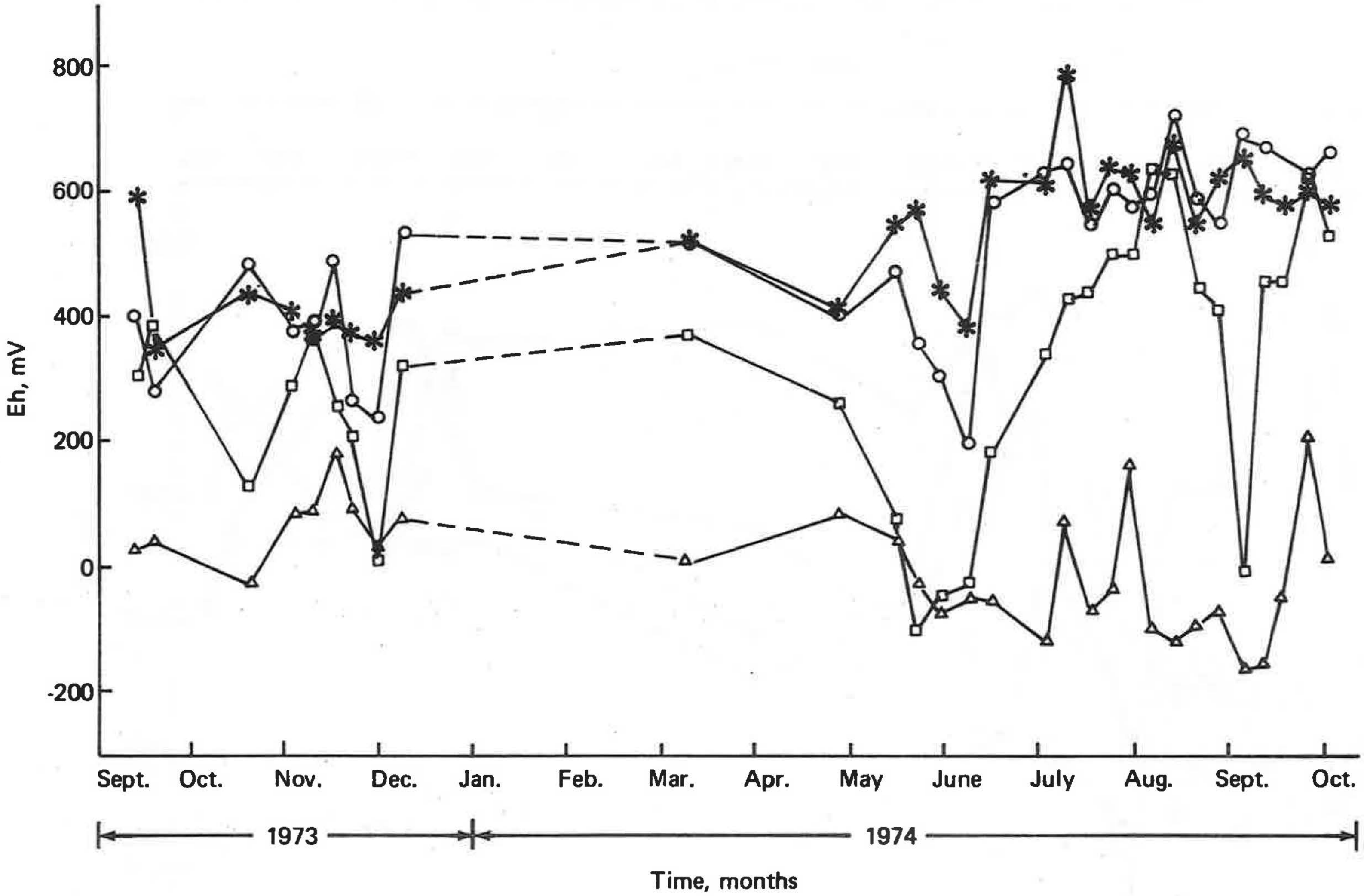

Figure 5. Yearly Eh changes in a Mexico soil with 145 kg N/ha + sewage sludge + excess water.

early September, just after the application of water had stopped. The Eh of treatment 2 at the 60 cm depth remained low throughout the year, reaching a high of 210 mV in late August. The Eh at the 30 cm depth in treatment 1 was in all cases higher than at the 60 cm depth. The Eh at 30 cm showed a greater variability than the Eh at the other depths by going from highly reduced to oxidized. At 7.5 and 15 cm depths, the Eh indicated the soil to be oxidized through most of the year, and in some cases the Eh at 15 cm showed a more oxidized situation than at 7.5 cm.

Figures 6 and 7 show the change in the oxidation-reduction potential with time and depth in the non irrigated treatments. The pattern of change is consistent at each depth, except for late May - early June at the 30 cm depth, where the treatment with 290 kg of N/ha shows a lower Eh than does the treatment with 145 kg N/ha. The Eh at 60 cm showed a gradual increase throughout June, July and August, as the soil became dry. Then in early September the Eh dropped. This drop occurred after a total rainfall of 3.84 inches during August 28 to 31. Once the soil became aerated the oxidation-reduction potential immediately increased. Scott (17) observed a similar situation in an experiment in which platinum electrodes were imbedded in soil at the top of a hill, two locations midway between the top and the bottom, and at the bottom. He observed high Eh throughout the year

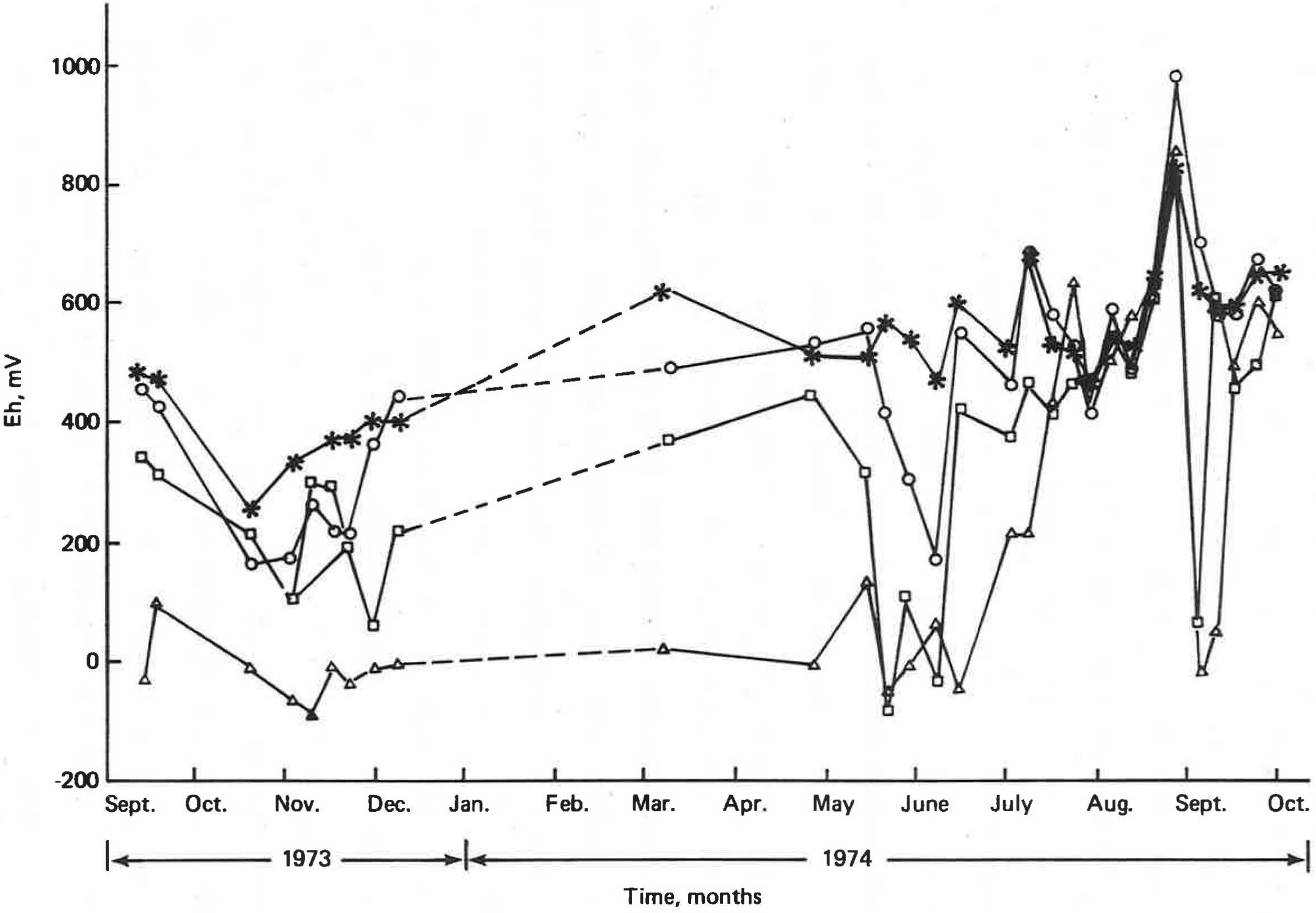

Figure 6. Yearly Eh changes in a Mexico soil with 290 kg N/ha.

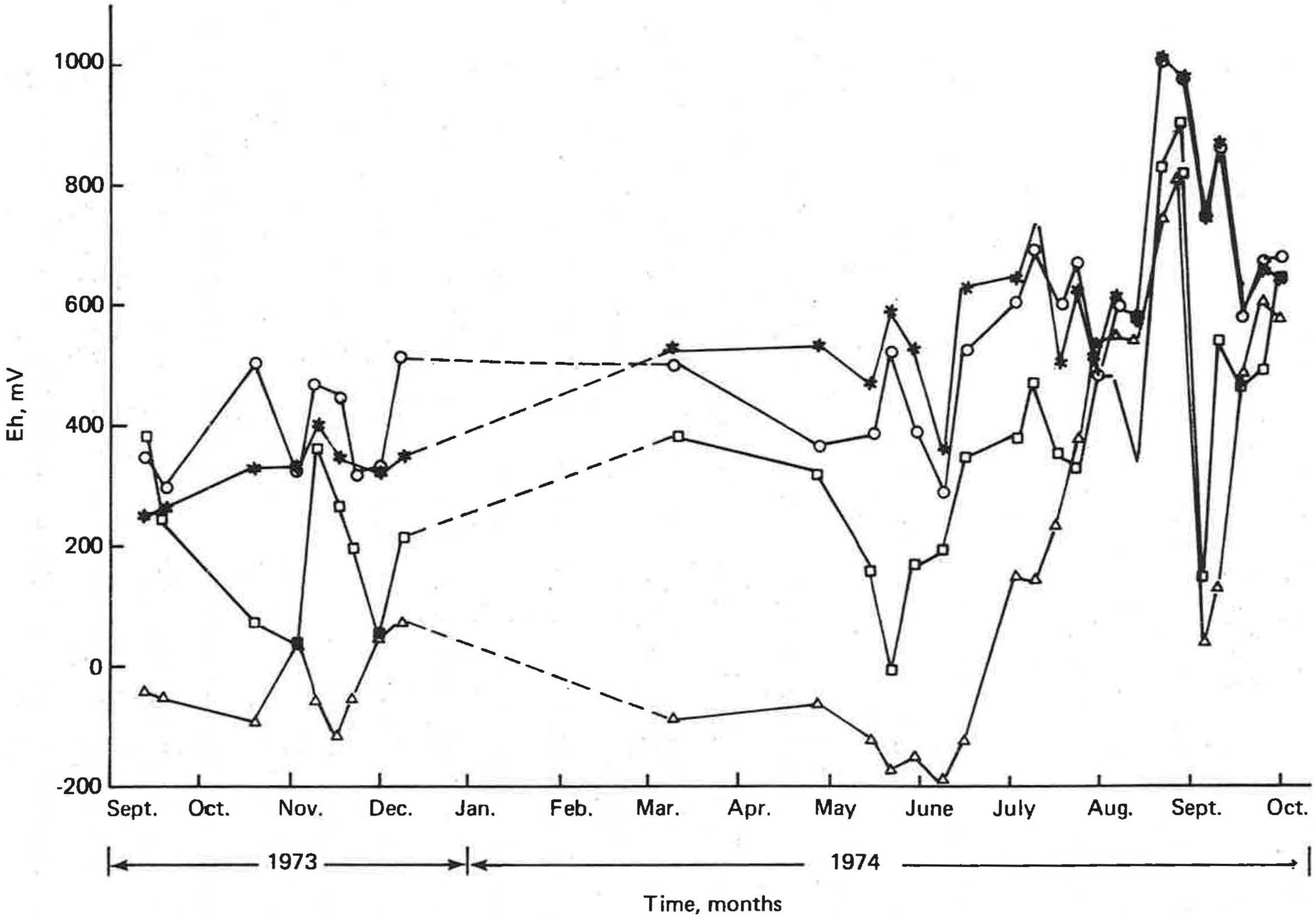

Figure 7. Yearly Eh changes in a Mexico soil with 145 kg N/ha.

in the upper three plots, but in the lowland plot the potential remained low throughout the spring and into the late summer. He also measured the moisture content of the soil and suggested that the fluctuation of the oxidation-reduction potential coincided with the fluctuation in moisture content. This study, as indicated in Figures 4-7 confirms his suggestion. The results of this study and those of Scott (17) indicate that if platinum electrodes are imbedded in the soil and left, they will give a consistent measurement of the oxidation-reduction potential.

Figures 8 and 9 show the limits of pH and Eh established on the Mexico soil in this experiment for normal rainfall and where 7.5 cm of water was added per week during the summer. Figure 8 also showed the Eh-pH measurements from the Sharpsburg soil during the anaerobic-aerobic experiment discussed in Chapter 6, and Figure 9 shows the measurements for the Menfro soil. All of the points fall within the range that occurs in the soil in natural systems. The deeper the measurement is taken in the soil, the lower the oxidation-reduction potential will be. These results indicate that the potential in the natural system becomes low enough to reduce arsenate to arsenite, and even to arsine under low partial pressures of arsine. Mukhopadhyay et al. (14) showed that after 14 days a submerged Lebanon soil had Eh values

○	15 g of soil was equilibrated with 30 ml of water.
□	15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried and maintained in contact with air.
△	15 g of soil was equilibrated with 30 ml of water for 21 days, freeze dried, the water adjusted to 26.7%, and maintained in contact with air.
●	15 g of soil was equilibrated with 30 ml of 1% dextrose.
■	15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried and maintained in contact with air.
▲	15 g of soil was equilibrated with 30 ml of 1% dextrose for 21 days, freeze dried, the water adjusted to 26.7% and maintained in contact with air.

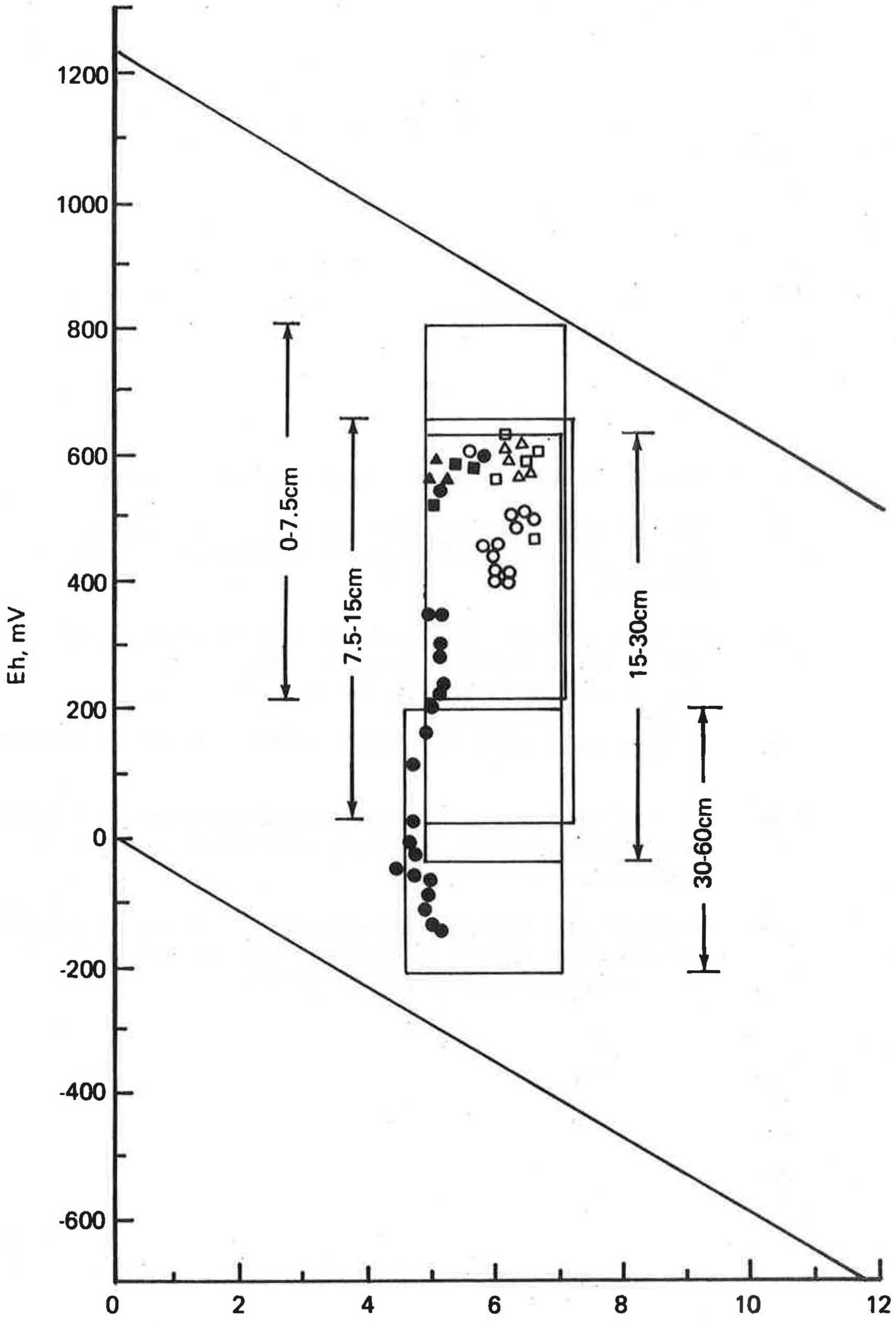

Figure 8. The distribution of Eh and pH values observed in the field for the Mexico soil compared to the Sharpsburg soil studied in Chapter 6.

