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ELMER R. KIEHL, DIRECTOR

Arsenic Determination and Arsenic, Lead and Copper Content of Missouri Soils

R.E. HESS AND R.W. BLANCHAR

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R.E. Hess and R.W. Blanchar

ABSTRACT

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. 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 solubilizing the As from plant and soil samples.

Arsenic, lead, and copper levels were determined in soils from several orchards and former potato fields in Missouri 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.

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 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 canary grass was harvested six 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

Compounds of arsenic have been applied to many soils in the past as desiccants, as insecticides, as herbicides in cotton, orchards, silviculture, and as soil sterilants. It has been assumed that the added arsenics have been hydrolyzed, oxidized, and finally precipitated as aluminum, calcium or iron orthoarsenates. Recent studies have shown that many soils in the United States contain in excess of 50 ppm As. In Missouri large amounts of lead arsenate were used to control pests in apple and peach orchards. Few problems had been encountered until these soils were used for different purposes. New land use practices which alter the chemical environment of the soil can potentially dissolve hitherto harmless arsenates to toxic levels.

As an example, systems to dispose of sewage effluent and animal lagoon effluent as irrigation water are being developed; some may be on former orchard soils contaminated with arsenic. The degree to which additions of effluent to soils alters the oxidation-reduction status and pH of the system can be controlled by amounts and frequency of application. It is known that in soil contaminated with arsenic, a period of anerobic conditions in the soil increases the solubility and phytotoxicity of arsenic. The potential to dissolve toxic levels of arsenic and to threaten the success of these soil-sewage system exists.

Specifically, our objectives are as follows:

1. To develop criteria for sampling soils which have been contaminated with arsenic.
2. To provide a reliable method for analyzing soils and plants for arsenic.
3. To determine the approximate levels of arsenic, lead, and copper in soils which had a long history of arsenic application.
4. To predict the impact of changed soil chemical environment on the solubility and possible toxicity of these arsenates.

ARSENIC LEVELS IN SOILS AND PLANTS

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, 9, 11, 22, 25, 32, 55) which surveyed soils for total As content have been summarized by Woolsen, Axley, and Kearney (59). 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 (3 1) reported levels of 30.3 ao 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 (49), and several reports confirmed that the natural level of Pb in soils ranged from 5-25 ppm Pb (8, 15, 17, 24, 34, 36, 38, 49, 60). 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 (28). Other reports confirm this as the natural level of Cu in soils (3, 14, 38, 60).

ANALYTIC PROCEDURE FOR ARSENIC IN SOIL

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 developed in 1879 where the arsine is evolved in a hydrogen gas stream by the action of HCl on Zn (35).

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 (59). Polargraphic methods have 1 μg sensitivity, but only 75± 4% of the original As was recovered (5, 37). Using a deuterium arc or an air-acetylene flame, as little as 0.8 μg/ml As has been determined (7), and using nitrogen entrained air-hydrogen flames, As has been determined to 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. By 1901 (10) investigators were using dry paper impregnated with mercuric chloride to absorb the arsine. The test was made more quantitative in 1907 (45) 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 (29) 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 (12, 43, 51, 53). 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 (12, 33, 59), in which As replaces an equivalent amount of Ag from the AgDDC (6). 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 (33).

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 g As sample, have been developed (18, 23, 57). 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 (6, 46, 50). Schmidt and Royer (46) 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

(39). The purpose of part of this research was to verify the accuracy of current colorimetric methods being used for arsenic determinations.

It has been shown that 1 ppm soluble As caused injury to cowpeas (1), 2 ppm As to barley (54), 7 ppm As for rice (6), 9 ppm As for peas, beans, and barley (11), and 4.4 and 1.0 ppm As for soybeans and cotton (19). 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 (44).

Jones and Hatch (30) 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 (40). Only 39-67% of the As added to soils as monosodium methanearsonate was reported recovered (27). 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 (58). Soil As levels higher than 69.5 ppm As have been found to significantly reduce the growth of lowbush blueberry (4). Another purpose for this research was to estimate the impact of changes in Eh and pH on As uptake by Canary Grass under field conditions in Missouri.

PROCEDURE

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. The county from which the samples were taken is indicated in Table 7. The samples were taken from each site, and each sample was run in duplicate.

Sample Decomposition

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 700 cc Coors evaporating dish. Ten ml of a thoroughly mixed magnesium oxide-magnesium nitrate slurry were 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° overnight, transferred to a muffle furnace, 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

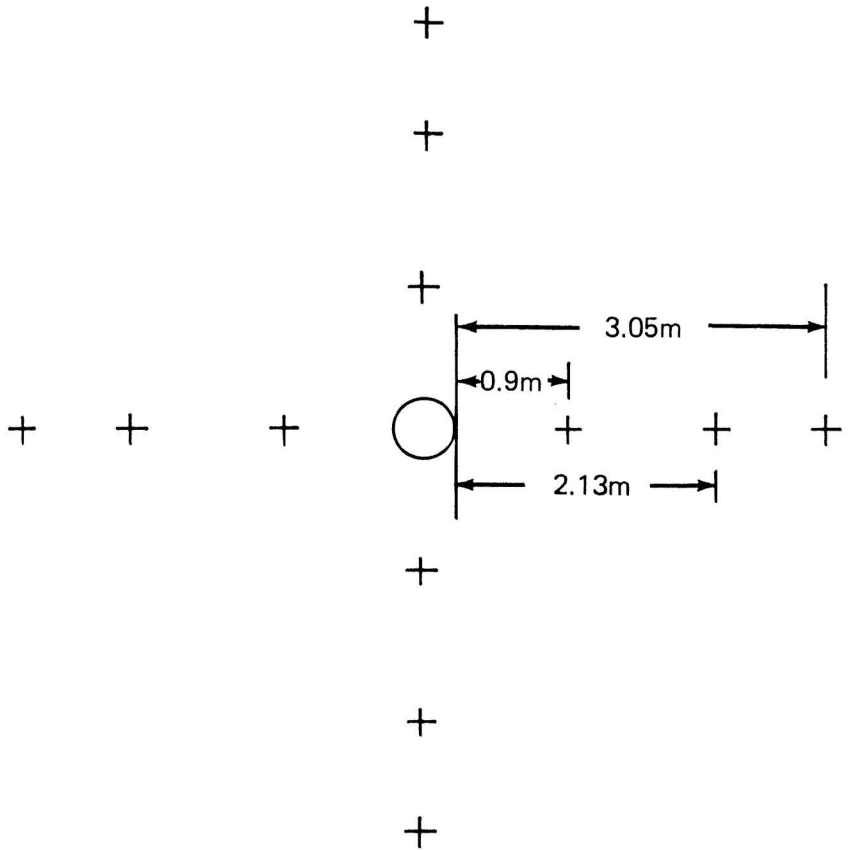

Figure 1. Sampling positions used for obtaining a composite sample around orchard trees.