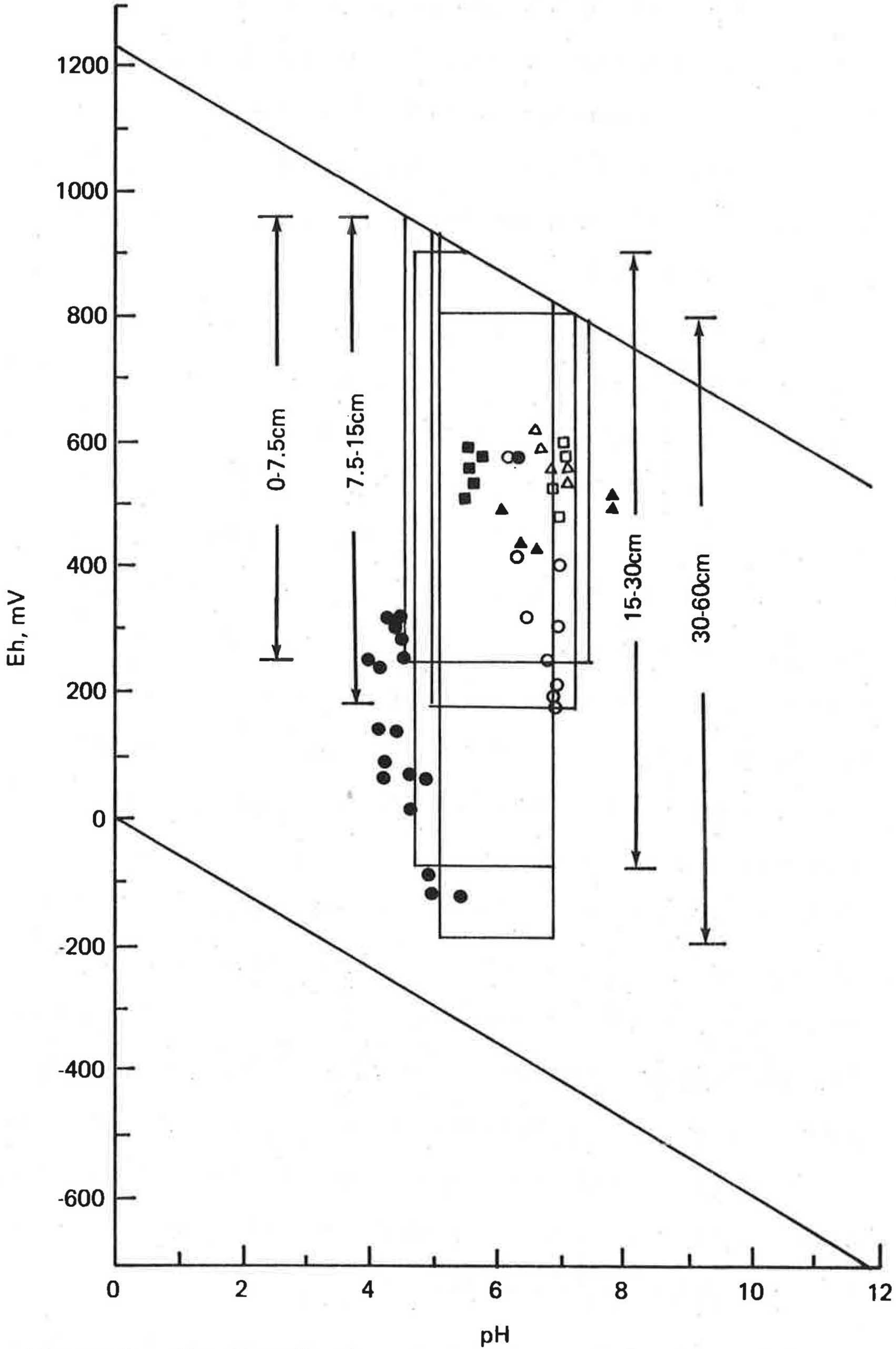

Figure 9. The distribution of Eh and pH values observed in the field for the Mexico soil compared to the Menfro soil studied in Chapter 6.

of -115 mV which also would cause arsenate reduction.

The observation on As dissolution in the laboratory were made on Eh and pH conditions created in an artificial system. A comparison of the fluctuations observed in the field and those in the laboratory indicate that the laboratory conditions are representative of what may occur under field conditions (Figures 8 and 9).

Table 1 lists the values of As in the soil to a depth of 30 cm at the beginning and end of the experiment. The table shows the normal concentration of As in the Mexico soil to be 4.5 ppm. In the watered treatments, the As concentration was higher at depths of 15-22.5 cm, and 7.5-15 cm than in unwatered plots. The results listed in Table 1 show that the treatments were not tilled in thoroughly. The As applied to the Mexico soil was in a more soluble form than was used in the orchards and it would be expected to be more mobile, as it was, however, the mobility was low enough so that As remained in the upper 22.5 cm of the soil. The unwatered treatments show very little movement of the As into deeper horizons, suggesting that the As will remain in the upper horizon unless an outside force such as flooding is applied. The Eh-pH measurements of the unwatered treatments imply that the arsenite was converted to more insoluble arsenate.

Table 1. Arsenic concentration in a Mexico soil at the beginning and the end of the experiment.

Depth	Treatment 1		Treatment 2		Treatment 3		Treatment 4	
	Before	After	Before	After	Before	After	Before	After
cm	µg As/g soil							
0 - 7.5	4	105	5	114	6	176	4	188
7.5-15	6	80	4	63	4	32	5	20
15 -22.5	5	23	6	22	4	7	4	6
22.5-30	4	14	4	9	4	4	4	6

Table 2 lists the dry weight and As content of the Reed's canary grass. The total µg As found per gram of plant tissue did not vary with treatments but the total amount removed from the soil did due to a yield increase from increased nitrogen fertilizer. Analysis of grass grown within the experimental area where the soil had not been treated with arsenic indicated values of 5, 4, and 2 ppm As on 7/18/74, 8/15/74, and 10/30/74, respectively. The highest levels observed in the As treated soils was around 20 ppm As at the earliest harvest. By the last harvesting period the level of As in the plant tissue was around 2 ppm As, these levels are very close to those of the untreated areas.

Table 3 lists the moisture content of the watered and the unwatered treatments one week after watering had stopped. According to the data presented in Chapter 6 on samples at 27 percent water the levels in the Mexico soil

Table 2. Amount of Reed's canary grass (dry weight) harvested from a Mexico soil during 1974 after the addition of 100 ppm As to depth of 15 cm.

Treatment	4/19/74		5/20/74		6/17/74		7/18/74		8/15/74		10/30/74		Totals		
	kg/ ha	µg As/ g	kg/ ha	µg As/ g	kg/ ha	µg As/ g	kg/ ha	µg As/ g	kg/ ha	µg As/ g	kg/ ha	µg As/ g	kg/ ha	mean µg/g	g As/ ha
1	321	21	545	9	519	6	557	4	588	2	296	2	2826	7	19
2	146	18	304	8	282	7	215	3	162	3	112	2	1221	7	8
3	242	18	727	7	447	7	465	6	313	2	282	2	2476	7	17
4	181	18	225	5	200	6	319	4	180	3	100	2	1205	6	8
LSD	200	3	163	6	125	2	102	3	74	1	79	1			

are not high enough to cause the oxidation-reduction potential to decrease, and suggest that the As in the soil will remain as arsenate, and may therefore be precipitated.

Table 3. Comparison of moisture content in a Mexico soil after addition of 8 cm water per week throughout the growing season and no addition.

Depth	Treatment 1	Treatment 2	Treatment 3	Treatment 4
cm	% moisture			
0 - 7.5	24.7	25.4	15.0	15.1
7.5-15	24.3	24.3	10.1	12.6

CONCLUSION

The oxidation-reduction potential and the pH of the soil show seasonal fluctuations. When the soil is watered heavily, but not flooded, the Eh at depths below 60 cm remains low throughout the year, but above 60 cm, it increases during the summer months and decreases in the late autumn. The pH at 15, 30 and 60 cm depths remains constant on any given day but showed a fluctuation from week to week, and was lower in the late autumn and early spring months than in the summer.

The concentration of As in Reed's canary grass was a constant at any sampling period, but the more abundant the growth of the crop, the more As removed per hectare.

The oxidation-reduction potential in the upper 30 cm did not become low enough to reduce arsenate to arsenite, and the As found in the soil indicated very little loss. In the lower horizons, below 60 cm, the potential became low enough to reduce arsenate to arsenite in the winter months, and remains low in the summer months if excess water is applied to the soil. This indicates that in flooded soils, the potential may become low enough for the arsenate to be reduced to arsenite, and for possible formation of trimethylarsine by soil microorganisms.

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CHAPTER 8

SUMMARY AND CONCLUSIONS

Ion products of aluminum, calcium, iron, manganese, and lead arsenates synthesized in the laboratory were used to construct stability diagrams of the arsenate salts. Manganese and lead arsenates were found to be the stable arsenates in Sharpsburg and Menfro soils, with the following equations representing the equilibrium between manganese and lead arsenates:

$$50.67Eh + 6pH = 66.84 \qquad [1]$$

$$25.47Eh + 4.5pH = 42.21 \qquad [2]$$

In Equation [1], the manganese arsenate is formed from MnO_2, and from Mn_2O_3 in Equation [2]. The data indicated that ferric and aluminum arsenates are not stable with respect to manganese arsenate in the soil system when sufficient manganese oxides are present. Ferric and aluminum arsenates are stable only at lower pH values and oxidation potentials than found in natural environments (1).

The As concentration under anaerobic conditions was of a transient nature and rapidly decreased when the system was made aerobic. This may suggest the reason for the lack of leaching of As in well drained loam and silt loam soils. Our study showed that manganese arsenate at Eh values less than 600 mV at pH 6.0 was more stable than lead arsenate in the soils that we examined (Equation 1 and 2). Since the As was applied in the form of lead arsenate, then during the extreme wet periods or flooding, when the Eh fell below 600 mV, lead arsenate would dissolve and manganese arsenate form. In highly aerated systems, Eh $>$ 600 mV more stable lead arsenate compounds would reform.

The Eh of the 7.5 cm soil layer of the Mexico soil was found to vary from approximately +800 to 300 mV at pH 6.0. Under the more oxidized conditions lead arsenate would be stable and under the more reduced conditions manganese arsenate would be stable. The observation presented indicate that seasonal fluctuations in Eh may result in a system with stable phases of both lead and manganese arsenates. High concentrations of As in systems reduced with dextrose are interpreted as non equilibrium which occur when pH, Eh, and the amount of chelating substances present in the system are changed. Another possibility is that production of carbon dioxide results in lower than predicted levels of Mn^{2+} due to manganese carbonate formation (3).

After 24 hours incubation of the soils with 1% dextrose the Eh reached a minimum of -150 mV. This Eh value compares with those found at a depth of 60 cm in the soil at the Agronomy Research Farm when 7.5 cm water were applied weekly. The low at the farm was -200 mV, with an average close to -100 mV throughout the growing period. Mukhopadhyay et al. (3) found that in a submerged Lebanon silt loam, the Eh reached -30.6 mV after 32 days with no liming, -138.3 mV after 14 days with moderate liming, and -115.8 mV after 14 days with heavy liming. Their pH reached an equilibrium level of 7.0, and the minimum Eh value was -211.8, -264.9, and -264.0 mV for unlimed, moderately limed and heavily limed soils. The Eh and pH determined in peat bogs in England had a low of 75 mV and a pH of 3.5 at a depth of 10 cm (5). Examination of Figures 11 and 12 in Chapter 6 show that at these values, most of the As in solution will have been converted to $HAsO_2$, which is a more toxic form of As. Yamane and Sato (6) have shown the Eh values of flooded soils to range from -300 to 600 mV. They stated that when H_2 is evolved, the Eh reaches a low of -420 mV at a pH of 7.0. This point falls on the H_2-H_2O stability line. Soils containing high levels of total As would be expected to have high As solubility and perhaps toxicity in these Eh-pH ranges.

Arsenic is generally two times as mobile as lead in the soil as indicated by comparing levels from the 0-5 cm horizon to the 5-10 cm horizon of As contaminated soils.

The experiment at the Agronomy Research Farm showed that the mobility of As increased with increasing water supplied. The leaching of As in the soil has been found to be a function of the adsorptive capacity of the soil (2). Sandy soils exhibit a much greater loss of As to leaching than do loamy soils. This was confirmed by comparing the depth of As found in various orchard soils. In the Baxter gravelly loam As had moved at least to a depth of 30 cm. The other soils tested, with finer sized particles, and more clay, contained most of the As in the upper 10 cm.

The study at the Agronomy Research Farm showed that when the soil was kept moist by weekly application of 7.5 cm of water the As does not inhibit the growth of Reed's canary grass, nor does the grass take up more As than when the soil was not kept excessively wet. Some Missouri orchards where cropping practices were changed after many years of treatment with lead arsenate experienced growth problems with the new crops. These were generally areas of poor drainage where the As with the grass cover may have been plowed to a deeper layer. Periods of low Eh in poorly drained soils have been indicated (4), and as this study has shown under these conditions As is more soluble, and may be converted from arsenate to arsenite.

Areas that have been treated with large amounts of lead arsenate should be kept well drained, and maintained with an oxidation-reduction potential, as high as possible which will help to maintain As insolubility. These areas should not be plowed so that the As will remain concentrated in the upper 5-10 cm of the soil, where it is less likely to be reduced to arsenite, and will therefore be less detrimental to crops.

APPENDIX

Table I. Eh, pH, and As content of 30 ml distilled water mixed with 15 g of the 0-15 cm layer of the Menfro soil for various periods of time at 25 ± 2° C.

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
0	824	825		6.23	6.25		0.1	0.1	
	824	825		6.27	6.20		0.0	0.1	
Total	1648	1650	3298	12.50	12.45	24.95	0.1	0.2	0.3
Mean	824	825	825	6.25	6.23	6.24	0.05	0.1	0.1
1	458	434		6.10	6.10		0.2	0.1	
	487	479		6.05	6.29		0.2	0.1	
Total	945	913	1858	12.15	12.39	24.54	0.4	0.2	0.6
Mean	473	457	465	6.08	6.20	6.14	0.2	0.1	0.2
2	363	374		6.36	6.27		0.7	1.4	
	381	379		6.23	6.37		0.6	1.5	
Total	744	753	1497	12.59	12.64	25.23	1.3	2.9	4.2
Mean	372	377	374	6.30	6.32	6.31	0.7	1.5	1.1
3	383	372		6.24	6.48		0.6	1.8	
	377	323		6.27	6.49		0.4	1.7	
Total	760	695	1455	12.51	12.97	25.48	1.0	3.5	4.5
Mean	380	348	364	6.26	6.49	6.37	0.5	1.8	1.1
4	402	395		6.41	6.36		1.8	2.6	
	420	419		6.52	6.37		1.7	1.8	
Total	822	814	1636	12.93	12.73	25.66	3.5	4.4	7.9
Mean	411	407	409	6.47	6.37	6.42	1.8	2.2	2.0
5	378	383		6.41	6.41		2.1	3.2	
	387	394		6.41	6.38		2.3	3.3	
Total	765	777	1542	12.82	12.79	25.61	4.4	6.5	10.0
Mean	383	389	386	6.41	6.40	6.40	2.2	3.3	2.7
6	328	363		6.58	6.72		1.9	3.5	
	346	358		6.49	6.51		2.2	3.7	
Total	674	721	1395	13.07	13.23	26.30	4.1	7.2	11.3
Mean	337	361	349	6.54	6.62	6.58	2.1	3.6	2.8
7	383	380		6.62	6.63		1.6	2.6	
	367	370		6.65	6.65		2.2	2.4	
Total	700	750	1450	13.27	13.28	26.55	3.8	5.0	8.8
Mean	350	375	362	6.64	6.64	6.64	1.9	2.5	2.2

Table I. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
8	345	305		6.60	6.60		2.8	4.6	
	340	267		6.51	6.52		3.1	5.2	
Total	685	572	1257	13.11	13.12	26.23	5.9	9.8	15.7
Mean	343	286	314	6.56	6.56	6.56	3.0	4.9	3.9
9	324	301		6.53	6.65		4.0	6.0	
	302	263		6.55	6.63		2.8	6.5	
Total	626	564	1190	13.08	13.28	26.36	6.8	12.5	19.3
Mean	313	282	298	6.54	6.54	6.59	3.4	6.3	4.8
10	340	272		6.62	6.64		4.4	5.3	
	328	285		6.66	6.83		3.5	5.7	
Total	668	557	1225	13.28	13.47	26.75	7.9	11.0	18.9
Mean	334	279	306	6.64	6.74	6.69	4.0	5.5	4.7
11	317	296		6.64	6.68				
	254	247		6.68	6.83				
Total	571	543	1114	13.32	13.51	26.83			
Mean	286	272	279	6.66	6.76	6.71			
12	434	336		6.98	6.99		6.6	6.9	
	436	385		7.05	7.25		6.6	6.6	
Total	870	721	1591	14.03	14.24	28.27	13.2	13.5	26.7
Mean	435	361	398	7.02	7.12	7.07	6.6	6.8	6.7
13	251	208		6.93	6.89				
	271	217		6.83	6.94				
Total	522	425	945	13.76	13.83	27.59			
Mean	261	213	237	6.88	6.92	6.90			
14	214	183		6.98	7.03		6.2	7.0	
	317	252		7.02	7.13		6.4	5.8	
Total	531	435	966	14.00	14.16	28.16	12.6	12.8	25.4
Mean	266	218	242	7.02	7.08	7.04	6.3	6.4	6.4
15	152	189		6.70	6.89				
	222	301		6.74	7.14				
Total	374	490	864	13.44	14.03	27.47			
Mean	187	245	216	6.72	7.02	6.87			

Table I. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
16	214	181		7.00	7.07		8.2	7.9	
	226	198		7.05	7.15		8.7	8.2	
Total	440	379	819	14.05	14.22	28.27	16.9	16.1	33.0
Mean	220	190	205	7.03	7.11	7.07	8.5	8.1	8.3
17	161	180		6.78	7.12				
	164	199		6.83	7.27				
Total	325	379	704	13.61	14.39	28.00			
Mean	163	190	176	6.81	7.20	7.00			
18	210	204		6.89	7.14		5.3	8.0	
	213	144		6.99	7.07		5.3	9.8	
Total	423	348	771	13.88	14.21	28.09	10.6	17.8	28.4
Mean	212	174	193	6.94	7.11	7.02	5.3	8.9	7.1
19	280	224		6.82	7.12				
	322	164		6.89	7.20				
Total	602	388	990	13.71		28.03			
Mean	301	194	248	6.86	7.16	7.01			
20	311	274		7.09	7.11		5.3	8.2	
	256	318		7.02	7.20		5.3	7.3	
Total	567	592	1159	14.11	14.31	28.42	10.6	15.5	26.6
Mean	284	296	290	7.06	7.16	7.11	5.3	7.8	6.7

*1 and 2 are field replicates of the soil.

Table II. Al, Ca, Fe, Mn, and Pb content of 30 ml distilled water mixed with 15 g of the 0-15 cm layer of the Menfro soil for various periods of time at 25 ± 2° C.

Time	Al	Ca	Fe	Mn	Pb
Days	ppm				
0	5.84	34	2.6	1.4	3.0
	6.00*	29	1.7	1.3	3.3
Total	11.84	63	4.3	2.7	6.3
Mean	5.92	32	2.2	1.4	3.2
4	18.9	52	15.5	6.0	5.5
	13.9	29	9.7	0	6.0
Total	32.8	81	25.2	6.0	11.5
Mean	16.4	41	12.6	3.0	5.8
8	6.4	138	14.2	18	2.5
	6.0	189	16.2	14	1.4
Total	12.4	327	30.4	32	3.9
Mean	6.2	164	15.2	16	2.0
12	6.5	229	15.3	24	3.3
	5.6	212	16.0	21	3.7
Total	12.1	441	31.3	45	7.0
Mean	6.1	221	15.7	23	3.5
16	6.8	258	22.4	29	4.9
	7.3	235	23.1	22	6.1
Total	14.1	493	45.5	51	11.0
Mean	7.1	247	22.8	26	5.5
20	5.3	568	16.4	21	4.6
	10.9	224	19.3	23	5.2
Total	16.2	792	35.7	44	9.8
Mean	8.1	396	17.9	22	4.9

*Field replicates of the soil.

Table III. Eh, pH, and As content of 30 ml (dextrose 1% and urea 100 ppm N) solution mixed with 15 g of the 0-15 cm layer of the Menfro soil for various periods of time at 25 ± 2° C.

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
0	823	825		6.48	6.25		0.1	0.4	
	826	827		6.38	6.20		0.1	0.4	
Total	1649	1652	3301	12.86	12.45	25.31	0.2	0.8	1.0
Mean	825	826	825	6.43	6.23	6.33	0.1	0.4	0.3
1	-151	-122		5.63	5.50		1.3	0.2	
	-137	-102		5.72	5.27		1.2	0.4	
Total	-288	-224	-512	11.35	10.77	22.12	2.5	0.6	3.1
Mean	-144	-112	-128	5.67	5.39	5.53	1.3	0.3	0.8
2	-152	- 61		5.17	5.00		6.3	12.0	
	-154	-106		5.16	5.08		6.4	12.6	
Total	-306	-167	-473	10.33	10.08	20.37	12.7	24.6	37.3
Mean	-153	- 84	-118	5.17	5.04	5.09	6.4	12.3	9.3
3	-124	- 73		4.95	5.07		10.8	21.2	
	-142	- 49		5.15	5.06		11.6	16.5	
Total	-266	-122	-388	10.10	10.13	20.23	22.4	37.7	60.1
Mean	-133	- 61	- 97	5.05	5.07	5.06	11.2	18.9	15.0
4	40	86		4.84	4.98		15.1	22.1	
	48	45		4.85	4.90		15.9	24.2	
Total	88	131	219	9.69	9.88	19.57	31.0	46.3	77.3
Mean	44	66	55	4.85	4.94	4.89	15.5	23.2	19.3
5	19	22		4.77	4.69		17.1	23.9	
	0	0		4.69	4.87		14.8	29.1	
Total	19	22	41	9.46	9.56	19.02	31.9	53.0	84.9
Mean	10	11	10	4.73	4.78	4.76	15.9	26.5	21.2
6	-101	117		4.70	4.66		16.5	25.0	
	- 11	206		4.67	4.67		15.8	28.9	
Total	-112	323	211	9.37	9.33	18.70	32.3	53.9	86.2
Mean	- 56	162	53	4.69	4.67	4.68	16.2	26.9	21.6
7	- 23	265		4.47	4.41		19.0	25.4	
	- 24	303		4.47	4.57		16.2	27.0	
Total	- 47	568	521	8.94	8.98	17.92	35.2	52.4	87.6
Mean	- 24	284	130	4.47	4.49	4.48	17.6	26.2	21.9

Table III. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
8	91	99		4.44	4.42		22.5	26.2	
	27	272		4.39	4.27		22.0	27.7	
Total	118	371	245	8.83	8.69	17.52	44.5	53.9	98.4
Mean	59	186	61	4.42	4.35	4.38	22.3	27.0	24.6
9	16	189		4.32	4.64		24.0	33.4	
	13	324		4.26	4.09		24.9	32.1	
Total	29	513	542	8.58	8.73	17.31	48.9	65.5	114.4
Mean	15	257	136	4.29	4.37	4.33	24.5	32.8	28.6
10	191	340		4.16	4.10		27.3	27.5	
	92	363		4.15	4.34		27.2	30.9	
Total	283	703	986	8.31	8.44	16.75	54.5	58.4	112.9
Mean	142	352	247	4.16	4.22	4.19	27.3	29.2	28.2
11	88	278		4.06	4.60				
	297	237		4.20	4.61				
Total	395	515	910	8.26	9.21	17.47			
Mean	198	258	228	4.13	4.61	4.37			
12	359	340		4.09	4.67		30.0	27.3	
	353	207		4.19	4.84		24.5	23.9	
Total	712	547	1259	8.28	9.51	17.79	54.5	51.2	105.7
Mean	356	274	315	4.14	4.76	4.45	27.3	25.6	26.4
13	285	339		4.22	4.61				
	146	179		4.26	5.14				
Total	431	518	949	8.48	9.75	18.23			
Mean	216	259	237	4.24	4.88	4.56			
14	344	343		4.23	4.62		26.9	33.1	
	361	28		4.26	5.29		29.4	31.1	
Total	705	371	1076	8.49	9.91	18.40	56.3	64.2	120.5
Mean	353	186	269	4.25	4.96	4.60	28.2	32.1	30.1
15	322	229		4.18	5.21				
	79	224		4.13	4.29				
Total	401	453	854	8.31	9.50	17.81			
Mean	201	227	214	4.16	4.75	4.45			

Table III. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
16	317	314		4.36	5.32		27.1	31.1	
	303	324		4.29	4.49		27.8	30.7	
Total	620	638	1258	8.65	9.81	18.46	54.9	61.8	116.7
Mean	310	319	315	4.33	4.91	4.62	27.5	30.9	29.2
17	170	359		4.14	4.10				
	59	320		4.32	4.80				
Total	229	679	908	8.46	8.90	17.36			
Mean	115	340	227	4.23	4.45	4.34			
18	305	361		4.17	4.09		27.9	38.8	
	185	321		4.46	5.03		29.1	37.8	
Total	490	682	1172	8.63	9.12	17.75	57.0	76.6	133.6
Mean	245	341	293	4.32	4.56	4.44	28.5	38.3	33.4
19	78	261		4.28	5.03				
	132	283		4.19	4.49				
Total	210	544	754	8.47	9.52	17.99			
Mean	105	274	189	4.24	4.76	4.50			
20	194	339		4.33	5.08		30.0	31.9	
	353	342		4.18	4.52		27.2	31.4	
Total	547	681	1228	8.51	9.60	18.11	57.2	63.3	120.5
Mean	274	341	307	4.26	4.80	4.53	28.6	31.7	30.1

*1 and 2 are field replicates of the soil.

Table IV. Al, Ca, Fe, Mn, and Pb content of 30 ml (dextrose 1% and urea 100 ppm N) solution mixed with 15 g of the 0-15 cm layer of the Menfro soil for various periods of time at 25 ± 2° C.

Time	Al	Ca	Fe	Mn	Pb
Days	ppm				
0	0.4	201	2.4	13	3.7
	5.9*	126	2.1	8	3.1
Total	6.3	327	4.5	21	6.8
Mean	3.2	164	2.3	11	3.4
4	7.8	981	341	187	13.3
	9.9	281	88	28	6.0
Total	17.7	1262	429	215	19.3
Mean	8.9	631	215	108	9.7
8	19.0	866	370	161	10.4
	20.9	1130	562	262	14.7
Total	39.9	1996	932	423	25.1
Mean	20.0	998	466	212	12.6
12	4.6	1003	484	180	15.1
	12.9	1003	614	196	13.3
Total	17.5	2006	1098	376	28.4
Mean	8.8	1003	549	188	14.2
16	19.0	998	378	174	14.7
	12.3	981	392	193	15.1
Total	31.3	1979	770	367	29.8
Mean	15.7	980	385	184	14.9
20	16.4	820	387	152	13.6
	10.7	843	528	166	13.3
Total	27.1	1663	915	318	26.9
Mean	13.6	832	458	159	13.5

*Field replicates of the soil.

Table V. Eh, pH, and As content of 30 ml distilled water mixed with 15 g of the 0-15 cm layer of the Sharpsburg soil for various periods of time at 25 ± 2° C.

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
0	847	852		5.65	5.33		0.1	0.1	
	848	852		5.66	5.62		0.0	0.3	
Total	1695	1704	3399	11.31	10.95	22.26	0.1	0.4	0.5
Mean	848	852	850	5.66	5.47	5.57	0.1	0.2	0.1
1	499	457		5.65	5.77		0.2	0.4	
	434	419		5.53	5.47		0.2	0.3	
Total	933	876	1809	11.18	11.24	22.42	0.4	0.7	1.1
Mean	467	438	452	5.59	5.62	5.61	0.2	0.4	0.3
2	412	403		5.60	5.68		0.2	0.4	
	431	413		5.77	5.61		0.2	0.1	
Total	843	816	1659	11.37	11.29	22.66	0.4	0.5	0.9
Mean	422	408	415	5.69	5.65	5.67	0.2	0.3	0.2
3	424	413		5.77	5.64		0.7	1.6	
	419	425		5.75	5.54		0.6	1.3	
Total	843	838	1681	11.52	11.18	22.70	1.3	2.9	4.2
Mean	422	419	420	5.76	5.59	5.68	0.7	1.5	1.0
4	467	448		5.77	5.59		0.6	1.2	
	492	461		5.78	5.59		0.9	1.1	
Total	959	909	1868	11.55	11.18	22.73	1.5	2.3	3.8
Mean	480	455	467	5.78	5.59	5.68	0.8	1.2	1.0
5	403	433		5.85	5.63		1.3	1.6	
	434	440		5.84	5.59		1.1	1.6	
Total	837	873	1710	11.69	11.22	22.91	2.4	3.2	5.6
Mean	419	437	428	5.85	5.61	5.73	1.2	1.6	1.4
6	398	388		5.90	5.80		0.9	1.4	
	405	400		6.03	5.80		1.0	0.8	
Total	803	788	1591	11.93	11.60	23.55	1.9	2.2	4.1
Mean	402	394	398	5.97	5.80	5.88	1.0	1.1	1.0
7	388	388		6.02	6.01		0.7	0.5	
	404	414		5.92	5.87		1.0	0.6	
Total	792	802	1594	11.94	11.88	23.89	1.7	1.1	2.8
Mean	396	401	399	5.97	5.94	5.96	0.9	0.6	0.7

Table V. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
8	452	453		5.92	5.68		1.0	1.9	
	474	460		5.90	5.65		1.3	2.0	
Total	926	913	1839	11.82	11.33	23.25	2.3	3.9	6.2
Mean	463	457	460	5.91	5.64	5.81	1.2	2.0	1.6
9	420	403		6.00	5.74		1.3	2.2	
	443	414		5.82	5.69		1.4	2.1	
Total	863	817	1680	11.82	11.43	23.25	2.7	4.3	7.0
Mean	432	409	420	5.91	5.72	5.81	1.4	2.2	1.8
10	415	397		6.03	5.78		1.6	2.3	
	423	403		6.12	5.88		1.7	2.3	
Total	838	800	1638	12.15	11.66	23.94	3.3	4.6	7.9
Mean	419	400	410	6.08	5.83	5.99	1.7	2.3	2.0
11	473	431		6.19	5.91				
	554	342		6.33	5.88				
Total	1027	773	1800	12.52	11.79	24.31			
Mean	514	387	450	6.46	5.90	6.08			
12	530	456		6.26	6.01		1.7	2.3	
	537	473		6.38	6.01		2.0	2.8	
Total	1067	929	1996	12.64	12.02	24.66	3.7	5.1	8.8
Mean	534	465	499	6.32	6.01	6.17	1.9	2.6	2.2
13	514	447		6.41	6.03				
	525	467		6.32	6.02				
Total	1039	914	1953	12.73	12.05	24.74			
Mean	520	557	488	6.37	6.03	6.20			
14	603	454		6.64	6.13		2.0	2.6	
	610	569		6.57	6.19		2.0	2.5	
Total	1213	1023	2236	13.21	12.32	25.53	4.0	5.1	9.1
Mean	607	512	559	6.61	6.16	6.38	2.0	2.6	2.3
15	301	435		6.18	5.89				
	513	450		6.27	5.99				
Total	814	885	1699	12.45	11.88	24.33			
Mean	407	443	425	6.23	5.94	6.08			

Table V. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
16	523	502		6.54	6.25		2.1	3.6	
	522	515		6.57	6.27		2.3	3.1	
Total	1045	1017	2062	13.11	12.52	25.63	4.4	6.7	11.1
Mean	523	509	516	6.56	6.26	6.41	2.2	3.4	2.8
17	528	435		6.56	6.00				
	542	464		6.53	6.03				
Total	1070	899	1969	13.09	12.03	25.12			
Mean	535	450	492	6.55	6.02	6.28			
18	415	381		6.63	6.14		2.3	3.8	
	405	389		6.48	6.28		2.9	3.6	
Total	820	770	1590	13.11	12.42	25.53	5.2	7.4	12.6
Mean	410	385	398	6.56	6.21	6.38	2.6	3.7	3.2
19	272	392		6.42	6.31				
	284	408		6.53	6.08				
Total	556	800	1356	12.95	12.39	25.34			
Mean	278	400	339	6.48	6.20	6.34			
20	565	544		6.56	6.43		2.3	4.5	
	309	587		6.60	6.31		1.5	3.0	
Total	874	1131	2005	13.16	12.74	25.90	3.8	7.5	11.3
Mean	437	566	501	6.58	6.37	6.48	1.9	3.8	2.8

*1 and 2 are field replicates of the soil.

Table VI. Al, Ca, Fe, Mn, and Pb content of 30 ml distilled water mixed with 15 g of the 0-15 cm layer of the Sharpsburg soil for various periods of time at 25 ± 2° C.

Time	Al	Ca	Fe	Mn	Pb
Days	ppm				
0	8.2	23	2.6	0.3	3.7
	6.6*	34	2.2	1.2	4.9
Total	14.8	57	4.8	1.5	8.6
Mean	7.4	29	2.4	0.8	4.3
4	7.0	69	3.4	5	6.0
	7.4	92	3.4	5	4.3
Total	14.4	161	6.8	10	10.3
Mean	7.2	81	3.4	5	5.2
8	15.5	75	13.1	7	4.0
	13.8	166	22.2	14	4.0
Total	29.3	241	35.3	21	8.0
Mean	14.7	121	17.7	11	4.0
12	12.6	92	19.2	10	3.7
	5.9	149	28.2	14	1.4
Total	19.5	241	47.4	24	5.1
Mean	9.8	121	23.7	12	2.6
16	11.6	69	12.7	8	4.3
	14.8	92	19.7	10	3.3
Total	26.4	161	32.4	18	7.6
Mean	13.2	81	16.2	9	3.8
20	8.9	97	20.0	11	4.9
	7.1	149	22.5	21	4.3
Total	16.0	246	42.5	33	9.2
Mean	8.0	123	21.3	17	4.6

*Field replicates of the soil.

Table VII. Eh, pH, and As content of 30 ml (dextrose 1% and urea 100 ppm N) solution mixed with 15 g soil of the 0-15 cm layer of the Sharpsburg soil for various periods of time at 25 ± 2°C.

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
0	834	848		5.73	5.58		0.1	0.4	
	855	848		5.84	5.75		0.1	0.5	
Total	1689	1696	3384	16.57	11.33	22.70	0.2	0.9	1.1
Mean	845	848	846	5.79	5.67	5.73	0.1	0.5	0.3
1	-194	-127		5.16	4.90		0.4	4.1	
	-149	-112		5.17	4.96		0.4	3.4	
Total	-343	-239	-582	10.33	9.86	20.19	0.8	7.5	8.3
Mean	-172	-120	-146	5.17	4.93	5.05	0.4	3.8	2.1
2	-130	- 82		5.00	5.01		1.9	7.0	
	-103	-104		4.98	4.94		1.5	6.8	
Total	-233	-186	-419	9.98	9.95	19.93	3.4	13.8	17.2
Mean	-117	- 93	-105	4.99	4.98	4.98	1.7	6.9	4.3
3	-137	-156		4.94	5.14		3.2	8.2	
	-121	-141		4.91	5.06		3.1	7.5	
Total	-258	-297	-555	9.85	10.20	20.50	6.3	15.7	22.0
Mean	-129	-149	-139	4.93	5.10	5.01	3.2	7.9	5.5
4	- 74	- 42		4.89	5.10		4.5	7.9	
	- 85	- 16		4.98	4.96		4.8	10.7	
Total	-159	- 58	-217	9.87	10.06	19.93	9.3	18.6	27.9
Mean	- 80	- 29	- 54	4.94	5.03	4.98	4.7	9.3	7.0
5	- 93	- 72		4.85	4.91		2.8	11.2	
	- 76	- 82		4.86	4.79		4.2	13.4	
Total	-169	-154	-323	9.71	9.70	19.41	7.0	24.6	31.6
Mean	- 85	- 77	- 81	4.86	4.85	4.85	3.5	12.3	7.9
6	0	91		4.88	4.64		4.7	10.3	
	- 51	-115		4.87	4.73		3.9	12.2	
Total	- 51	- 24	- 75	9.75	9.37	19.12	8.6	22.5	31.1
Mean	- 26	- 12	- 19	4.88	4.69	4.78	4.3	11.3	7.8
7	- 31	- 36		4.79	4.62		5.5	16.5	
	76	53		4.79	4.56		4.7	17.2	
Total	45	17	62	9.58	9.18	18.76	10.2	33.7	43.9
Mean	23	9	16	4.79	4.59	4.69	5.1	16.9	11.0

Table VII. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
8	- 81	- 50		4.67	4.59		6.30	16.9	
	- 16	- 14		4.76	4.33		5.7	18.5	
Total	- 97	- 64	-161	9.43	8.92	18.35	12.0	35.4	47.4
Mean	- 49	- 32	- 40	4.72	4.46	4.59	6.0	17.7	11.9
9	- 44	- 59		4.83	4.72		3.1	18.5	
	- 34	- 64		4.85	4.43		2.7	17.7	
Total	- 78	-123	-201	9.68	9.15	18.83	5.8	36.2	42.0
Mean	- 39	- 62	- 50	4.84	4.58	4.77	2.9	18.1	10.5
10	30	- 39		4.87	4.82		5.7	18.3	
	29	- 56		4.89	4.50		5.9	23.1	
Total	59	- 95	- 36	0.76	9.32	19.08	11.6	41.4	53.0
Mean	30	- 48	- 9	4.88	4.66	4.77	5.8	20.7	13.3
11	379	- 35		5.06	4.88				
	258	+ 14		4.94	4.70				
Total	637	- 21	616	10.00	9.58	19.58			
Mean	329	- 11	154	5.00	4.79	4.90			
12	348	190		5.11	5.04		7.9	21.2	
	333	138		5.03	4.81		5.7	15.6	
Total	681	228	909	10.14	9.85	19.99	13.6	36.8	50.4
Mean	341	114	227	5.07	4.93	5.00	6.8	18.4	12.6
13	338	165		5.17	4.90				
	289	128		5.00	5.15				
Total	627	293	920	10.17	10.05	20.22			
Mean	314	147	230	5.04	5.03	10.11			
14	378	312		5.20	4.36		7.6	20.0	
	337	335		5.06	5.20		8.3	19.5	
Total	715	647	1362	10.26	9.56	19.82	15.9	39.5	55.4
Mean	358	329	341	5.13	4.78	4.96	8.0	19.8	13.9
15	199	260		4.95	5.11				
	298	50		5.08	4.79				
Total	497	310	807	10.03	9.80	19.83			
Mean	249	155	202	5.02	4.90	4.96			

Table VII. (continued)

Time	Eh			pH			As		
	1*	2		1	2		1	2	
Days	mV						ppm		
16	353	345		5.08	5.17		7.5	18.1	
	342	186		5.19	5.04		8.5	23.9	
Total	695	531	1226	10.27	10.21	20.48	16.0	42.0	58.0
Mean	348	261	307	5.14	5.11	5.12	8.0	21.0	14.5
17	330	217		5.14	5.10				
	327	286		5.20	5.10				
Total	657	503	1160	10.34	10.20	20.54			
Mean	329	252	290	5.17	5.10	5.14			
18	268	354		5.11	5.07		8.40	19.7	
	340	367		5.17	5.07		9.7	19.6	
Total	608	721	1329	10.28	10.14	20.42	18.1	39.3	57.4
Mean	304	361	332	5.14	5.07	5.11	9.1	19.7	14.4
19	314	263		5.07	5.14				
	276	225		5.21	5.15				
Total	590	488	1078	10.28	10.29	20.57			
Mean	295	244	270	5.14	5.15	5.14			
20	361	332		5.08	5.13		9.9	17.5	
	356	337		5.20	5.15		9.8	16.5	
Total	717	669	1386	10.28	10.28	20.56	19.7	34.0	53.7
Mean	359	335	347	5.14	5.14	5.14	9.9	17.0	13.4

*1 and 2 are field replicates of the soil.