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 (12) 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, 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 as Arsine

Collection in Iodine: An amount of solution containing less than 120 μg As was placed in the 125 ml evolution flask. 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 of 30 mesh Zn (0.00001% As) were added and the evolution flask immediately connected to a collection vessel containing 4 ml iodine solution. The reaction was allowed to proceed for at least two hours. 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. When the arsine evolution was completed, 1 ml of the single solution used for the determination of phosphate was added (42). 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 hours after adding the single solution light absorbance was measured at a wavelength of 840 nm.

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 soldium 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 desiccator. The pyridine solution of AgDDC was prepared by dissolving 1.0 g of AgDDC in a 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.

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

Eh, pH, and Arsenic Measurements in a Mexico Soil

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 20 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.

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

The electrode (Figure 2) 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

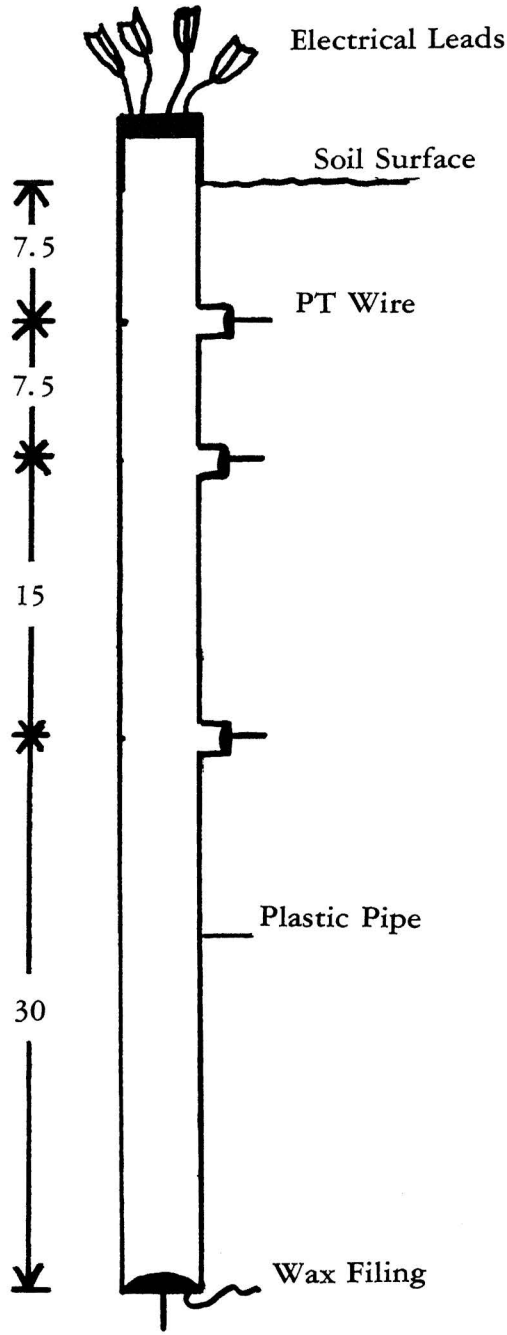

Figure 2. The electrode used to measure the oxidation-reduction potential.

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 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.

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

Comparison of Sample Decomposition Techniques

Sodium arsenate standards were prepared and carried through both decomposition procedures. The results of digesting standards by wet digestion and dry ashing are listed in Table 1. The percent recovery was calculated by summing the absorbance values of the non-digested standards and dividing the result into the sum of the absorbance minus blank values of the wet oxidation or those from the dry ashing shown in Table 1. The

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

Amount of As	Standards	Ashed			
		Wet		Dry	
μg	Absorbance				
			% Recovery		% Recovery
0	0.000	0.006		0.011	
0.067	0.006	0.010	67	0.020	150
0.250	0.023	0.024	78	0.028	83
0.500	0.049	0.047	84	0.045	69
1.000	0.098	0.095	91	0.090	81
2.000	0.198	0.205	101	0.185	88
4.000	0.405	0.395	96	0.345	82
8.000	0.815	0.795	97	0.710	86
Σ	1.594	1.529	96	1.346	84

percent recovery of the wet oxidation is 96% and of the dry ashing 84%. 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 was 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. 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 digestion procedure appears superior as an agent for solubizing the arsenic from solid samples.

Table 2. Comparison of arsenic concentration in Menfro soil and Reed 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.

Comparison of silver diethyldithiolcarbamate with iodine as arsine absorbing agents

Standards additions of 0, 1, 2, 4, and 8 μg As were placed in 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 3. Absorption of arsine into 4 ml of 0.004 M iodine solution results in a more sensitive method than absorption into either the pyridine or the chloroform solutions. For this reason, and because of the strong odor of both the pyridine and the chloroform, it was

Table 3. 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.

decided to use the iodine solution as the absorbing solution throughout this study.

Standards were prepared from a stock solution made by dissolving sodium arsenate in water. The reason for using sodium arsenate as the standard was because the reaction of arsine with iodine in water is (57)

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

which gives arsenate as a product. Standard curves run at several dates are presented 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 laboratory conditions, positioning of the absorbance cell, and other variables which could not be absolutely controlled. To account for these variations, standards were included at the beginning and end of each batch of samples to be run.

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 (13, 42, 46, 57). 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, 4g 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 was added and 15 ml of concentrated HCl diluted to 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 4.