Table VIII. Al, Ca, Fe, Mn, and Pb content of 30 ml (dextrose 1% and urea 100 ppm N) solution mixed with 15 g of the 0-15 cm layer of the Sharpsburg soil for various periods of time at 25 ± 2° C.

Time	Al	Ca	Fe	Mn	Pb
Days	ppm				
0	6.4	143	1.9	4.5	4.9
	7.8*	109	2.5	1.1	3.3
Total	14.2	252	4.4	5.6	8.2
Mean	7.1	126	2.2	2.8	4.1
4	8.4	499	91	66	6.0
	8.4	442	65	57	6.6
Total	16.8	941	156	123	12.6
Mean	8.4	471	78	62	6.3
8	8.9	1061	632	237	6.3
	20.5	682	570	129	8.3
Total	29.4	1743	1202	366	14.6
Mean	14.7	872	601	183	7.3
12	6.3	751	492	166	4.9
	4.7	946	1218	215	12.7
Total	11.0	1697	1710	381	17.6
Mean	5.5	849	855	191	8.8
16	6.9	1072	936	278	8.9
	10.1	837	818	180	9.2
Total	17.0	1909	1754	458	18.1
Mean	8.5	956	877	229	9.1
20	6.6	877	588	190	7.5
	6.8	883	896	182	12.0
Total	13.4	1760	1494	372	19.5
Mean	6.7	880	747	186	9.8

*Field replicates of the soil.

Table IX. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of air dry Sharpsburg soil incubated for various times in contact with the atmosphere at 25 ± 2° C.

Time	Eh			pH			As			Al	Ca	Fe	Mn	Pb
	1	2		1	2		1	2						
Days	mV						ppm							
4	616	592		6.63	6.16		1.0	1.8						
	582	603		6.50	6.04		1.3	1.6						
Total	1208	1195	2403	13.13	12.20	25.33	2.3	3.4	5.7					
Mean	604	598	601	6.57	6.10	6.33	1.2	1.7	2.9					
8	628	608		5.69	6.15		0.8	1.2						
	607	594		6.29	6.07		1.0	1.5						
Total	1235	1202	2437	11.98	12.32	24.30	1.8	2.7	4.5					
Mean	618	601	609	5.99	6.16	6.1	0.9	1.4	1.1					
12	564	542		6.30	6.10		0.4	2.0						
	569	547		6.30	6.13		0.5	2.2						
Total	1133	1089	2222	12.60	12.23	24.83	0.9	4.2	5.1					
Mean	567	545	556	6.30	6.12	6.21	0.5	2.1	1.3					
24	494	483		6.32	6.14		1.0	1.9						
	448	497		6.36	6.24		1.1	1.8						
Total	992	990	1992	12.68	12.38	25.06	2.1	3.7	5.8					
Mean	496	495	496	6.34	6.19	6.27	1.1	1.9	1.5					
48	558	548		6.22	6.03		1.1	2.5		5.06	34	4.4	6.2	1.04
	564	555		6.16	6.03		0.8	2.6		6.00	23	4.0	4.9	0.53
Total	1122	1103	2225	12.38	12.06	24.44	1.9	5.1	7.0	11.06	57	8.4	11.1	1.57
Mean	561	552	556	6.19	6.03	6.11	1.0	2.6	1.8	5.53	29	4.2	5.6	0.8

*15 g of sample were incubated with 30 ml of water for 21 days and then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table X. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of air dry Sharpsburg soil incubated for various times in contact with the atmosphere at 25 ± 2° C.*

Treatment	Eh			pH			As			Al	Ca	Fe	Mn	Pb
	1	2		1	2		1	2						
Days	mV						ppm							
4	586	588		5.27	5.10		0.9	1.6						
	589	587		5.34	5.11		0.4	1.5						
Total	1175	1175	2350	10.61	10.21	20.82	1.3	3.1	4.4					
Mean	588	588	588	5.31	5.11	5.21	0.7	1.6	1.1					
8	581	589		5.18	5.71		1.0	2.0						
	570	592		5.29	5.92		0.7	1.7						
Total	1151	1181	2332	10.47	11.63	22.1	1.7	3.7	5.4					
Mean	576	591	583	5.24	5.82	5.53	0.9	1.9	1.4					
12	584	576		5.30	5.08		0.6	2.2						
	583	587		5.26	5.09		0.6	1.9						
Total	1167	1163	2330	10.56	10.17	20.73	1.2	4.1	5.3					
Mean	584	582	583	5.28	5.09	5.18	0.6	2.1	1.3					
24	550	538		5.18	4.99		0.9	1.8						
	547	541		5.08	4.99		1.0	1.9						
Total	1097	1079	2176	10.26	9.98	20.24	1.9	3.7	5.6					
Mean	549	540	544	5.13	4.99	5.06	1.0	1.9	1.4					
48	527	516		4.97	5.01		1.2	2.2		14.1	16.3	7.1	66	0.84
	527	518		4.97	4.97		1.0	1.4		18.5	16.6	9.5	52	1.27
Total	1054	1034	2088	9.94	9.98	19.92	2.2	3.6	5.8	32.6	32.9	16.6	118	2.11
Mean	527	517	522	4.97	4.99	4.98	1.1	1.8	1.6	16.3	16.5	8.3	59	1.06

*15 g of sample were incubated with 30 ml of 1% dextrose and 100 ppm N urea for 21 days then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table XI. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of air dry Menfro soil incubated for various times in contact with the atmosphere at 25 ± 2° C.*

Treatment	Eh			pH			As			Al	Ca	Fe	Mn	Pb
	1	2		1	2		1	2						
Days	mV						ppm							
4	546	538		7.27	7.34		1.2	0.9						
	545	544		7.31	7.14		1.0	1.3						
Total	1091	1082	2173	14.58	14.48	29.06	2.2	2.2	4.4					
Mean	546	541	543	7.29	7.24	7.27	1.1	1.1	1.1					
8	536	532		7.39	7.30		1.2	1.3						
	549	529		7.09	7.37		0.6	1.1						
Total	1085	1061	2146	14.48	14.67	29.15	1.8	2.4	4.2					
Mean	543	531	572	7.24	7.34	7.29	0.9	1.2	1.1					
12	530	530		6.91	7.01		1.0	0.9						
	525	522		6.98	7.02		1.3	1.2						
Total	1055	1052	2107	13.89	14.03	27.92	2.3	2.1	4.4					
Mean	528	526	527	6.95	7.02	6.98	1.2	1.1	1.1					
24	495	444		7.01	7.00		0.6	1.3						
	489	449		7.10	7.12		1.6	1.5						
Total	984	893	1877	14.11	14.12	28.23	2.2	2.8	5.0					
Mean	492	447	469	7.06	7.06	7.06	1.1	1.4	1.3					
48	528	506		6.91	6.86		1.4	1.8		6.6	1.7	3.0	8.4	0.53
	527	512		6.92	6.91		1.4	1.6		5.2	1.4	1.1	6.0	0.71
Total	1055	1018	2073	13.83	13.77	27.60	2.8	3.4	6.2	11.8	3.1	4.1	14.4	1.24
Mean	528	509	518	6.92	6.89	6.90	1.4	1.7	1.6	5.9	1.6	2.1	7.2	0.62

*15 g of sample were incubated with 30 ml of water for 21 days and then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table XII. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of air dry Menfro soil incubated for various times in contact with the atmosphere at 25 ± 2° C. *

Treatment	Eh			pH			As			Al	Ca	Fe	Mn	Pb
	1	2		1	2		1	2						
Days	mV						ppm							
4	564	565		5.85	5.85		1.2	1.5						
	569	569		5.92	5.92		1.2	1.1						
Total	1133	1134	2267	11.77	11.77	23.54	2.4	2.6	5.0					
Mean	567	567	567	5.89	5.89	5.89	1.2	1.3	1.3					
8	554	551		5.85	5.84		0.5	0.8						
	559	564		5.70	5.84		0.6	1.2						
Total	1113	1115	2228	11.55	11.68	23.23	1.1	2.0	3.1					
Mean	557	558	557	5.78	5.84	5.81	0.6	1.0	0.8					
12	546	555		5.78	5.72		6.4	1.0						
	546	549		5.76	5.74		1.2	0.3						
Total	1092	1104	2196	11.54	11.46	23.00	8.6	1.3	9.9					
Mean	546	552	549	5.77	5.73	5.75	4.3	0.7	2.5					
24	518	524		5.73	5.72		2.1	1.3						
	518	520		5.73	5.71		1.2	1.5						
Total	1036	1044	2080	11.46	11.43	22.89	3.3	2.8	6.1					
Mean	518	522	520	5.73	5.72	5.73	1.7	1.4	1.5					
48	501	493		5.67	5.61		1.4	1.3		7.4	4.0	3.0	6	2.49
	497	498		5.69	5.59		1.2	1.5		6.8	29.0	1.8	80	1.61
Total	998	991	1989	11.36	11.20	22.54	2.6	2.8	5.4	14.2	33	4.8	86	4.10
Mean	499	496	497	5.68	5.60	5.64	1.3	1.4	1.4	7.1	17	2.4	43	2.05

*15 g of sample were incubated with 30 ml of 1% dextrose and 100 ppm N urea for 21 days then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table XIII. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of Sharpsburg soil at 26.7% moisture incubated for various times in contact with the atmosphere at 25 ± 2° C.*

Time	Eh	pH	As	Al	Ca	Fe	Mn	Pb	Cond.
Days	mV		ppm						μ mhos
4	569	6.46	0.2	25.3	34	7.6	2.8	0.86	229
	584	6.32	0.4	39.4	23	30.9	2.3	1.75	131
Total	1153	12.78	0.6	64.7	57	38.5	5.1	2.61	360
Mean	577	6.39	0.3	32.4	29	19.3	2.6	1.31	180
8	617	6.09	0.3	23.1	34	6.7	2.2	0.80	178
	606	6.25	0.3	32.6	23	24.9	2.1	0.97	156
Total	1223	12.34	0.6	55.7	57	31.6	4.3	1.77	334
Mean	612	6.17	0.3	27.9	29	15.8	2.2	0.89	167
12	554	6.30	0.7	20.5	34	6.6	2.0	0.62	162
	609	6.16	0.2	28.7	23	22.0	1.5	0.90	155
Total	1163	12.46	0.9	49.2	57	28.6	3.5	1.52	317
Mean	582	6.23	0.5	24.6	29	14.3	1.8	0.76	159
24	577	6.36	0.3	17.0	34	4.4	0.7	0.50	172
	565	6.24	0.1	27.9	23	9.1	1.5	0.49	143
Total	1142	12.60	0.4	44.9	57	13.5	2.2	0.99	314
Mean	571	6.30	0.2	22.5	29	6.8	1.1	0.50	157
48	640	5.39	0.1	14.5	32	6.8	4.1	0.48	425
	683	5.21	0.1	4.9	35	2.7	4.3	0.52	412
Total	1323	10.60	0.2	19.4	67	9.5	8.4	1.00	837
Mean	662	5.30	0.1	9.7	34	4.8	4.2	0.50	419

*15 g of sample were incubated with 30 ml of water for 21 days and then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table XIV. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of Sharpsburg soil at 26.7% moisture incubated for various times in contact with the atmosphere at 25 ± 2° C.*

Time	Eh	pH	As	Al	Ca	Fe	Mn	Pb	Cond.
Days	mV		ppm						µ mhos
4	550	4.96	1.2	6.1	258	1.7	57	0.77	1530
	562	4.98	1.5	18.1	218	2.4	48	1.45	1100
Total	1112	9.94	2.7	22.2	476	4.1	105	2.22	2630
Mean	556	4.97	1.4	11.1	238	2.1	53	1.11	1315
8	563	4.95	1.3	5.7	292	1.5	50	0.48	1600
	554	4.93	1.1	8.1	258	3.8	43	1.36	1410
Total	1117	9.88	2.4	13.8	550	5.3	93	1.84	3010
Mean	559	4.94	1.2	6.9	275	2.7	47	0.92	1505
12	578	4.96	1.1	5.5	258	1.2	49	0.59	1190
	566	4.92	1.5	5.8	235	2.5	39	0.90	1260
Total	1144	9.88	2.6	11.3	493	3.7	88	1.49	2450
Mean	572	4.94	1.3	5.7	247	1.9	44	0.75	1225
24	587	5.01	0.9	5.5	195	1.2	35	0.69	1370
	595	5.16	1.0	5.6	206	1.2	40	0.48	1900
Total	1182	10.17	1.9	11.1	401	2.4	75	1.17	3270
Mean	591	5.09	1.0	5.6	201	1.2	38	0.59	1635
48	555	5.16	0.8	2.8	160	1.5	50	1.13	1070
	560	5.14	1.1	2.0	174	0.8	57	1.56	1160
Total	1115	10.30	1.9	4.8	334	2.3	107	2.69	2230
Mean	558	5.15	1.0	2.4	167	1.2	54	1.35	1115

*15 g of sample were incubated with 30 ml of 1% dextrose and 100 ppm N urea for 21 days then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table XV. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of Menfro soil at 26.7% moisture incubated for various times in contact with the atmosphere at 25 ± 2° C.*

Time	Eh	pH	As	Al	Ca	Fe	Mn	Pb	Cond.
Days	mV		ppm						µ mhos
4	535	7.33	0.3	10.5	23	5.6	2.4	0.81	278
	558	7.10	0.2	11.2	29	7.4	2.3	0.78	245
Total	1093	14.43	0.5	22.7	52	13.0	4.7	1.59	523
Mean	547	7.22	0.3	11.4	26	6.5	2.4	0.80	262
8	542	7.15	0.2	11.0	29	5.6	3.4	0.98	269
	525	7.09	0.2	13.2	29	5.3	3.3	0.71	253
Total	1067	14.24	0.4	24.2	58	10.9	6.7	1.69	522
Mean	534	7.12	0.2	12.1	29	5.5	3.4	0.85	261
12	574	6.81	0.1	8.1	46	2.1	3.9	0.36	302
	575	6.98	1.1	6.8	29	4.1	3.9	0.49	279
Total	1149	13.79	1.2	14.9	75	6.2	7.8	0.85	581
Mean	575	6.89	0.6	7.5	38	3.1	3.9	0.43	291
24	581	6.82	0.2	8.0	63	2.2	4.8	0.32	329
	528	7.02	0.2	9.3	29	4.9	3.2	0.85	231
Total	1109	13.84	0.4	17.3	92	7.1	8.0	1.17	560
Mean	555	6.92	0.2	8.7	46	3.6	4.0	0.59	280
48	602	6.78	0.1	7.2	71	3.6	8.5	0.61	558
	605	6.85	0.1	4.5	64	2.6	7.1	0.82	470
Total	1207	13.63	0.2	11.7	135	6.2	15.6	1.43	1028
Mean	604	6.82	0.1	5.9	68	3.1	7.8	0.72	512

*15 g of sample were incubated with 30 ml of water for 21 days and then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table XVI. Eh, pH, and the concentration of elements in 1 to 2 soil to water extracts of the 0-15 cm layer of Menfro soil at 26.7% moisture incubated for various times in contact with the atmosphere at 25 ± 2° C.*

Time	Eh	pH	As	Al	Ca	Fe	Mn	Pb	Cond.
Days	mV		ppm						μ mhos
4	434	6.30	0.8	7.8	533	3.4	54.4	0.76	2390
	528	5.95	0.8	7.9	575	12.9	76.2	1.36	2580
Total	962	12.25	1.6	15.7	1108	16.3	130.6	2.12	4970
Mean	481	6.13	0.8	7.9	554	8.2	65.3	1.06	2485
8	490	6.64	0.6	6.9	355	3.4	33.6	0.45	2290
	387	6.35	0.9	4.5	476	5.5	48.9	0.93	2450
Total	877	12.99	1.5	11.4	831	8.9	82.5	1.38	4740
Mean	439	6.50	0.8	5.7	416	4.5	41.3	0.69	2370
12	574	7.01	0.6	4.7	235	1.5	13.1	0.46	1910
	293	6.34	1.3	4.7	453	2.8	43.4	0.47	2060
Total	867	13.35	1.9	9.4	688	4.3	56.5	0.93	3970
Mean	434	6.68	1.0	4.7	344	2.2	28.3	0.47	1985
24	492	8.02	0.2	4.5	69	4.9	2.5	0.19	380
	504	7.79	0.3	4.7	109	1.9	31.6	0.44	530
Total	996	15.81	0.5	9.2	178	6.8	34.1	0.63	910
Mean	498	7.91	0.3	4.6	89	3.4	17.1	0.32	455
48	489	7.95	0.1	6.1	76	4.6	2.9	1.35	470
	497	7.86	0.1	4.9	82	1.8	6.8	0.68	503
Total	986	15.81	0.2	11.0	158	6.4	9.7	2.03	973
Mean	493	7.91	0.1	5.5	79	3.2	4.9	1.02	487

*15 g of sample were incubated with 30 ml of 1% dextrose and 100 ppm N urea for 21 days then freeze dried. Time refers to the number of days after the freeze dried sample was exposed to the atmosphere.

Table XVII. The concentration of various elements in solution after equilibration of the Sharpsburg soil with HCl and NaOH solutions.

Initial pH	Final pH	Eh	As	Al	Ca	Fe	Mn	Pb
		mV	ppm					
2	3.80	657	0.3	6.2	259	9.2	38.4	23.4
	3.42	713	0.4	5.8	309	1.9	29.4	48.1
Total	7.22	1370	0.7	12.0	568	11.1	67.8	71.5
Mean	3.61	685	0.4	6.0	284	5.6	33.9	35.8
3	6.40	568	3.1	7.0	45	8.1	4.4	9.0
	3.37	716	2.0	13.9	34	10.5	1.8	13.2
Total	9.77	1284	5.1	20.9	79	18.6	6.2	22.2
Mean	4.89	642	2.6	10.5	40	9.3	3.1	11.1
4	6.52	552	3.6	10.1	40	12.2	3.0	9.0
	4.58	647	5.5	119.8	27	37.2	2.4	21.1
Total	11.10	1199	9.1	129.9	67	49.4	5.4	30.1
Mean	5.55	600	4.6	65.0	34	24.7	2.7	15.1
5	6.68	547	3.4	9.9	37	13.9	2.9	10.5
	6.18	580	2.2	18.2	14	15.5	0.7	12.2
Total	12.86	1127	5.6	28.1	51	29.4	3.6	22.7
Mean	6.43	564	2.8	14.1	26	14.7	1.8	11.4
6	6.51	552	3.1	10.5	26	11.1	0.2	8.7
	6.25	594	1.1	27.9	13	23.9	0.4	15.0
Total	12.76	1146	4.1	38.4	39	35.0	0.6	23.7
Mean	6.38	573	2.1	19.2	20	17.5	0.3	11.9
7	6.13	569	3.0	29.5	26	24.4	2.4	12.4
	6.71	540	4.4	16.5	23	59.1	1.2	28.4
Total	12.84	1109	7.4	46.2	49	83.5	3.6	36.8
Mean	6.42	555	3.7	23.1	25	41.8	1.8	18.4
8	6.36	556	3.6	21.5	30	19.7	2.8	12.1
	6.42	543	4.8	31.4	39	29.4	2.7	13.8
Total	12.78	1099	8.4	52.9	69	49.1	5.5	25.9
Mean	6.39	550	4.2	26.5	35	24.6	2.8	13.0

*Equilibrated for 7 days at 25° C with constant shaking.

Table XVIII. The concentration of various elements in solution after equilibration of the Menfro soil with HCl and NaOH solutions.

Initial pH	Final pH	Eh	As	Al	Ca	Fe	Mn	Pb
		mV	ppm					
2	6.72	544	3.2	3.4	371	4.2	25.4	0.14
	6.96	502	4.2	3.9	361	4.8	24.6	†
Total	13.68	1046	7.4	7.3	732	9.0	50.0	
Mean	6.84	523	3.7	3.7	366	4.5	25.0	
3	7.23	500	4.5	3.9	115	5.5	9.1	0.11
	7.60	469	6.3	4.5	117	4.2	9.7	†
Total	14.83	969	10.8	8.4	232	9.7	18.8	
Mean	7.42	485	5.4	4.2	116	4.8	9.4	
4	7.29	494	3.4	3.3	84	3.4	5.4	0.11
	7.40	478	4.2	3.5	81	4.1	7.0	†
Total	14.69	972	7.6	6.8	165	7.5	12.4	
Mean	7.35	486	3.8	3.4	83	3.8	6.2	
5	7.17	496	3.3	5.1	88	4.2	7.1	0.13
	7.16	486	4.8	3.0	81	5.3	7.6	†
Total	14.33	982	8.1	8.1	169	8.6	14.7	
Mean	7.17	491	4.1	4.1	85	4.3	7.4	
6	7.49	489	2.5	3.9	75	3.1	6.0	0.12
	7.20	483	6.3	2.4	85	6.2	8.5	†
Total	14.69	972	8.8	6.3	160	9.3	14.5	
Mean	7.35	486	4.4	3.2	80	5.7	7.3	
7	7.29	485	4.0	3.9	92	5.5	8.1	0.13
	7.34	478	5.5	2.8	94	6.4	9.6	†
Total	14.63	963	9.5	6.7	186	12.0	17.7	
Mean	7.32	482	4.8	3.4	93	6.0	8.9	
8	7.41	482	3.6	3.7	85	4.5	6.7	0.15
	7.10	486	5.1	2.5	76	5.6	6.8	†
Total	14.51	968	8.7	6.2	161	10.1	13.5	
Mean	7.26	484	4.4	3.1	81	5.1	6.8	

*Equilibrated for 7 days at 25° C with constant shaking.

†Less than 0.075 ppm.

Table XIX. The concentration of various elements in solution after equilibration of the Sharpsburg soil (3 g) with 0.01 M $CaCl_2$ and various concentrations of $Na_2HAsO_4 \cdot 7H_2O$ at pH 4.5 (30 ml solution).

Time	Added As	Eh	pH	Cond.	As	Al	Ca	Fe	Mn	Pb
Hours	µg/g soil	mV		µ mhos	ppm					
24	0	589	5.07	2060	0.1	0.18	324	2.3	4.8	0.24
		628	4.91	2280	0.2	0.30	335	2.5	4.2	0.20
	Mean	609	4.99	2170	0.2	0.24	330	2.4	4.6	0.22
	10	600	5.03	2550	0.2					
		635	4.87	2590	0.2					
	Mean	618	4.95	2570	0.2					
	20	610	4.99	2120	0.3					
		635	4.85	2040	0.2					
	Mean	623	4.92	2080	0.3					
	40	615	5.06	2490	0.3	0.16	328	2.4	5.0	0.15
		636	4.88	2590	0.3	0.27	335	6.1	4.0	0.17
	Mean	626	4.97	2540	0.3	0.22	332	4.3	5.0	0.16
	80	621	5.02	2130	0.3	0.15	325	2.0	5.5	0.28
		639	4.89	2110	0.3	0.30	340	4.1	3.9	0.15
	Mean	630	4.96	2120	0.3	0.23	333	3.1	4.7	0.22
	160	621	5.03	2220	0.6	0.13	330	1.5	5.2	0.20
		640	4.88	2070	1.4	0.24	342	5.8	3.6	0.14
	Mean	631	4.96	2145	1.0	0.19	336	3.7	4.4	0.117

Table XIX. (continued)

Time	Added As	Eh	pH	Cond.	As	Al	Ca	Fe	Mn	Pb
Hours	µg/g soil	mV		µ mhos	ppm					
48	0	634	5.11	2110	0.2	0.15	327	1.9	5.2	0.19
		648	4.93	2610	0.2	0.19	315	1.8	5.3	0.25
	Mean	641	5.02	2360	0.2	0.17	321	1.9	5.3	0.22
	10	635	5.12	2060	0.1					
		648	4.92	2380	0.3					
	Mean	642	5.02	2220	0.2					
	20	637	5.08	2200	0.2					
		651	4.90	2200	0.3					
	Mean	644	4.99	2200	0.3					
	40	617	5.07	2600	0.3	0.20	325	2.1	5.2	0.17
		650	4.92	2900	0.2	0.21	340	6.5	3.8	0.16
	Mean	634	5.00	2750	0.3	0.21	333	4.3	4.5	0.17
	80	635	5.09	2200	0.5	0.16	333	0.9	5.7	0.25
		652	4.92	2150	0.3	0.28	342	3.5	4.1	0.14
	Mean	644	5.01	2175	0.4	0.22	338	2.2	4.9	0.20
	160	639	5.04	2030	0.8	0.13	328	1.2	5.2	0.22
		652	4.93	2200	1.5	0.20	342	6.4	3.5	0.13
	Mean	646	4.99	2115	1.2	0.17	335	3.8	4.4	0.18

Table XIX. (continued)

Time	Added As	Eh	pH	Cond.	As	Al	Ca	Fe	Mn	Pb
Hours	µg/g soil	mV		µ mhos	ppm					
96	0	620	5.30	2110	0.2	0.13	330	2.2	5.4	0.28
		638	4.98	2110	0.3	0.18	339	2.7	3.9	0.12
	Mean	629	5.14	2110	0.3	0.16	335	2.5	4.7	0.20
	10	625	5.18	3130	0.3					
		642	5.02	1810	0.3					
	Mean	634	5.10	2470	0.3					
	20	627	5.19	2200	0.6					
		643	4.93	2200	0.4					
	Mean	635	5.06	2200	0.5					
	40	598	5.15	2150	0.3	0.15	330	2.2	5.1	0.18
		643	4.95	2180	0.4	0.28	345	6.4	3.9	0.19
	Mean	621	5.05	2165	0.4	0.22	338	4.3	4.5	0.19
	80	624	5.13	2100	0.4	0.17	330	1.1	5.6	0.31
		642	4.96	2100	0.7	0.24	345	3.9	3.6	0.13
	Mean	633	5.05	2100	0.6	0.21	338	2.0	4.6	0.22
	160	628	5.12	2110	1.1	0.14	330	1.1	5.0	0.21
		645	4.93	2190	1.2	0.22	339	7.3	3.7	0.13
	Mean	637	5.03	2150	1.2	0.18	335	4.2	4.4	0.17

Table XX. The concentration of various elements in solution after equilibration of the Menfro soil (3 g) with 0.01 M $CaCl_2$ and various concentrations of $Na_2HAsO_4 \cdot 7H_2O$ at pH 5.5 (30 ml solution).

Time	Added As	Eh	pH	Cond.	As	Al	Ca	Fe	Mn	Pb*
Hours	µg/g soil	mV		µ mhos	ppm					
24	0	589	6.31	2320	0.2	0.21	372	3.8	0.1	
		599	6.08	2190	0.2	0.09	386	3.7	0.2	
	Mean	594	6.20	2255	0.2	0.15	380	3.8	0.2	
	10	589	6.30	1800	0.2					
		597	6.14	2060	0.2					
	Mean	593	6.22	1930	0.2					
	20	589	6.34	1870	0.2					
		596	6.23	2190	0.2					
	Mean	593	6.23	2030	0.2					
	40	586	6.45	2270	0.4	0.14	392	4.0	0.1	
		599	6.10	2080	0.2	0.14	370	4.0	0.3	
	Mean	593	6.28	2175	0.3	0.14	381	4.0	0.2	
	80	594	6.18	2190	0.6	0.14	375	2.5	0.4	
		590	6.33	2140	0.4	0.13	369	3.7	0.3	
	Mean	592	6.26	2165	0.5	0.14	372	3.1	0.4	
	160	596	6.14	2080	1.2	0.13	367	4.2	0.2	
		593	6.31	2220	1.0	0.15	388	4.0	0.1	
	Mean	594	6.23	2150	1.1	0.14	378	4.1	0.2	

*Less than 0.075 ppm.

Table XX. (continued)

Time	Added As	Eh	pH	Cond.	As	Al	Ca	Fe	Mn	Pb*
Hours	µg/g soil	mV		µ mhos	ppm					
48	0	583	6.44	2460	0.2	0.15	372	3.8	0.3	
		592	6.29	1920	0.2	0.14	368	3.8	0.2	
	Mean	588	6.37	2190	0.2	0.15	370	3.8	0.3	
	10	588	6.31	2220	0.2					
		592	6.23	2210	0.2					
	Mean	590	6.28	2215	0.2					
	20	586	6.38	2090	0.3					
		589	6.35	2050	0.2					
	Mean	588	6.37	2070	0.3					
	40	591	6.19	2120	0.4	0.13	390	4.1	0.2	
		597	6.15	2200	0.4	0.15	391	3.9	0.2	
	Mean	594	6.17	2160	0.4	0.14	391	4.0	0.2	
	80	588	6.36	2200	0.3	0.14	382	4.0	0.4	
		592	6.26	2120	0.4	0.16	355	4.0	0.4	
	Mean	590	6.31	2160	0.4	0.15	369	4.0	0.4	
	160	599	6.05	2100	1.2	0.12	386	3.2	0.3	
		596	6.13	1880	1.3	0.14	367	3.7	0.2	
	Mean	598	6.09	1990	1.3	0.13	377	3.5	0.3	

*Less than 0.075 ppm.

Table XX. (continued)

Time	Added As	Eh	pH	Cond.	As	Al	Ca	Fe	Mn	Pb*
Hours	µg/g soil	mV		µ mhos	ppm					
96	0	596	6.34	2310	0.2	0.14	369	3.9	0.2	
		598	6.37	2380	0.3	0.15	387	4.2	0.3	
	Mean	597	6.36	2345	0.3	0.15	378	4.1	0.3	
	10	594	6.41	2210	0.2					
		593	6.50	2300	0.3					
	Mean	594	6.46	2255	0.3					
	20	595	6.42	2180	0.4					
		596	6.39	2170	0.3					
	Mean	596	6.41	2175	0.4					
	40	595	6.42	2210	0.4	0.15	386	3.9	0.03	
		595	6.43	2250	0.2	0.13	374	3.4	0.3	
	Mean	595	6.43	2230	0.3	0.14	380	3.7	0.2	
	80	600	6.32	2240	0.3	0.13	379	3.9	0.2	
		597	6.33	2330	0.5	0.13	368	2.5	0.5	
	Mean	599	6.33	2285	0.4	0.13	374	3.2	0.4	
	160	598	6.31	2280	1.3	0.15	392	4.1	0.1	
		585	6.52	2300	0.9	0.13	368	4.1	0.3	
	Mean	592	6.42	2290	1.1	0.14	380	4.1	0.2	

*Less than 0.075 ppm.

Table XXI. The concentration of various elements in solution after equilibration of the Sharpsburg soil (3 g) with 0.01 M $CaCl_2$ and various concentrations of $NaAsO_2$ at pH 4.5 (30 ml solution).

Time (hours)	24				48				96			
Added As	Eh	pH	Cond.	As	Eh	pH	Cond.	As	Eh	pH	Cond.	As
μg/g soil	mV		μ mhos	ppm	mV		μ mhos	ppm	mV		μ mhos	ppm
0	680	4.94	1980	0.3	645	5.00	2180	0.3	646	5.17	2180	0.1
	663	4.92	2090	0.2	669	4.98	2180	0.3	681	4.94	2260	0.1
Mean	672	4.93	2035	0.3	657	4.99	2180	0.3	664	5.05	2220	0.1
10	673	5.01	2110	0.4	646	5.15	2240	0.2	653	5.11	2190	0.1
	674	4.91	2100	0.2	672	496	2110	0.3	681	4.95	2210	0.1
Mean	674	4.96	2105	0.3	659	5.06	2175	0.3	667	5.03	2200	0.1
20	670	5.04	2100	0.4	656	5.08	2200	0.3	656	5.12	2190	0.1
	674	4.91	2180	0.2	671	4.97	2170	0.4	682	4.93	2300	0.2
Mean	672	4.98	2140	0.3	664	5.03	2185	0.4	669	5.03	2245	0.2
40	660	5.03	2080	1.0	659	5.09	2210	0.4	659	5.12	2170	0.1
	671	4.92	2140	0.6	672	4.96	2090	0.3	670	4.95	2200	0.2
Mean	666	4.98	2110	0.8	666	5.03	2150	0.4	665	5.04	2185	0.2
80	629	5.03	2110	2.6	662	5.09	2210	0.5	664	5.08	2300	0.4
	654	4.95	2180	2.0	673	4.95	2150	0.5	678	5.03	2240	0.6
Mean	642	4.99	2145	2.3	667	5.02	2180	0.5	671	6.06	2270	0.5
160	605	5.06	2180	6.2	664	5.04	2170	2.0	667	5.11	2250	1.1
	610	4.93	2200	8.4	673	4.94	2200	2.1	679	5.01	2290	1.0
Mean	607	5.00	2190	7.3	669	4.99	2185	2.1	673	5.06	2270	1.1

Table XXII. The concentration of various elements in solution after equilibration of the Menfro soil (3 g) with 0.01 M $CaCl_2$ and various concentrations of $NaAsO_2$ at pH 5.5 (30 ml solution).

Time (hours)	24				48				96			
Added As	Eh	pH	Cond.	As	Eh	pH	Cond.	As	Eh	pH	Cond.	As
μg/g soil	mV		μ mhos	ppm	mV		μ mhos	ppm	mV		μ mhos	ppm
0	599	6.35	2300	0.25	624	6.32	2290	0.3	630	6.46	2440	0.1
	599	6.23	2300	0.51	608	6.39	2220	0.3	627	6.45	2465	0.1
Mean	599	6.29	2300	0.38	616	6.37	2255	0.3	627	6.45	2465	0.1
10	610	6.33	2100	0.3	615	6.46	2200	0.3	626	6.50	2340	0.1
	605	6.37	2100	0.3	612	6.39	2120	0.3	625	6.44	2310	0.1
Mean	607	6.35	2100	0.3	614	6.42	2160	0.3	626	6.47	2325	0.1
20	616	6.30	2110	0.3	616	6.45	2200	0.3	627	6.44	2380	0.2
	617	6.24	2180	0.3	617	6.33	2190	0.2	620	6.46	2410	0.3
Mean	617	6.27	2145	0.3	617	6.39	2195	0.3	624	6.45	2395	0.3
40	610	6.32	2190	0.6	617	6.45	2230	0.4	626	6.46	2420	0.3
	609	6.21	2100	0.9	619	6.31	2110	0.2	620	6.46	2410	0.3
Mean	610	6.27	2145	0.8	618	6.38	2170	0.3	623	6.46	2415	0.3
80	614	6.38	2200	2.0	622	6.33	2200	0.2	626	6.45	2350	0.4
	614	6.27	2100	2.2	615	6.42	2290	0.4	620	6.47	2420	0.6
Mean	614	6.33	2150	2.1	619	6.38	2245	0.3	623	6.46	2385	0.5
160	538	6.32	2140	7.9	595	6.36	2210	2.6	625	6.44	2430	1.3
	534	6.28	2290	6.1	615	6.45	2370	2.5	624	6.42	2300	1.3
Mean	536	6.30	2215	7.0	605	6.41	2290	2.6	625	6.43	2365	1.3

Table XXIII. Composition of the solution of various arsenate salts after equilibration with HCl and NaOH solutions for 7 days at 25° C.

	T1					T2				
Initial pH	Al	As	Eh	Final pH	Cond.	Al	As	Eh	Final pH	Cond.
	— ppm —		mV		μ mhos	— ppm —		mV		μ mhos
2	2.1	807	580	3.00	3200	9.9	930	524	2.72	2900
3	1.6	720	601	3.19	2910	4.0	2337	736	3.26	1310
4	0.4	602	640	3.00	836	1.5	1410	753	3.34	642
5	1.6	346	680	3.00	603	3.1	910	759	3.32	842
6	2.8	584	682	3.34	556	2.9	1122	760	3.34	718
7	0.3	824	682	3.36	617	3.0	1520	764	3.33	895
8	3.3	886	720	3.41	469	1.5	1050	768	3.37	610

	T3					T4				
Initial pH	Mn	As	Eh	Final pH	Cond.	Mn	As	Eh	Final pH	Cond.
	— ppm —		mV		μ mhos	— ppm —		mV		μ mhos
2	3.3	987	772	3.81	3200	55	1067	752	3.85	2370
3	5.3	96	627	7.01	1290	30.7	39	631	5.96	364
4	1.2	103	613	7.32	1290	10.7	21	597	6.69	55
5	4.9	106	608	7.40	1230	10.7	17	582	7.01	40
6	1.4	132	606	7.44	1510	6.0	19	555	6.91	35
7	1.5	125	601	7.44	1420	5.6	19	588	6.91	43
8	1.2	127	597	7.44	1370	5.6	17	572	7.00	62

T1 - 0.1 M $AlCl_3 \cdot 6H_2O$ added to 0.1 M $Na_2HA_3O_4 \cdot 7H_2O$ at 95° C, pH maintained at 4.0 to 5.0.

T2 - 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ added to 0.1 M $AlCl_3 \cdot 6H_2O$ at 95° C, pH maintained at 4.0 to 5.0.

T3 - 0.5 g Mn dissolved in 1:1 HNO_3/H_2O, diluted to 100 ml, added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH brought back to 6.0.

T4 - 0.5 g Mn dissolved in 1:1 HNO_3/H_2O, diluted to 100 ml, added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH maintained at 5.5 to 6.5.