In the temperature studies only the initial temperature was controlled and as it decreased, the percent As recovered increased. Increasing the concentration of alcohol

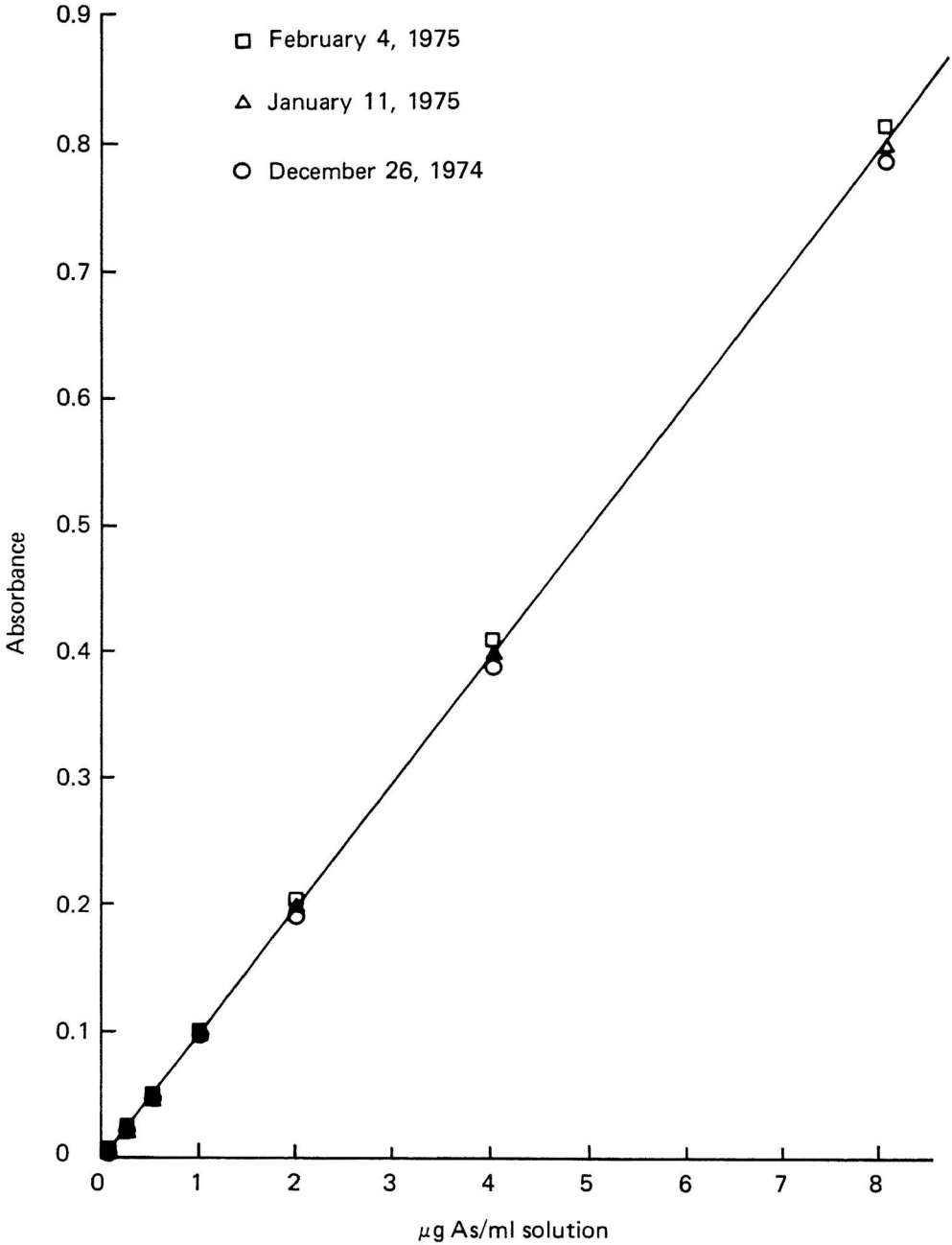

Figure 3. Relationship between arsenic concentration in solution and absorbance at a wavelength of 840 mm determined after developing the blue molybdenum-arsenic complex.

Table 4. 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

*No alcohol added and 2.4N HCl at all temperatures.
**Temperature was 25°C and 2.4N HCl at all alcohol levels.
***No alcohol added and temperature of 25°C.

increased the percent. As recovered to a point, and then it 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 more quantitative 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 and increasing As recovery.

Reaction vessels. Various reaction vessels were examined in the evolution of arsine to learn which would give the best recovery of the evolved arsine. 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 5. 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.

Sampling Soils for Arsenic

Arsenic Concentration as a Function of Depth and Distance from the Tree Trunk: Figure 4 shows the relationship between As concentration at various depths in the Menfro 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 from the tree trunk of 0.91, 2.13, and 3.05 m, respectively. 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 4). This showed that the As remains in the upper horizons of the Menfro soil.

Table 5. 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

On the basis of these analyses it was concluded that making a composite 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.

Table 6 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.

Although there was variation in the levels of nutrients between the various orchards, results presented in Table 6 can be used as a guide to sampling techniques for orchards. The levels of phosphorus, organic matter, and calcium in most cases were much higher in the upper 0-5 cm than the lower 5-30 cm. The steepness of the organic matter and phosphorus gradient between the 0-5 cm and 5-20 cm layer suggested that a single sample of 0-20 cm as conventionally taken would not be satisfactory. The data suggest that a better sampling procedure would be to take two samples, one 0-5 cm and the other 5-20 cm in depth. These samples would provide greater sensitivity for indicating soil test values for organic matter, phosphorus, and calcium as well as being useful for As or Pb analyses.

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 (47, 49, 52, 60), it was concluded that Pb would also be concentrated in the upper horizons. Table 7 lists the results of the analyses for the elements throughout

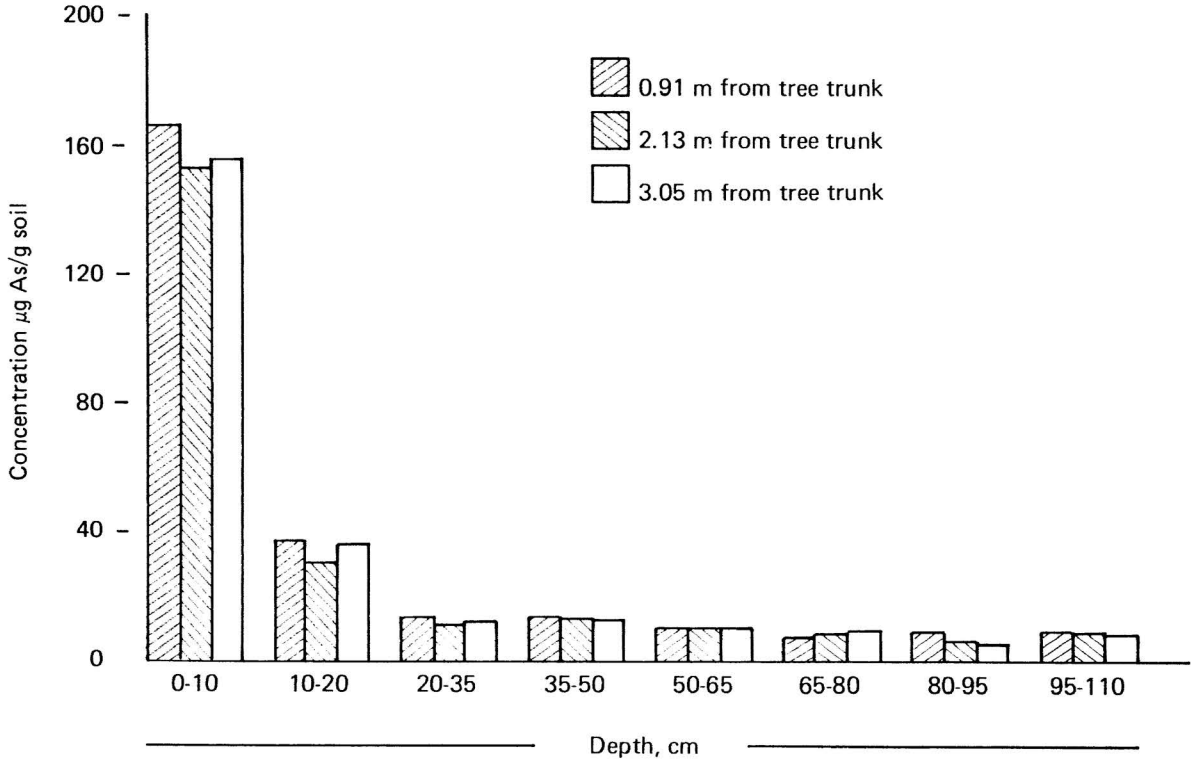

Figure 4. Arsenic concentration in a Menfro soil with depth and distance from the tree.

Table 6. Nutrient levels in Missouri soils.*

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
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	26.00	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	4.80	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	i87	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 6. (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
6a	Pioneer Orchard	0- 5	188	312	3.8	6.7	6.1	1.5	3400	230	410	11.5
		5-10	848	1470	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 6. (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.

Missouri. 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 occuring 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.

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 tend to 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 had 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 three 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. Hess (26) has shown that waterlogging increased the solubility of Pb and As that has been added to the soil, and others (1, 2, 13, 21) have shown that these levels can be toxic to plant growth.

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 five times yearly since 1952. Sample 6b was pasture until 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 7).

Table 7. 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 7. (continued)

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

Table 7. (continued)

Sample	Location	Soil Type	Depth	Lead	Arsenic	Copper	Lead/Arsenic	Current Use
	County		cm		μg/g soil*			
10	Lindsay Orchard		0- 5	131	20	6	6.55	Apple/peach
	Scott		5-10	78	24	6	3.25	orchard
			10-20	36	43	6	0.84	
			20-30	22	20	6	1.10	
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							

Table 7. (continued)

Sample	Location	Soil Type	Depth	Lead	Arsenic	Copper	Lead/Arsenic	Current Use
	County		cm	——	μg/g soil*	——		
17	Artman Farm Ray		0-30	18	10	3	1.80	Corn/soybeans

*Field replicates.
†Treated with lead arsenate.
‡Not treated with lead arsenate.

The relationships of the concentrations of Pb, As, and Cu of the Pioneer Orchard are shown in Figure 5, 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 8, but it still affords comparison over the time span discussed.

Table 8. 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
5	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.

Lead and arsenic levels for the Unity Village and Carver Orchards are shown in Figure 6. The Unity Village Orchard soil contained the highest amounts of lead and arsenic of any of the soils examined. This orchard is the oldest one observed, and the greater amount of lead and arsenic over the Carver Orchard may be attributed to the number of years of application. It is also indicated in Figure 6 that very little lead or arsenic had moved below 20 cm even after nearly 100 years of addition to the soil.

The Pb/As ratios found in Table 8 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 versus the As concentration in these horizons. In considering the Sharpsburg silt loam sample,