Table XXIII. (continued)

	T5					T6				
Initial pH	Mn	As	Eh	Final pH	Cond.	Ca	As	Eh	Final pH	Cond.
	— ppm —		mV		µ mhos	— ppm —		mV		µ mhos
2	56	1078	735	3.83	2580	352	3.0	567	12.45	2120
3	41.7	45	646	5.81	426	259	1.6	333	12.41	2900
4	19.5	33	609	5.33	85	240	0.7	330	12.23	2590
5	15.8	28	588	6.61	47	236	1.8	329	12.15	2300
6	11.8	30	580	6.56	51	234	0.8	322	12.33	2650
7	11.6	27	582	6.60	50	184	1.2	335	12.42	2150
8	11.0	26	585	6.58	60	176	0.5	346	12.31	1910

	T7				
Initial pH	Pb	As	Eh	Final pH	Cond.
			mV		µ mhos
2	3.6	231	825	1.82	5950
3	1.3	207	800	2.90	725
4	1.0	21.8	764	3.64	94
5	0.2	18.2	700	6.23	15
6	0.3	12.7	689	6.40	14
7	0.4	31.5	722	5.46	14
8	0.2	42.6	749	4.23	41

T5 - 0.1 M $MnCl_2 \cdot 4H_2O$ added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH maintained at 5.5 to 6.5.

T6 - 0.1 M $CaCl_2$ added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH maintained at 5.5 to 6.5.

T7 - 0.1 M $Pb(NO_3)_2$ added to 0.1 M Na_2HAsO_4 at 95° C, pH maintained at 5.5 to 6.5.

Table XXIV. Composition of the solution after equilibration with HCl and NaOH solutions for 7 days at 25° C.

	T1					T2					T3				
Initial pH	Fe	As	Eh	Final pH	Cond.	Fe	As	Eh	Final pH	Cond.	Fe	As	Eh	Final pH	Cond.
	— ppm —		mV		μ mhos	— ppm —		mV		μ mhos	— ppm —		mV		μ mhos
2	29.1	687	801	1.87	5280	6.9	28.9	827	1.68	6750	286	392	744	2.40	4510
3	27.8	767	687	5.33	1410	2.9	9.1	762	3.10	542	282	549	755	2.35	3230
4	27.6	610	668	5.61	845	1.4	8.6	771	3.59	95	217	279	740	2.31	1020
5	25.2	628	667	5.62	915	0.5	11.2	744	4.66	27	198	372	748	2.31	560
6	24.4	555	683	5.69	765	7.8	11.4	737	4.81	16	205	448	740	2.25	348
7	21.3	571	687	5.70	695	9.0	10.0	704	5.17	16	414	239	732	2.22	180
8	19.2	627	662	5.73	720	1.5	11.4	735	5.74	35	86	354	739	2.18	32
	T4					T5					T6				
2	28.6	333	603	5.36	2500	10.5	42.6	656	5.42	2880	17.2	40.2	653	2.08	2610
4	114.2	464	567	5.42	188	8.6	27.4	671	5.15	142	6.5	39.4	642	4.61	94
6	28.6	587	510	5.64	135	9.7	26.5	594	5.15	21	16.5	33.4	618	5.41	19
8	14.3	571	496	6.59	79	3.8	19.9	634	5.30	36	5.9	51.4	497	5.80	48

T1 - 0.1 M $FeCl_3 \cdot 6H_2O$ added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH allowed to drop to 2.5.

T2 - 0.1 M $FeCl_3 \cdot 6H_2O$ added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH maintained at 5.5 to 6.5.

T3 - 0.1 M $FeCl_3 \cdot 6H_2O$ added to 0.1 M $NaAsO_2$ at 95° C, pH maintained at 5.5 to 6.5.

T4 - 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ added to 0.1 M $FeCl_3 \cdot 6H_2O$ at 95° C, pH maintained at 4.0 to 5.0.

T5 - 0.1 M $FeCl_3 \cdot 6H_2O$ added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH maintained at 4.0 to 5.0.

T6 - 0.1 M $FeCl_3 \cdot 6H_2O$ added to 0.1 M $Na_2HAsO_4 \cdot 7H_2O$ at 95° C, pH maintained at 4.5 to 5.5.

Table XXV. Eh and pH of the Mexico soil at various depths on September 12, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	304	409	354	424	1491	373	7.5	5.6	6.4	5.3	24.8	6.2
	15	564	274	-126	44	756	189	6.0	7.9	7.0	5.5	26.4	6.6
	30	214	804	114	234	1366	342	4.5	7.0	5.2	6.4	24.0	6.0
	60	-26	194	- 76	-36	56	14	6.4	5.2	6.8	6.5	24.9	6.2
2	7.5	504	764	654	434	2356	589	4.8	7.0	4.5	5.3	21.6	5.4
	15	24	529	709	324	1586	397	6.0	4.6	6.6	6.2	23.4	5.9
	30	-36	454	574	254	1246	312	6.5	5.8	5.7	6.3	24.3	6.1
	60	-26	254	- 16	-76	136	34	6.4	6.2	6.6	6.6	25.8	6.5
3	7.5	254	354	484	819	1911	478	6.0	6.4	6.3	6.7	25.4	6.4
	15	329	364	364	554	1811	453	5.9	5.9	5.2	5.1	22.1	5.5
	30	209	754	164	214	1341	335	5.9	6.0	4.8	4.9	21.6	5.4
	60	-46	- 6	- 36	-16	-104	-26	5.6	5.6	5.6	5.3	22.1	5.5
4	7.5	364	134	194	264	986	247	6.3	5.4	6.1	6.9	24.7	6.2
	15	774	334	64	324	1496	374	6.0	6.9	6.3	6.0	25.2	6.3
	30	424	303	379	404	1511	378	5.3	5.5	6.1	5.6	22.4	5.6
	60	- 6	-86	4	-71	-159	-40	5.2	4.7	5.1	4.8	19.8	5.0

Table XXVI. Eh and pH of the Mexico soil at various depths on September 17, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	104	254	394	384	1136	284	5.1	5.0	5.1	5.2	20.4	5.1
	15	- 6	244	-106	34	166	42	4.7	4.8	5.0	5.1	19.6	4.9
	30	14	744	94	154	1006	252	4.9	5.0	5.0	5.1	20.0	5.0
	60	-76	474	-116	84	366	92	4.4	5.0	5.2	5.5	20.1	5.0
2	7.5	364	44	614	374	1396	349	4.6	6.1	5.5	5.7	21.9	5.5
	15	134	44	644	299	1121	280	4.9	6.0	5.6	5.6	22.1	5.5
	30	- 6	474	574	479	1521	380	5.0	5.9	5.2	5.5	21.6	5.4
	60	- 6	124	44	- 8	154	39	5.3	5.7	5.1	5.4	21.5	5.4
3	7.5	214	364	644	664	1886	472	5.0	5.1	5.8	5.6	21.5	5.4
	15	234	584	484	394	1696	424	4.9	5.3	5.9	5.5	21.6	5.4
	30	224	539	94	364	1221	305	5.2	5.3	6.3	5.8	22.6	5.7
	60	-56	504	-61	-11	376	94	5.2	5.4	6.2	5.3	22.1	5.5
4	7.5	514	114	214	194	1036	259	4.6	5.2	5.4	5.5	20.7	5.2
	15	654	414	34	264	1176	294	5.2	5.5	5.4	5.6	21.7	5.4
	30	424	- 6	264	274	956	239	5.4	5.3	5.2	5.0	20.9	5.2
	60	-36	-76	-36	-71	-219	-55	5.3	5.3	5.1	5.1	20.8	5.2

Table XXVII. Eh and pH of the Mexico soil at various depths on October 18, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	334	244	159	374	1111	278	4.9	5.0	4.8	4.9	19.6	4.9
	15	174	314	156	254	898	225	5.0	6.2	5.1	5.5	21.8	5.5
	30	- 46	314	- 19	- 76	173	43	5.1	5.65	5.2	5.6	21.6	5.4
	60	-111	54	- 6	- 36	- 99	-25	5.2	5.7	5.5	5.6	22.0	5.5
2	7.5	449	379	459	484	1771	443	4.6	6.1	4.7	4.8	20.2	5.1
	15	409	584	504	404	1901	475	4.9	6.1	4.9	5.0	20.9	5.2
	30	74	-106	554	- 61	461	115	5.0	5.8	5.4	5.3	21.5	5.4
	60	59	- 1	- 51	-101	- 94	-24	5.2	5.75	5.2	5.1	21.3	5.3
3	7.5	309	329	164	214	1016	254	4.9	5.05	5.9	5.8	21.7	5.4
	15	199	354	49	49	651	163	5.0	5.25	6.3	5.7	22.3	5.6
	30	234	359	-126	459	826	207	5.1	5.2	6.4	5.6	22.3	5.6
	60	- 36	64	-136	54	- 54	-14	5.1	5.35	6.15	5.5	22.2	5.6
4	7.5	389	144	544	249	1326	332	4.4	5.1	5.2	5.4	20.1	5.0
	15	769	574	484	189	2016	504	5.15	5.6	5.3	5.5	21.6	5.4
	30	14	224	- 46	74	266	67	5.3	5.4	4.9	4.7	20.3	5.1
	60	-106	- 6	-126	-101	-339	-85	5.4	5.2	4.8	5.0	20.4	5.1

Table XXVIII. Eh and pH of the Mexico soil at various depths on November 2, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	144	424	164	264	996	249	—	—	—	—		
	15	74	64	-166	314	286	72	5.9	5.91	6.35	6.0	24.2	6.1
	30	224	-26	4	- 6	192	48	5.35	5.45	5.71	5.43	22.0	5.5
	60	-76	19	-116	- 36	-209	-52	5.5	5.73	5.94	5.85	23.0	5.8
2	7.5	514	204	544	384	1646	412	—	—	—	—		
	15	134	534	454	409	1531	383	5.2	5.82	6.48	6.05	23.6	5.9
	30	244	79	464	- 26	761	190	5.1	5.41	6.41	5.89	22.8	5.7
	60	- 1	44	- 16	329	356	89	5.4	5.61	6.0	5.81	22.8	5.7
3	7.5	254	529	254	294	1331	333	—	—	—	—		
	15	199	344	94	54	691	173	5.0	5.71	6.45	5.8	23.0	5.8
	30	129	354	- 66	- 36	381	95	5.09	5.48	5.52	5.65	21.8	5.5
	60	-36	-86	-116	- 6	-244	-61	5.5	5.87	5.8	5.9	23.1	5.8
4	7.5	354	124	534	324	1336	334	—	—	—	—		
	15	670	524	224	-106	1312	328	5.1	5.9	6.2	6.2	23.4	5.9
	30	-46	- 6	294	-114	128	32	5.25	5.62	5.3	5.75	21.9	5.5
	60	454	-36	-126	-126	166	42	5.5	5.71	5.56	5.9	22.7	5.7

Table XXIX. Eh and pH of the Mexico soil at various depths on November 9, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	94	384	134	259	871	218	—	—	—	—		
	15	194	264	-186	124	396	99	7.10	6.43	6.44	6.35	26.32	6.58
	30	314	314	194	339	1161	290	5.90	5.70	5.80	5.70	23.10	5.78
	60	-111	24	-141	- 76	-304	-76	5.85	6.00	6.00	6.10	23.95	5.99
2	7.5	299	304	499	364	1466	367	—	—	—	—		
	15	359	589	434	404	1546	387	5.2	5.85	6.35	6.35	23.75	5.94
	30	329	204	499	484	1516	379	5.4	5.25	6.0	6.0	22.65	5.66
	60	- 76	59	- 31	414	366	92	5.75	5.7	5.9	6.15	23.30	5.83
3	7.5	189	469	254	299	1211	303	—	—	—	—		
	15	164	499	154	249	1066	267	5.55	6.00	6.39	6.45	24.39	6.10
	30	174	384	304	344	1206	302	5.41	5.30	5.69	5.80	22.2	5.55
	60	- 46	-136	-126	- 26	-334	-84	5.56	5.80	5.90	6.15	23.41	5.85
4	7.5	364	239	529	464	1596	399	—	—	—	—		
	15	704	444	274	434	1856	464	5.79	6.1	6.3	6.3	24.49	6.12
	30	464	304	464	224	1456	364	5.33	5.55	5.75	5.9	22.53	5.63
	60	-116	114	- 96	-126	-224	-56	5.58	5.85	6.0	6.1	23.53	5.88

Table XXX. Eh and pH of the Mexico soil at various depths on November 13, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	94	384	514	234	1226	307	—	—	—	—		
	15	194	264	-166	164	456	114	4.35	5.55	6.21	5.85	21.96	5.49
	30	314	314	124	314	1066	267	4.45	4.60	5.43	4.60	19.08	4.77
	60	-111	24	204	- 86	31	8	5.25	3.35	5.55	4.20	18.35	4.59
2	7.5	299	304	504	414	154	380	—	—	—	—		
	15	359	589	394	444	1786	447	4.55	5.25	5.7	5.5	21.00	5.25
	30	329	204	474	404	1411	353	4.0	4.4	5.62	3.8	17.82	4.46
	60	- 76	59	234	369	586	147	3.05	5.2	5.5	5.0	18.46	4.61
3	7.5	189	469	434	354	1446	362	—	—	—	—		
	15	164	399	199	249	1011	253	4.0	5.4	4.8	5.74	19.94	4.99
	30	174	384	209	274	1041	260	3.79	4.35	5.2	5.35	18.69	4.67
	60	- 46	-136	179	214	211	53	3.7	2.8	5.4	5.71	17.61	4.40
4	7.5	364	239	494	484	1581	395	—	—	—	—		
	15	704	444	239	444	1831	458	4.70	4.60	5.60	6.00	20.90	5.23
	30	464	304	204	379	1351	338	4.53	2.25	4.70	5.00	16.48	4.12
	60	-116	114	-106	-106	-214	-54	4.90	3.55	5.45	4.50	18.40	4.60

Table XXXI. Eh and pH of the Mexico soil at various depths on November 16, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	64	384	469	214	1131	283	—	—	—	—		
	15	239	224	- 96	84	643	161	5.75	5.85	5.65	5.45	22.70	5.68
	30	194	264	24	324	806	202	4.75	5.30	5.45	5.23	20.73	5.18
	60	-96	- 6	-136	- 56	-294	- 74	4.67	5.35	5.40	5.83	21.25	5.31
2	7.5	289	394	524	334	1541	385	—	—	—	—		
	15	424	634	424	394	1931	483	4.75	5.90	6.35	5.9	22.90	5.73
	30	29	244	479	254	1006	252	4.90	5.05	5.75	5.49	21.19	5.30
	60	-76	74	434	294	726	182	5.30	5.61	5.65	5.71	22.27	5.57
3	7.5	164	544	464	314	1486	372	—	—	—	—		
	15	104	424	124	214	866	217	4.80	5.69	6.00	6.00	22.49	5.62
	30	334	309	229	304	1176	294	5.00	5.23	5.30	5.42	20.95	5.24
	60	-16	-126	-106	179	- 69	- 17	5.35	5.50	5.50	5.59	21.93	5.48
4	7.5	359	184	504	324	1371	343	—	—	—	—		
	15	699	434	204	444	1781	445	5.00	5.45	5.90	5.75	22.1	5.23
	30	484	94	264	194	1036	259	5.10	5.30	5.35	5.30	21.05	5.26
	60	-86	-106	-136	-146	-474	-119	5.40	5.60	5.37	5.65	22.02	5.51

Table XXXII. Eh and pH of the Mexico soil at various depths on November 21, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	84	364	474	184	1106	277	—	—	—	—		
	15	124	54	- 96	- 66	16	4	6.05	5.03	5.80	5.20	22.08	5.52
	30	264	124	24	264	676	169	4.60	4.73	5.10	5.25	19.68	4.92
	60	-96	24	-116	104	- 84	-21	5.20	5.15	5.39	5.40	21.14	5.29
2	7.5	174	344	544	424	1486	372	—	—	—	—		
	15	-76	564	389	204	1081	270	4.55	5.60	6.55	5.50	22.20	5.55
	30	-96	234	424	279	841	210	4.60	4.79	5.79	5.00	20.18	5.05
	60	-96	104	154	234	396	99	5.15	5.40	5.50	5.25	21.30	5.33
3	7.5	204	589	414	274	1481	370	—	—	—	—		
	15	64	384	164	199	811	203	4.45	5.65	5.90	6.01	22.01	5.50
	30	324	259	- 26	194	751	188	4.65	4.80	5.00	5.00	19.45	4.86
	60	-46	-151	-126	194	-129	-32	5.13	5.39	5.25	5.48	21.25	5.31
4	7.5	334	134	524	344	1336	334	—	—	—	—		
	15	664	464	234	- 46	1316	329	5.15	5.37	5.60	5.70	21.82	5.46
	30	264	14	244	244	766	192	4.70	5.05	5.00	5.15	19.90	4.98
	60	84	- 36	-116	-146	-214	-54	5.20	5.49	5.30	5.40	21.39	5.35

Table XXXIII. Eh and pH of the Mexico soil at various depths on November 30, 1973.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	104	204	514	344	1166	292	—	—	—	—		
	15	109	224	-156	214	391	98	5.8	6.4	6.6	5.7	24.5	6.1
	30	- 66	- 86	- 46	124	- 74	-19	5.6	5.6	5.9	5.6	22.7	5.7
	60	-106	14	-126	- 31	-249	-62	5.9	6.0	6.1	6.2	24.2	6.1
2	7.5	284	294	474	404	1456	364	—	—	—	—		
	15	- 81	484	414	124	941	235	5.3	6.35	6.7	6.0	24.4	6.1
	30	-116	-106	314	- 31	61	15	5.4	5.6	6.0	5.1	22.1	5.5
	60	- 86	- 16	44	204	146	37	5.5	5.9	6.2	5.3	22.9	5.7
3	7.5	289	454	484	369	1596	399	—	—	—	—		
	15	284	484	364	304	1436	359	5.4	5.7	6.2	6.2	23.5	5.9
	30	114	54	- 96	144	216	54	5.4	5.5	5.7	5.5	22.1	5.5
	60	- 81	- 56	-126	224	- 39	-10	5.7	5.7	5.7	5.6	22.7	5.7
4	7.5	284	234	604	154	1276	319	—	—	—	—		
	15	644	514	284	-116	1326	332	5.4	6.0	6.0	6.2	23.6	5.9
	30	- 96	54	164	64	186	47	5.3	5.6	5.5	5.8	22.2	5.6
	60	-106	534	-136	-136	156	39	6.0	5.9	5.9	5.7	23.5	5.9

able XXXIV. Eh and pH of the Mexico soil at various depths on December 7, 1973.

reatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	——— mV ———											
1	7.5	314	264	364	134	1076	269	—	—	—	—		
	15	314	419	-126	144	751	188	5.1	5.7	5.6	5.5	21.9	5.5
	30	164	-26	504	54	696	174	4.7	5.0	4.9	4.9	19.5	4.9
	60	- 46	34	-106	- 51	-169	-42	5.1	5.2	5.2	5.4	20.9	5.2
2	7.5	424	434	494	394	1746	437	—	—	—	—		
	15	494	654	534	444	2126	532	4.9	5.8	6.0	5.6	22.3	5.6
	30	204	379	584	99	1266	317	5.2	5.0	5.2	4.7	20.1	5.0
	60	- 66	104	94	184	316	79	5.5	5.4	5.2	5.3	21.4	5.4
3	7.5	404	494	524	174	1596	399	—	—	—	—		
	15	364	474	474	424	1736	434	5.2	5.2	5.8	5.6	21.8	5.5
	30	324	154	4	374	856	214	4.9	5.0	4.9	5.1	19.9	5.0
	60	24	39	-126	34	- 29	- 7	5.2	5.3	5.1	5.3	20.9	5.2
4	7.5	459	224	494	204	1381	345	—	—	—	—		
	15	664	559	374	419	2016	504	4.9	5.6	5.6	5.8	21.9	5.5
	30	344	254	274	- 26	846	212	4.1	5.1	4.9	5.0	19.1	4.8
	60	-106	94	464	-156	296	74	5.1	5.2	5.1	5.3	20.8	5.2

Table XXXV. Eh and pH of the Mexico soil at various depths on March 8, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	—	534	734	204	1472	491	6.4	5.2	4.8	3.3	19.7	4.9
	15	309	454	194	34	991	248	5.6	5.7	5.7	5.0	22.0	5.5
	30	304	514	554	314	1686	422	5.1	5.2	5.0	4.8	20.1	5.0
	60	-86	- 16	-186	- 26	-314	-79	5.3	5.3	4.8	4.9	20.2	5.1
2	7.5	584	454	614	434	2086	522	4.5	5.9	5.4	6.1	21.9	5.5
	15	484	714	434	464	2096	524	5.95	6.7	6.7	6.0	25.4	6.4
	30	104	394	674	304	1476	369	5.1	5.7	4.5	5.5	20.8	5.2
	60	54	114	-156	- 6	6	2	4.65	5.5	4.7	5.2	20.1	5.0
3	7.5	704	694	384	694	2476	619	4.8	5.2	5.2	6.2	21.4	5.4
	15	274	654	494	534	1956	489	4.7	5.7	5.5	6.2	22.1	5.5
	30	414	114	574	384	1486	372	4.7	5.5	5.2	5.6	21.0	5.3
	60	-26	- 6	-176	294	86	22	5.0	5.5	5.2	5.2	20.9	5.2
4	7.5	489	534	634	434	2091	523	5.5	5.6	5.9	5.5	22.5	5.6
	15	634	494	384	494	2006	502	4.8	6.2	5.8	5.5	22.3	5.6
	30	434	354	374	374	1576	384	5.1	5.3	5.3	4.8	20.5	5.1
	60	54	-116	-156	-146	-364	-91	5.2	5.5	5.3	4.7	20.7	5.2

Table XXXVI. Eh and pH of the Mexico soil at various depths on April 26, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	114	504	394	514	1526	382	6.8	6.9	4.2	4.5	22.4	5.6
	15	364	494	—	404	1262	421	5.4	6.4	5.6	5.7	23.1	5.8
	30	314	604	194	339	1451	363	3.9	5.4	4.9	5.2	19.4	4.9
	60	4	54	—	124	182	61	4.1	5.9	5.4	5.4	21.1	5.3
2	7.5	614	434	314	264	1626	407	4.0	5.3	5.5	5.3	20.1	5.0
	15	434	524	234	409	1601	400	4.3	5.9	5.6	5.4	21.2	5.3
	30	164	—	464	144	772	257	4.0	5.5	5.3	5.2	20.0	5.0
	60	104	104	—	64	272	91	4.1	6.0	4.9	4.8	19.8	5.0
3	7.5	754	524	494	274	2046	512	6.5	6.75	6.6	6.3	26.2	6.6
	15	589	484	484	514	2116	529	5.4	6.5	5.7	5.6	23.2	5.8
	30	659	84	554	484	1781	445	5.8	5.3	5.2	4.9	21.2	5.3
	60	-16	14	- 96	74	- 24	- 6	5.7	5.7	5.7	5.5	22.6	5.7
4	7.5	594	314	679	534	2121	530	5.3	6.1	6.6	6.2	24.2	6.1
	15	564	414	354	134	1466	367	6.0	6.8	6.2	4.0	23.0	5.8
	30	424	234	294	334	1286	322	5.1	5.9	5.5	4.5	21.0	5.3
	60	-16	- 6	-146	-86	-254	-64	5.8	5.7	5.4	6.8	23.7	5.9

Table XXXVII. Eh and pH of the Mexico soil at various depths on May 14, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	154	334	474	464	1426	357	6.9	6.8	5.5	4.3	23.5	5.9
	15	304	254	-156	394	796	199	5.4	6.3	5.5	5.6	22.8	5.7
	30	-36	84	-166	254	136	34	4.8	5.5	4.7	5.2	20.2	5.1
	60	39	4	-186	- 46	-189	- 47	4.4	5.6	5.0	4.9	19.9	5.0
2	7.5	594	789	414	384	2181	545	4.2	5.3	5.5	5.3	20.3	5.1
	15	334	839	274	434	1881	470	4.5	5.6	5.4	5.9	21.4	5.4
	30	-61	499	- 26	- 76	336	84	4.2	5.8	5.3	5.5	20.8	5.2
	60	34	309	- 96	- 36	211	53	4.2	5.2	5.2	4.1	18.7	4.7
3	7.5	524	644	639	234	2041	510	6.3	6.8	6.5	6.6	26.2	6.6
	15	484	754	734	244	2216	554	5.6	6.5	5.4	5.7	23.2	5.8
	30	474	544	214	4	1236	309	4.9	5.3	5.8	5.2	21.2	5.3
	60	54	104	184	174	516	129	5.5	5.7	5.7	5.7	22.6	5.7
4	7.5	554	104	654	524	1836	459	6.6	6.2	6.3	5.4	24.5	6.1
	15	584	244	324	354	1506	377	6.2	6.6	4.2	5.8	22.8	5.7
	30	464	114	-236	284	626	157	5.5	5.8	4.8	5.2	21.3	5.3
	60	4	24	-286	-216	-474	-119	5.4	5.5	6.9	5.8	23.6	5.9

Table XXXVIII. Eh and pH of the Mexico soil at various depths on May 20, 1974.

Treatment	Depth	Eh						pH*					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	534	724	584	574	2416	604	6.8	5.5	6.5	6.3	25.1	6.3
	15	194	294	44	444	976	244						
	30	- 86	- 66	-176	194	-134	- 34						
	60	-126	- 36	-156	- 46	-364	- 91						
2	7.5	674	579	594	434	2281	570	5.7	5.0	6.9	6.2	23.8	6.0
	15	364	624	234	234	1456	364						
	30	-106	- 76	-106	-116	-404	-101						
	60	- 76	14	-176	144	- 94	- 24						
3	7.5	484	654	554	594	2286	572	6.15	6.5	5.9	6.0	24.6	6.2
	15	524	214	434	474	1646	412						
	30	-106	24	- 96	-136	-314	- 79						
	60	- 66	- 96	-156	114	-204	- 51						
4	7.5	534	574	554	674	2336	584	5.4	5.9	6.7	6.2	24.2	6.1
	15	624	574	294	564	2056	514						
	30	94	- 96	-166	124	- 44	- 11						
	60	-116	-126	-206	-236	-684	-171						

*Because the soil was saturated with water, it was not practical to take all the pH measurements.

Table XXXIX. Eh and pH of the Mexico soil at various depths on May 31, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	604	604	474	644	2326	582	7.0	7.1	6.9	6.8	27.8	7.0
	15	464	84	54	- 96	506	127	6.8	6.8	6.6	6.7	26.9	6.7
	30	194	164	-126	154	386	97	5.0	5.2	5.4	5.7	21.3	5.3
	60	-86	-111	-156	- 46	-399	-100	5.5	5.1	5.2	5.3	21.1	5.3
2	7.5	554	594	24	584	1756	439	5.6	5.9	6.2	6.3	24.0	6.0
	15	234	474	179	329	1216	304	4.2	4.9	5.8	6.0	20.3	5.1
	30	-26	24	- 46	-129	-177	- 44	4.0	5.2	5.0	5.9	20.1	5.0
	60	-36	14	-166	- 96	-284	- 71	4.9	5.0	5.1	4.9	19.9	5.0
3	7.5	464	444	594	664	2166	542	7.0	7.1	7.0	6.9	28.0	7.0
	15	394	194	189	444	1221	305	6.9	6.8	6.6	6.7	27.0	6.8
	30	394	104	- 46	- 46	406	102	5.4	5.5	5.2	5.6	21.7	5.4
	60	-36	- 46	-146	179	- 49	- 12	5.1	4.9	5.0	5.7	20.7	5.2
4	7.5	464	624	624	364	2076	519	6.8	7.2	7.1	6.9	28.0	7.0
	15	384	504	179	484	1551	388	5.4	5.4	5.4	5.5	21.5	5.4
	30	284	- 6	164	214	656	164	5.2	5.6	5.7	5.1	21.6	5.4
	60	-36	-101	-176	-281	-594	-149	4.9	5.2	5.8	5.0	20.9	5.2

Table XL. Eh and pH of the Mexico soil at various depths on June 7, 1974.

Treatment	Depth	Eh						pH*					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	184	424	334	434	1376	344	7.2	6.8	6.95	7.5	28.5	7.1
	15	404	- 56	4	- 96	256	64						
	30	144	134	-161	94	211	53						
	60	-146	-181	-146	- 76	-549	-137						
2	7.5	689	374	84	374	1521	380	5.85	6.4	7.6	6.15	26.1	6.5
	15	184	189	114	289	776	194						
	30	-121	4	4	- 6	-119	- 30						
	60	-106	- 26	44	- 86	-174	- 44						
3	7.5	444	734	354	354	1886	472	7.3	7.7	7.7	7.15	29.9	7.5
	15	204	204	49	214	671	168						
	30	184	-146	- 86	- 86	-134	- 34						
	60	24	204	-161	164	231	58						
4	7.5	524	- 86	554	414	1406	352	6.0	7.1	7.4	6.6	27.1	6.8
	15	314	234	254	324	1126	282						
	30	184	74	214	274	746	187						
	60	-146	-126	-206	-301	-779	-195						

*Because the soil was saturated with water, it was not practical to take all the pH measurements.

Table XLI. Eh and pH of the Mexico soil at various depths on June 14, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	684	634	524	624	2466	617	6.7	6.2	6.1	5.0	24.0	6.0
	15	439	594	144	424	1601	400	5.1	6.2	5.8	5.4	22.5	5.6
	30	289	594	164	269	1316	329	5.2	6.1	5.7	4.7	21.7	5.4
	60	-156	-156	-126	14	-424	-106	5.4	5.7	5.9	4.6	21.6	5.4
2	7.5	654	674	604	524	2456	614	5.1	5.7	6.2	4.8	21.8	5.5
	15	634	664	534	494	2326	582	5.8	6.1	6.4	4.2	22.5	5.6
	30	- 26	324	344	76	718	180	5.8	5.9	6.3	4.1	22.1	5.5
	60	- 66	- 16	-176	44	-214	- 54	5.8	5.8	6.1	3.8	21.5	5.4
3	7.5	654	594	624	534	2406	602	6.4	6.1	5.7	4.4	22.6	5.7
	15	604	484	524	594	2206	552	5.6	5.9	5.8	4.6	21.9	5.5
	30	504	454	394	314	1666	417	5.4	5.9	5.8	4.5	21.6	5.4
	60	-126	4	-146	64	-204	-51	5.4	5.6	5.6	4.3	20.9	5.2
4	7.5	614	534	694	674	2516	629	5.5	5.5	4.9	5.3	21.2	5.3
	15	594	474	444	584	2096	524	5.9	6.0	5.4	5.2	22.5	5.6
	30	274	334	394	364	1366	342	5.8	5.9	5.0	5.1	21.8	5.5
	60	-126	34	-156	-286	-534	-134	5.6	5.5	4.9	4.9	20.9	5.2

Table XLII. Eh and pH of the Mexico soil at various depths on July 1, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	764	674	624	694	2756	689	6.2	4.3	4.8	4.8	20.1	5.0
	15	464	624	204	594	1889	472	7.1	6.1	6.4	6.8	26.4	6.6
	30	304	684	404	469	1861	465	7.2	6.5	6.3	6.7	26.7	6.7
	60	254	359	484	359	1456	364	6.9	6.4	6.5	6.6	26.4	6.6
2	7.5	664	724	664	444	2466	617	5.5	5.4	5.7	5.9	22.5	5.6
	15	624	724	634	534	2516	629	6.5	6.8	6.5	6.2	26.0	6.5
	30	324	274	589	164	1351	338	6.2	6.4	6.5	5.8	24.9	6.2
	60	-116	-56	-176	-106	-454	-114	6.0	6.0	6.0	6.4	24.4	6.1
3	7.5	644	404	564	474	2086	522	4.7	4.4	5.3	4.1	18.5	4.6
	15	399	389	594	474	1856	464	6.8	5.9	5.1	6.5	24.3	6.1
	30	364	164	574	394	1496	374	6.7	6.0	4.5	6.6	23.8	6.0
	60	104	239	254	244	841	210	6.6	6.1	5.4	6.5	24.6	6.2
4	7.5	684	574	724	579	2561	640	5.5	5.2	4.4	5.4	20.5	5.1
	15	694	614	564	514	2386	597	6.1	6.3	6.5	6.4	25.3	6.3
	30	494	294	394	309	1491	373	5.6	6.0	6.0	6.2	23.8	6.0
	60	84	374	-121	259	596	149	5.4	6.1	5.8	6.2	23.5	5.9

Table XLIII. Eh and pH of the Mexico soil at various depths on July 8, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	804	954	824	804	3386	847	5.6	6.0	5.4	7.0	24.0	6.0
	15	544	1004	284	564	2396	599	6.4	6.4	7.5	6.9	27.2	6.8
	30	364	994	664	494	2516	629	6.1	6.4	7.7	6.7	26.9	6.7
	60	299	474	624	324	1721	430	6.1	6.4	7.7	6.8	27.0	6.8
2	7.5	934	899	714	564	3111	778	5.8	5.5	5.5	5.7	22.5	5.6
	15	554	724	594	694	2566	642	6.8	6.3	7.0	7.1	27.2	6.8
	30	364	634	254	444	1696	424	6.6	7.2	6.8	7.2	27.8	7.0
	60	74	24	94	64	256	64	6.2	7.5	6.4	7.2	27.3	6.8
3	7.5	764	674	804	414	2656	664	5.9	6.0	5.8	5.7	23.4	5.9
	15	704	854	574	544	2676	669	7.4	7.0	6.9	6.6	27.9	7.0
	30	614	120	564	524	1822	456	6.5	7.3	6.3	6.3	26.4	6.6
	60	-116	724	-86	304	826	207	6.2	6.9	6.2	6.4	25.7	6.4
4	7.5	744	844	864	464	2916	729	5.5	5.6	6.1	6.9	24.1	6.0
	15	634	774	704	604	2716	679	6.8	6.8	6.9	7.3	27.8	7.0
	30	624	479	389	364	1856	464	6.9	7.0	7.0	6.9	27.8	7.0
	60	-206	519	-76	314	551	138	6.8	6.7	6.9	6.8	27.2	6.8

Table XLIV. Eh and pH of the Mexico soil at various depths on July 15, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	74	514	544	629	1761	440	7.3	5.3	5.3	5.9	23.8	6.0
	15	464	554	74	554	1646	412	7.5	6.9	7.3	6.8	28.5	7.1
	30	274	594	164	389	1421	355	6.8	6.5	7.3	6.4	27.0	6.8
	60	324	204	524	144	1196	299	7.0	6.4	7.1	6.9	27.4	6.9
2	7.5	669	609	489	504	2271	568	6.4	5.8	6.7	5.0	23.9	6.0
	15	519	639	414	584	2156	539	7.0	6.7	7.8	7.2	28.7	7.2
	30	334	449	554	399	1736	434	6.6	6.4	7.9	6.4	27.3	6.8
	60	64	-86	14	-246	-254	-64	6.8	7.0	7.6	6.5	27.9	7.0
3	7.5	654	664	424	364	2106	527	6.0	4.8	5.0	6.3	22.1	5.5
	15	614	624	589	464	2291	573	6.2	6.9	7.3	7.1	27.5	6.9
	30	754	84	554	264	1656	414	6.2	6.5	7.0	7.3	27.0	6.8
	60	384	554	384	414	1736	434	6.3	6.5	7.0	7.3	27.1	6.8
4	7.5	764	524	724	- 16	1996	499	5.4	4.8	5.8	6.5	22.5	5.6
	15	804	574	674	344	2396	599	6.5	6.8	7.2	7.8	28.3	7.1
	30	464	234	294	384	1376	344	6.4	6.6	7.0	6.8	26.8	6.7
	60	34	444	14	404	896	224	6.4	6.7	6.9	6.5	26.5	6.6

Table XLV. Eh and pH of the Mexico soil at various depths on July 22, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	736	704	594	739	2773	693	6.2	5.2	4.8	6.3	22.5	5.6
	15	434	704	234	674	2046	512	7.0	6.5	7.0	7.3	27.8	7.0
	30	284	654	564	509	2011	502	6.3	6.4	6.4	6.8	25.9	6.5
	60	274	- 86	594	-126	656	164	6.3	6.6	6.6	6.9	26.4	6.6
2	7.5	789	654	659	449	2551	638	5.9	5.4	6.8	6.1	24.2	6.1
	15	624	624	539	544	2391	598	6.8	6.8	7.8	7.4	28.8	7.2
	30	379	534	534	524	1971	493	6.7	6.7	6.9	7.2	27.5	6.9
	60	224	-116	- 96	-176	-164	-41	6.5	6.8	6.9	7.1	27.2	6.8
3	7.5	604	514	384	564	2066	517	6.4	7.2	6.3	6.8	26.7	6.7
	15	489	504	574	569	2136	534	7.1	7.2	7.4	7.3	29.0	7.3
	30	614	244	549	439	1846	462	7.0	6.7	7.0	7.0	27.7	6.9
	60	589	494	684	734	2501	625	6.5	6.9	6.9	7.1	27.4	6.9
4	7.5	674	554	824	414	2466	617	6.0	5.9	5.9	6.2	24.0	6.0
	15	684	639	684	644	2651	663	6.4	6.7	7.2	7.4	27.7	6.9
	30	159	534	204	424	1321	330	6.5	6.7	7.2	7.1	27.5	6.9
	60	204	634	254	409	1501	375	6.6	6.3	7.0	7.2	27.1	6.8

Table XLVI. Eh and pH of the Mexico soil at various depths on July 29, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	664	674	564	599	2501	625	6.2	5.5	5.9	6.1	23.7	5.9
	15	439	614	194	564	1811	452	6.8	6.7	6.8	6.6	26.9	6.7
	30	299	605	594	484	1982	496	6.5	6.2	6.4	6.3	25.4	6.4
	60	339	-86	634	-126	761	190	6.4	6.5	6.0	6.2	25.1	6.3
2	7.5	624	634	634	644	2536	634	5.8	6.8	6.4	6.0	25.0	6.3
	15	524	724	569	604	2321	580	6.5	6.4	7.1	6.5	26.5	6.6
	30	379	574	464	584	2001	500	6.4	6.7	5.7	5.8	25.6	6.4
	60	234	364	54	- 46	606	152	6.7	6.8	5.7	5.7	24.9	6.2
3	7.5	554	343	484	384	1856	464	5.8	6.0	6.0	6.0	23.8	6.0
	15	364	484	404	394	1646	412	5.6	6.3	6.5	6.7	25.1	6.3
	30	614	444	364	444	1866	467	5.7	6.2	6.4	6.4	24.7	6.2
	60	594	464	554	74	1686	422	5.8	5.9	6.3	6.3	24.3	6.1
4	7.5	564	514	554	474	2106	527	5.7	5.3	6.0	5.8	22.8	5.7
	15	524	494	404	509	1931	483	5.6	5.4	5.9	6.1	23.0	5.8
	30	624	184	634	484	1926	482	5.8	6.4	6.4	6.2	24.8	6.2
	60	549	584	474	544	2151	538	6.0	5.2	6.0	6.4	23.6	5.9

Table XLVII. Eh and pH of the Mexico soil at various depths on August 5, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	cm	mV											
1	7.5	614	599	424	394	2031	508	6.4	6.6	6.3	6.7	25.5	6.4
	15	389	589	574	554	2106	527	6.3	6.5	5.9	5.0	22.7	5.9
	30	274	574	554	419	1821	455	5.9	6.8	5.8	6.0	24.5	6.1
	60	314	64	104	174	656	164	6.4	6.9	6.6	6.3	26.2	6.55
2	7.5	489	754	554	409	2206	552	6.8	6.6	6.3	6.3	26.0	6.5
	15	504	714	564	524	2346	587	6.4	6.1	7.0	6.4	25.9	6.5
	30	294	744	404	534	2540	635	5.6	6.1	6.6	6.3	24.6	6.2
	60	-166	-236	- 6	24	-384	-96	6.2	6.1	6.2	6.2	24.7	6.2
3	7.5	499	599	559	509	2166	542	6.2	6.0	6.2	5.8	24.2	6.1
	15	619	519	559	614	2311	578	6.3	6.2	6.2	6.4	25.1	6.3
	30	404	604	584	554	2146	537	6.4	6.2	6.2	6.3	25.1	6.3
	60	519	489	479	509	1996	499	6.5	6.3	6.2	6.0	25.0	6.3
4	7.5	619	614	609	604	2446	612	6.5	6.4	7.0	5.9	25.8	6.5
	15	614	524	654	559	2351	588	6.3	6.3	5.9	5.7	24.2	6.1
	30	824	314	359	424	1921	480	6.2	6.4	5.8	6.0	24.4	6.1
	60	619	559	504	519	2201	550	6.4	6.7	6.3	6.0	25.4	6.4

Table XLVIII. Eh and pH of the Mexico soil at various depths on August 12, 1974.