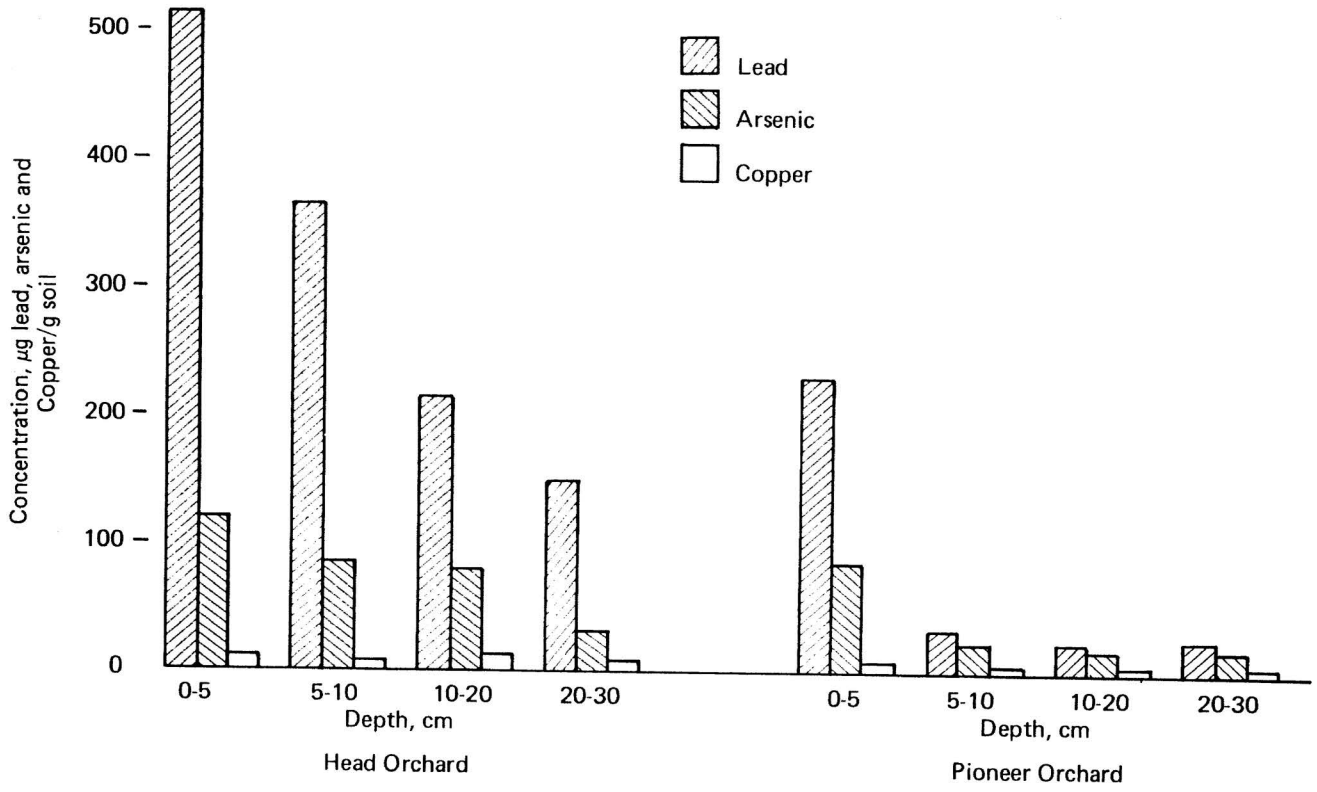

Figure 5. Comparison of lead arsenic and copper concentrations from the Head orchard treated with lead arsenate from about 1920 to 1955 with Pioneer orchard treated with lead arsenate since 1952.

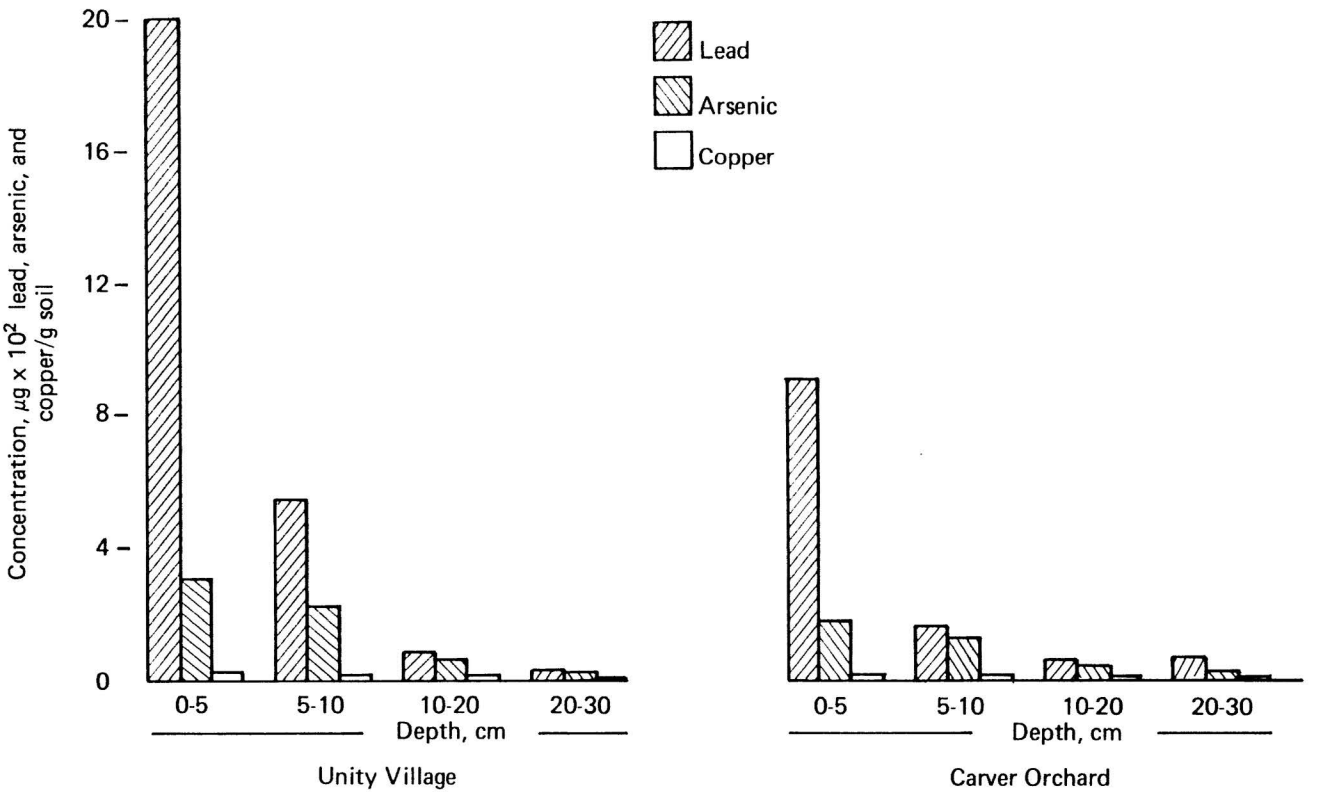

Figure 6. Comparison of lead, arsenic, and copper concentrations from Unity Village orchard, treated with lead arsenate for 75-80 years, with those from Carver orchard treated 40-50 years.

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

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

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 8, 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 from Lawrence County, and these are samples from the Head and Maples Orchards 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 (60) suggested plant transport as a possible cause, while Swain and Mitchell (52) and Schnitzer and Skinner (47) postulated that Pb forms stable complexes with fulvic acid and other organic molecules. Slinger and Hanson (49) found that Pb forms highly insoluble carbonates and sulfates in the soil. Lead may also be adsorbed 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 (38) 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 compounds that arsenate forms with Fe, Al, Mn and Ca may account for the immobility of arsenate in the soil. Johnson and Hiltbold (26) showed that arsenate was associated with Al in the soil, Deuel and Swoboda (13) indicated in the soil they worked with that As was precipitated as Fe compounds, and Hess (26) showed that Mn controls the solubility in the soils similar to those discussed here. This suggests that As forms Mn compounds readily after being applied to the soil, and that the As will remain near the surface as a Mn precipitate. A detailed evaluation of the forms of stable arsenates likely to occur in soil has been discussed by Hess (26).

Variations of pH and Eh in a Mexico Soil: Plots were established at the agronomy research farm to measure the seasonal variations in pH and Eh in a Mexico soil and to relate this to arsenic movement and uptake by plants. Figures 7 and 8 show the change in pH with depth and time according to the treatment applied. The pattern in all treatments appears 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

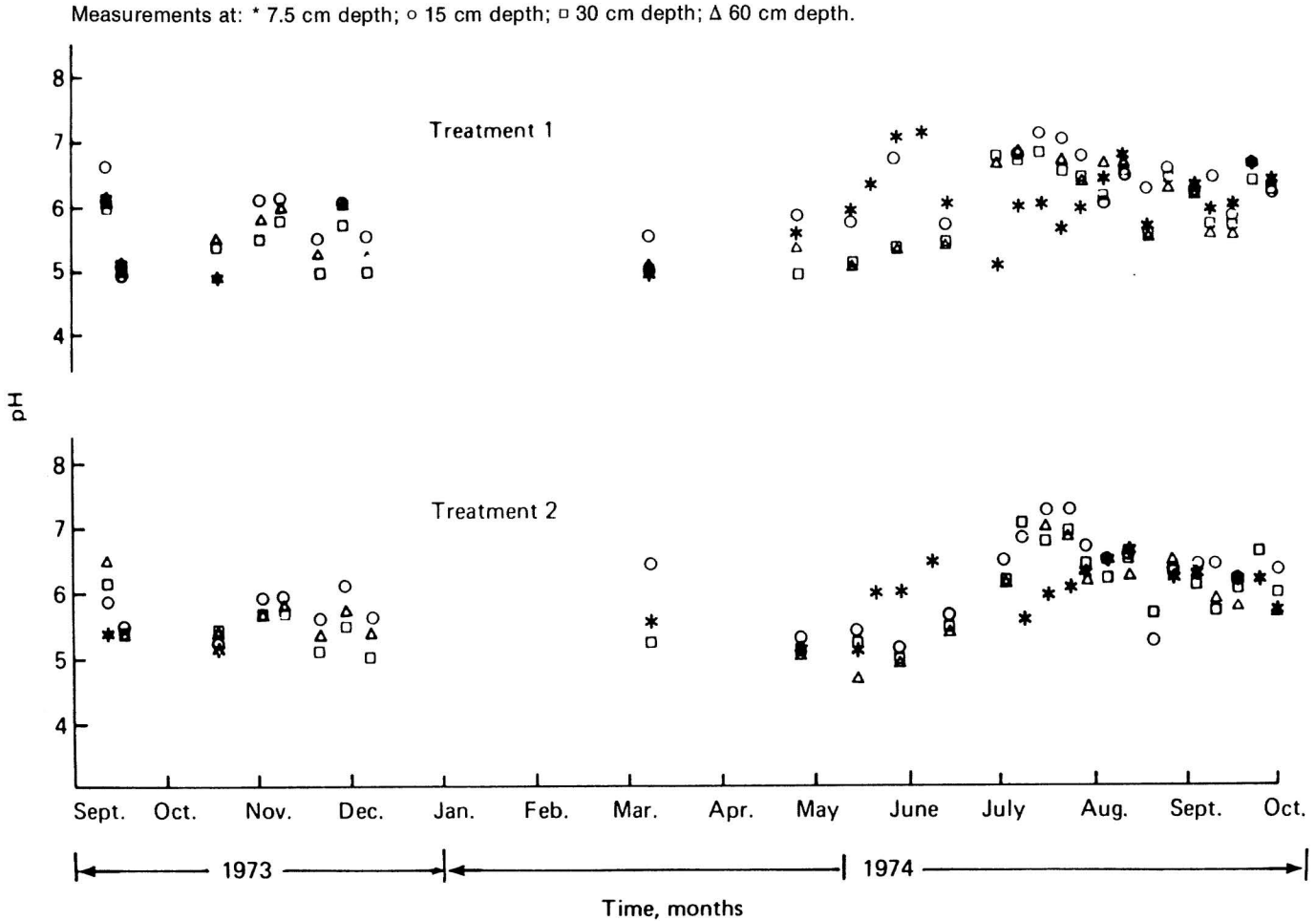

Figure 7. Yearly pH changes in a Mexico soil with depth and excess watering: Treatment 1, sewage sludge + 290 kg N/ha; Treatment 2, 145 kg N/ha.