Treatment	Depth	Eh						pH*					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	884	679	834	564	2961	740	6.9	6.4	6.5	6.8	26.6	6.7
	15	529	594	174	804	2101	525	7.1	6.6	6.3	5.6	25.6	6.4
	30	344	659	784	594	2381	595	7.2	6.5	6.4	5.8	25.9	6.5
	60	-126	264	-186	-26	- 74	- 19	7.0	6.4	6.3	6.5	26.2	6.6
2	7.5	834	624	814	424	2696	674	7.0	6.6	6.7	6.3	26.6	6.7
	15	779	724	649	699	2851	713	6.9	6.5	6.7	7.3	26.5	6.6
	30	354	854	644	649	2501	625	6.6	6.1	6.7	6.7	26.1	6.5
	60	-106	-86	-256	-36	-484	-121	6.4	6.1	6.3	6.3	25.1	6.3
3	7.5	454	574	519	539	2086	522	7.0	6.5	6.8	6.0	26.3	6.6
	15	424	549	484	509	1966	492	6.7	6.7	6.1	6.0	25.5	6.4
	30	514	494	439	494	1941	485	6.7	-	6.1	6.4	19.2	6.4
	60	599	524	604	574	2301	575	7.0	-	6.3	6.2	19.5	6.5
4	7.5	604	494	654	514	2266	567	6.8	6.8	6.2	6.3	26.1	6.5
	15	664	484	554	619	2316	579	6.3	6.2	6.3	7.0	25.8	6.5
	30	334	244	319	409	1306	327	6.4	6.3	-	6.6	19.3	6.4
	60	309	554	774	529	2166	542	6.4	6.2	-	6.7	19.3	6.4

*The soil was too dry to take all pH measurements.

Table XLIX. Eh and pH of the Mexico soil at various depths on August 19, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	759	544	564	624	2491	623	5.4	5.8	5.7	5.5	22.4	5.6
	15	634	494	674	664	2466	617	5.6	6.4	6.1	4.6	22.7	5.7
	30	199	594	204	684	1681	420	5.3	5.4	6.2	4.2	21.1	5.3
	60	-111	-141	-171	-126	-549	-137	5.7	4.4	6.4	4.7	21.2	5.3
2	7.5	494	569	624	504	2191	548	4.8	5.1	5.9	5.6	22.4	5.6
	15	444	604	629	659	2336	584	5.6	6.4	6.5	6.2	24.7	6.2
	30	424	634	374	354	1786	447	5.4	6.0	5.2	5.3	21.9	5.5
	60	- 51	- 36	-156	-146	-389	- 97	5.8	5.9	5.7	4.6	22.0	5.5
3	7.5	614	404	1014	579	2611	653	4.2	5.9	5.1	5.1	20.3	5.1
	15	674	574	854	464	2566	642	4.2	5.5	5.1	5.2	20.0	5.0
	30	564	534	854	484	2436	609	4.7	6.9	5.4	5.6	22.6	5.7
	60	529	454	919	664	2566	642	4.9	5.3	5.3	4.4	19.9	5.0
4	7.5	1014	1014	1014	1014	4056	1014	5.1	6.5	5.7	5.8	23.1	5.8
	15	1014	1014	1014	994	4036	1009	5.0	6.2	6.0	5.5	22.7	5.7
	30	734	994	764	834	3326	832	5.4	6.2	5.7	5.6	22.9	5.7
	60	724	504	964	759	2951	738	5.6	6.0	5.7	5.8	23.1	5.8

Table L. Eh and pH of the Mexico soil at various depths on August 26, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	654	604	774	684	2716	679	6.6	5.7	6.1	5.9	24.3	6.1
	15	624	584	134	494	1836	459	6.6	5.8	6.8	5.9	25.1	6.3
	30	464	559	734	514	2271	568	6.7	5.8	6.7	6.1	25.3	6.3
	60	-196	4	- 36	-156	-384	-96	6.9	5.8	6.7	6.0	25.4	6.4
2	7.5	634	599	624	614	2471	618	6.1	6.4	6.3	6.1	24.9	6.2
	15	374	609	619	589	2191	548	6.5	6.8	6.4	6.3	26.0	6.5
	30	294	514	389	414	1611	403	6.3	6.6	6.4	6.3	25.6	6.4
	60	14	-46	-166	- 81	-279	-70	6.2	6.4	6.2	6.2	25.0	6.3
3	7.5	734	844	999	764	3341	835	4.8	6.3	5.8	6.1	23.0	5.8
	15	1014	959	894	1014	3881	970	4.9	5.9	5.9	6.5	22.2	5.6
	30	894	869	764	754	3281	820	4.9	5.3	5.7	6.5	22.4	5.6
	60	884	874	734	814	3406	852	4.9	6.0	5.9	6.3	23.1	5.8
4	7.5	1014	1014	954	964	3946	987	5.5	6.0	5.7	6.2	23.4	5.9
	15	984	994	969	974	3921	980	5.7	6.6	5.9	6.3	24.5	6.1
	30	784	794	814	799	3191	798	5.7	6.5	6.0	6.2	24.4	6.1
	60	514	619	769	924	2826	707	5.9	6.4	6.2	6.1	24.6	6.2

Table LI. Eh and pH of the Mexico soil at various depths on September 4, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	719	814	634	714	2881	720	6.5	6.1	6.5	6.1	25.2	6.3
	15	359	734	114	844	2051	513	6.8	6.3	5.6	6.1	24.8	6.2
	30	99	-126	-196	224	1	1	6.9	5.4	5.6	6.4	24.3	6.1
	60	-226	-236	-206	-166	-834	-209	7.2	5.2	6.5	6.0	24.9	6.2
2	7.5	434	964	584	664	2646	662	6.2	6.7	5.9	6.2	25.0	6.3
	15	504	654	764	804	2726	682	6.7	6.5	6.0	6.3	25.5	6.4
	30	154	-196	-286	284	- 44	- 11	6.5	5.6	6.5	5.6	24.2	6.1
	60	-146	-186	-236	-106	-674	-169	6.4	5.8	6.1	5.9	24.2	6.1
3	7.5	554	544	864	534	2496	624	5.6	6.0	5.7	5.3	22.6	5.7
	15	414	784	994	584	2776	694	5.5	6.4	5.8	5.5	23.2	5.8
	30	294	170	-256	4	212	53	6.1	6.3	5.6	5.7	23.7	5.9
	60	-216	80	-226	264	- 98	- 25	5.7	6.5	5.8	5.9	23.9	6.0
4	7.5	574	644	909	764	2892	723	5.8	5.7	6.2	6.1	23.8	6.0
	15	594	704	1004	684	2986	747	5.9	6.3	5.9	5.8	23.9	6.0
	30	624	4	-286	204	546	137	5.7	6.0	6.0	6.1	23.9	6.0
	60	74	170	- 36	- 36	172	43	6.4	6.2	5.9	6.0	24.5	6.1

Table LII. Eh and pH of the Mexico soil at various depth on September 10, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	664	734	754	594	2746	687	6.0	5.5	6.0	6.1	23.6	5.9
	15	589	534	804	654	2581	645	6.2	6.5	6.4	6.3	25.4	6.4
	30	289	694	94	654	1731	433	5.7	5.6	6.1	5.4	22.8	5.7
	60	-166	-196	24	- 96	-434	-109	5.2	5.6	6.1	5.2	22.1	5.5
2	7.5	604	764	514	484	2366	592	6.1	5.2	6.1	5.7	23.1	5.8
	15	524	724	774	659	2681	670	6.3	6.3	6.5	6.5	25.6	6.4
	30	384	864	4	564	1816	454	5.7	5.6	6.0	5.6	22.9	5.7
	60	-146	- 76	-231	-146	-599	-150	5.8	5.9	5.9	5.8	23.4	5.9
3	7.5	704	484	684	474	2346	587	5.9	6.0	6.1	6.1	24.1	6.0
	15	714	564	574	484	2336	584	6.0	6.3	6.2	6.4	24.9	6.2
	30	764	664	564	454	2446	612	5.7	5.7	5.9	6.2	23.5	5.9
	60	- 66	224	-116	144	186	47	5.8	6.0	5.9	5.8	23.5	5.9
4	7.5	884	744	829	594	3051	763	6.1	5.5	5.6	5.7	22.9	5.7
	15	964	534	864	674	3036	759	6.0	6.4	6.3	6.5	25.2	6.3
	30	854	354	474	474	2156	539	5.7	5.8	5.6	5.8	22.9	5.7
	60	154	39	- 6	319	506	127	5.9	5.7	5.5	5.3	22.4	5.6

Table LIII. Eh and pH of the Mexico soil at various depths on September 17, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	694	674	484	794	2646	662	6.6	5.9	5.8	4.6	23.9	6.0
	15	594	654	594	654	2496	624	6.7	6.0	6.1	4.8	23.6	5.9
	30	74	664	684	604	2026	507	6.5	6.0	5.6	4.7	22.8	5.7
	60	-26	269	184	279	706	177	6.3	5.8	5.6	4.2	21.9	5.5
2	7.5	524	654	634	514	2326	582	6.2	6.6	5.0	6.9	24.7	6.2
	15	514	649	614	614	2391	598	5.8	6.3	5.8	7.0	24.9	6.2
	30	404	664	124	634	1826	457	5.7	6.0	6.1	6.5	24.3	6.1
	60	184	-91	-196	-81	-184	-46	5.8	5.9	5.2	6.2	23.1	5.8
3	7.5	504	599	664	574	2341	585	6.0	5.5	6.0	6.4	23.9	6.0
	15	514	574	514	304	1916	479	5.8	5.5	6.6	7.0	24.9	6.3
	30	664	574	504	384	2126	531	5.5	5.7	6.0	6.3	23.5	5.9
	60	564	444	334	364	1706	427	5.4	5.9	5.9	6.4	23.6	5.9
4	7.5	614	504	574	704	2396	599	5.1	6.2	5.9	5.5	22.7	5.7
	15	714	464	484	664	2326	582	5.4	6.4	5.6	5.7	23.1	5.8
	30	664	364	264	544	1836	459	5.3	6.2	5.6	5.7	22.8	5.7
	60	394	474	664	444	1976	494	5.6	6.2	5.6	5.4	22.8	5.7

Table LIV. Eh and pH of the Mexico soil at various depths on September 24, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	654	704	559	634	2551	638	6.4	6.5	6.9	6.7	26.5	6.6
	15	424	694	214	654	1986	497	6.3	6.9	6.7	6.3	26.2	6.6
	30	384	679	54	684	1801	450	6.1	6.7	6.6	6.3	25.7	6.4
	60	574	364	714	444	2096	524	6.1	6.1	6.4	6.4	25.0	6.3
2	7.5	564	659	664	524	2411	603	6.2	5.1	6.9	6.4	24.6	6.2
	15	539	659	644	609	2531	633	6.1	6.7	6.6	6.5	25.9	6.5
	30	514	754	664	574	2506	627	6.6	6.7	6.7	6.5	26.5	6.6
	60	354	-46	164	364	836	209	6.7	6.5	6.6	6.4	26.2	6.6
3	7.5	454	514	664	639	2271	568	6.7	6.6	6.5	6.6	26.3	6.6
	15	489	624	584	539	2236	559	6.4	6.6	6.0	6.7	25.2	6.3
	30	634	579	674	489	2376	594	6.3	6.7	6.1	6.1	25.2	6.3
	60	614	494	704	394	2206	552	6.4	6.6	6.1	6.3	25.4	6.4
4	7.5	654	549	694	719	2607	652	6.2	6.0	6.5	6.5	25.2	6.3
	15	779	624	564	699	2666	667	6.2	6.2	6.7	7.0	26.1	6.5
	30	704	394	304	549	1951	488	6.2	6.2	6.7	6.4	25.5	6.4
	60	584	574	779	474	2411	603	6.0	6.0	6.5	6.5	25.0	6.3

Table LV. Eh and pH of the Mexico soil at various depths on September 30, 1974.

Treatment	Depth	Eh						pH					
		R1	R2	R3	R4	Total	Mean	R1	R2	R3	R4	Total	Mean
	— cm —	mV											
1	7.5	644	679	584	624	2531	633	6.3	6.1	6.6	6.5	25.5	6.4
	15	404	714	594	634	2346	587	5.2	6.5	6.8	6.5	25.0	6.2
	30	394	419	194	684	1691	423	5.1	6.4	6.9	6.4	24.8	6.2
	60	299	174	664	239	1376	344	5.8	6.0	6.9	6.4	25.1	6.3
2	7.5	569	649	599	494	2311	578	6.1	5.3	6.1	5.4	22.9	5.7
	15	614	719	694	604	2631	658	6.5	6.0	7.0	5.8	25.3	6.3
	30	469	704	489	664	2326	528	5.7	5.9	6.7	5.8	24.1	6.0
	60	239	-66	-86	-26	61	15	5.9	5.6	5.8	5.6	21.9	5.7
3	7.5	559	654	694	714	2621	655	6.2	5.0	6.3	5.5	23.0	5.8
	15	624	684	564	594	2466	617	6.0	5.9	6.6	6.7	25.2	6.3
	30	714	624	614	479	2431	608	6.0	5.4	6.7	6.3	24.4	6.1
	60	634	494	694	399	2221	555	6.2	5.0	6.7	5.8	23.7	5.9
4	7.5	694	514	609	749	2566	642	6.0	5.0	6.1	6.5	23.6	5.9
	15	764	634	634	699	2731	683	6.5	6.0	6.4	6.3	25.2	6.3
	30	689	394	554	549	2566	642	6.2	5.7	5.9	6.7	24.5	6.1
	60	479	634	714	484	2311	578	6.1	5.9	5.9	6.5	24.4	6.1

Table LVI. Concentration of various elements from composite samples of Reeds canary grass harvested in 1974.

Treatment	Al					Ca				
	µg/g plant tissue									
1	390	357	217	353		5550	5290	6000	5740	
	385	357	217	360		5550	5290	6000	5740	
Total	775	714	434	713	2636	11100	10580	12000	11480	44960
Mean	387	357	217	357	330	5550	5290	6000	5740	5620
2	398	372	313	324		5100	6190	7540	7750	
	410	372	310	324		5420	6190	6450	6880	
Total	808	744	623	648	2823	10520	12380	14090	14630	51620
Mean	404	372	312	324	353	5160	6190	7045	7315	6453
3	625	600	416	324		4880	5420	5870	5550	
	626	605	416	324		5160	5610	5880	5360	
Total	1251	1205	832	648	3936	10040	11030	11750	10910	43730
Mean	626	603	416	324	492	5020	5515	5875	5455	5466
4	217	44	560	372		4520	4520	5810	4600	
	228	236	545	371		4580	4520	5480	4650	
Total	445	280	1105	743	1829	9100	9040	11290	9250	38680
Mean	223	140	553	372	229	4550	4520	5645	4625	4835

Table LVI. (continued)

Treatment			Fe					Mn					Pb		
	µg/g plant tissue										ng/g plant tissue				
1	1227	711	703	711		120	108	101	153		437	192	269	274	
	1227	711	703	711		127	108	101	148		437	192	245	303	
Total	2454	1422	1406	1422	6701	247	216	202	301	966	874	384	514	577	2349
Mean	1227	711	703	711	837	124	108	101	151	121	437	192	257	289	294
2	1196	805	766	635		171	155	106	104		245	192	240	202	
	1196	852	768	683		167	164	101	104		221	192	187	202	
Total	2392	1657	1534	1418	7001	338	319	207	208	1072	466	384	427	404	1681
Mean	1196	829	764	709	875	169	160	104	104	134	233	192	214	202	210
3	1712	649	735	414		197	174	154	124		307	163	264	255	
	1677	610	735	414		198	177	154	124		240	163	192	144	
Total	3389	1259	1470	828	6946	395	351	308	248	1302	547	326	456	399	1728
Mean	1695	630	735	414	868	198	176	154	124	163	274	163	228	200	216
4	969	719	1516	833		155	203	164	140		192	192	168	245	
	1001	719	1516	794		155	203	160	140		183	192	168	226	
Total	1970	1438	3032	1627	8067	310	406	324	280	1320	375	384	336	471	1566
Mean	985	719	1516	814	1008	155	203	162	140	165	188	192	168	236	196

TRAINING ACCOMPLISHED

Ronald E. Hess has done the research contained in this report as the research requirement for his Ph.D. degree. He has developed an understanding of the relationship between arsenic chemistry and water quality that he will put to use in his current position.

Kenneth Koelkebeck, a senior in the College of Agriculture, worked diligently on the project. He will continue to work in this laboratory on a water quality problem concerned with fragipan stability under sewage effluent irrigation.

William Brook a junior in the College of Agriculture has worked on various aspects of this project.