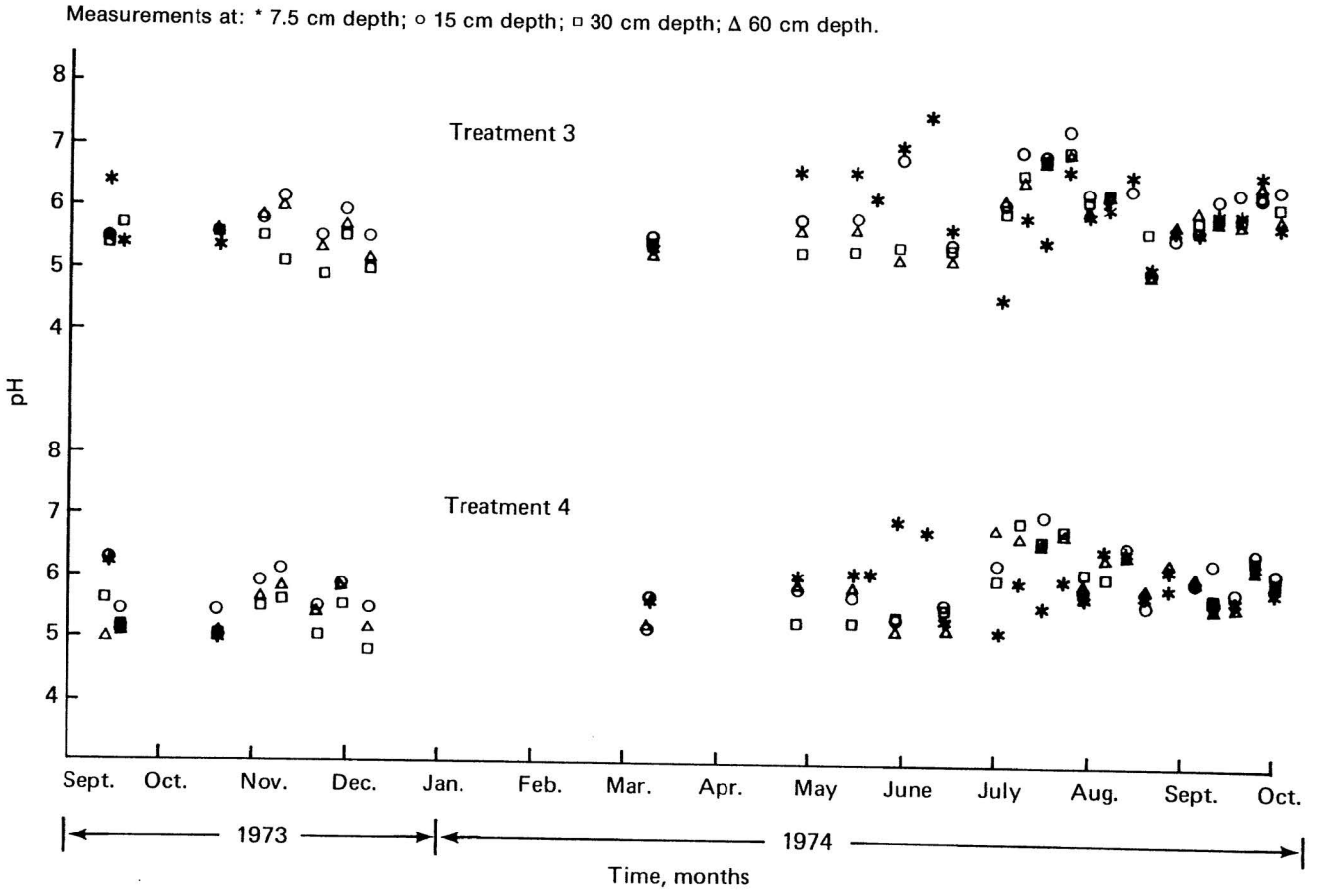

Figure 8. Yearly pH changes in a Mexico soil with depth: Treatment 3, 290 kg N/ha; Treatment 4, 145 kg N/ha.

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 was in the summer and early autumn months. Also, during the winter, spring, and later autumn, the soil had a higher percentage of water than it did during the summer and early fall. The highest surface pH was observed in late May, when the sewage sludge had been on the plots for about 1 month, and after an overnight heavy rain of about two inches fell.

Figures 9 and 10 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 the mid- to late June, and then it dropped to a low of -210 mV in 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 11 and 12 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 become aerated the oxidation-reduction potential immediately increased. Scott (48) 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 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 7 to 12, confirms his suggestion. The results of this study and those of Scott (48) indicate that if platinum electrodes are imbedded in the soil and left, they will give a consistent measurement of the oxidation-reduction potential.

Figure 13 shows the limits of pH and Eh established on the Mexico soil in this experiment for normal rainfall and where 7.5 cm of water is added per week during the summer. 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. (41) showed that after 14 days a submerged Lebanon soil had Eh values of -115 mV which also would cause arsenate reduction.

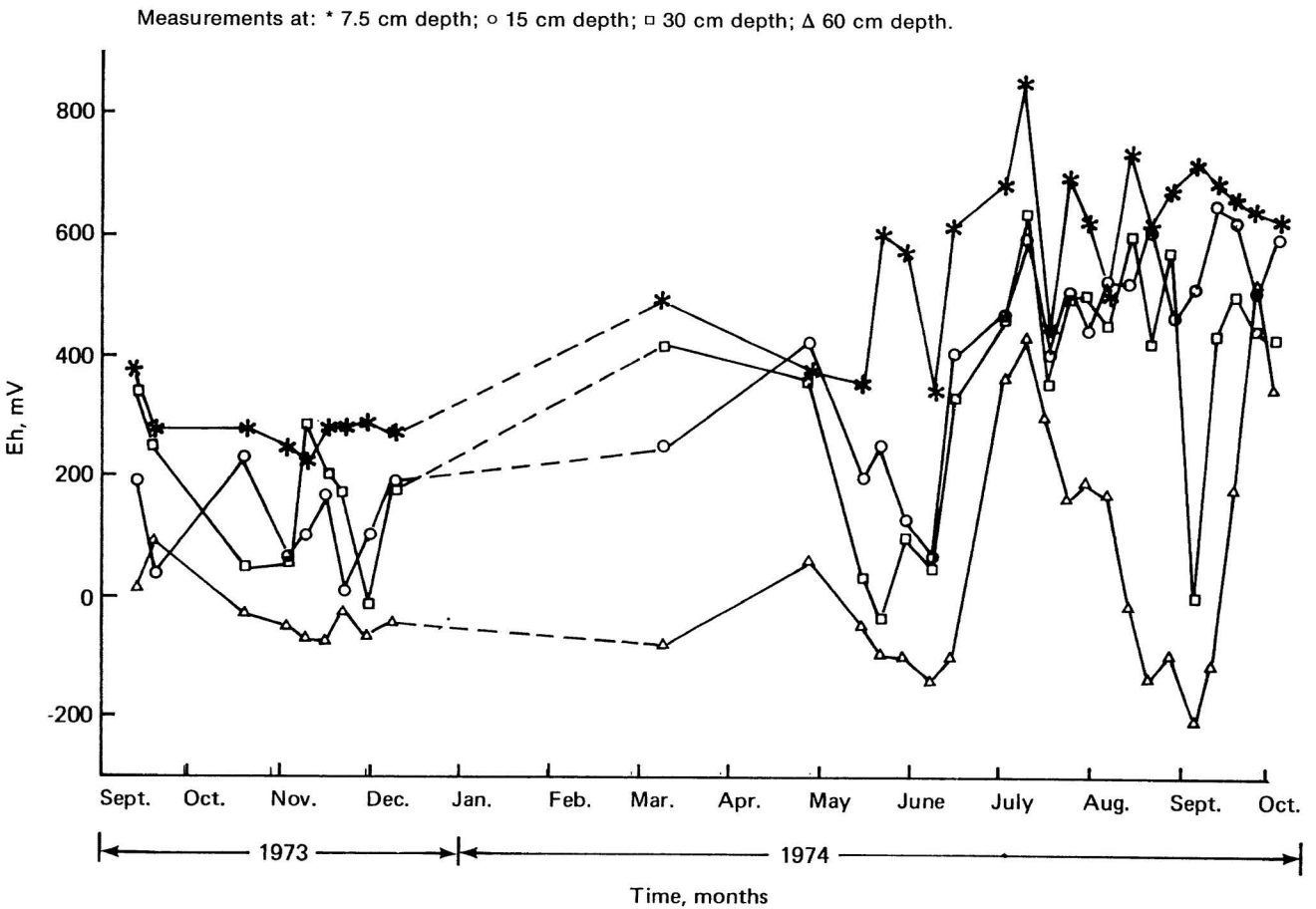

Figure 9. Yearly Eh changes in a Mexico soil with 290 kg N/ha + sewage sludge + excess water.

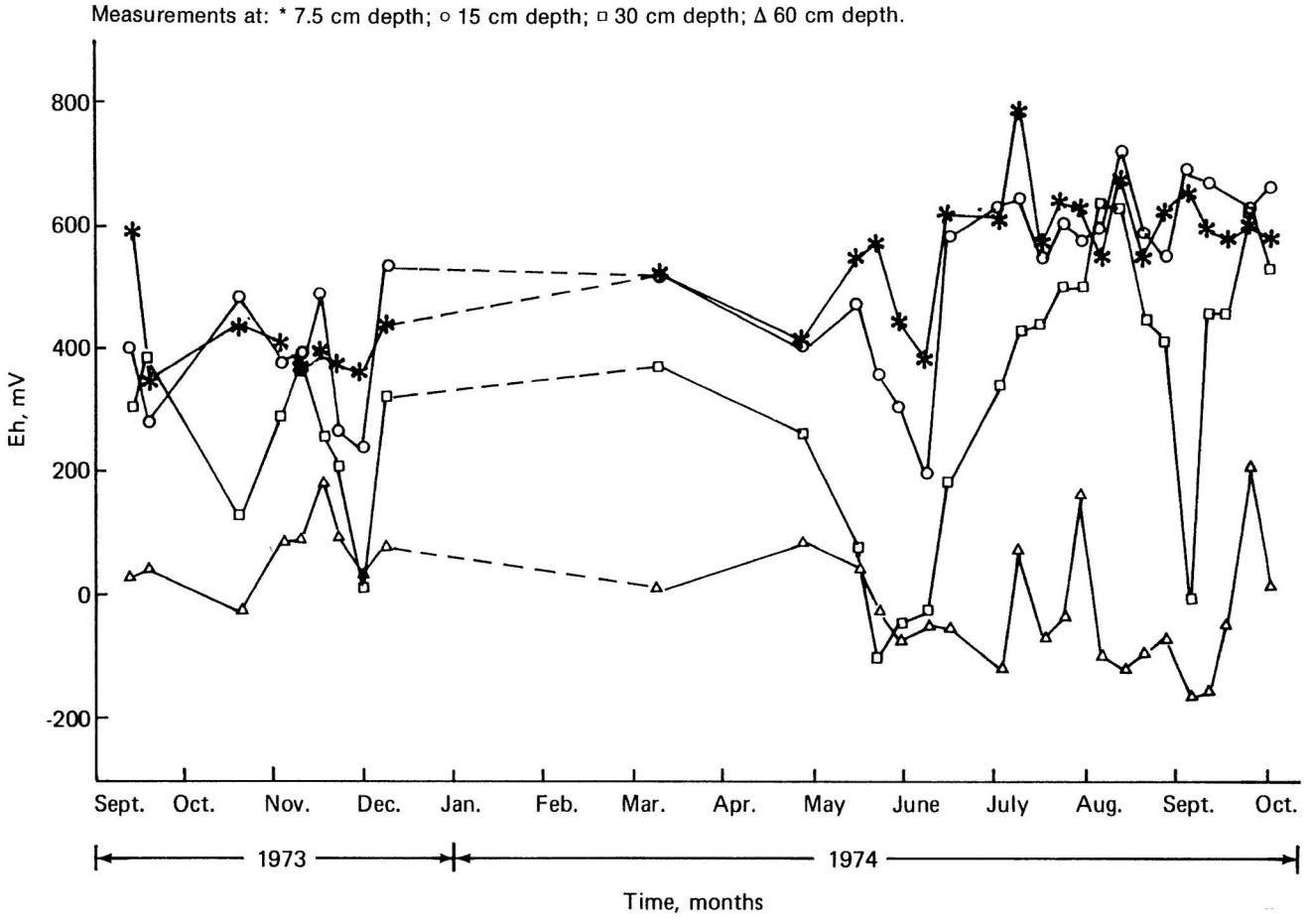

Figure 10. Yearly Eh changes in a Mexico soil with 145 kg N/ha + sewage sludge + excess water.

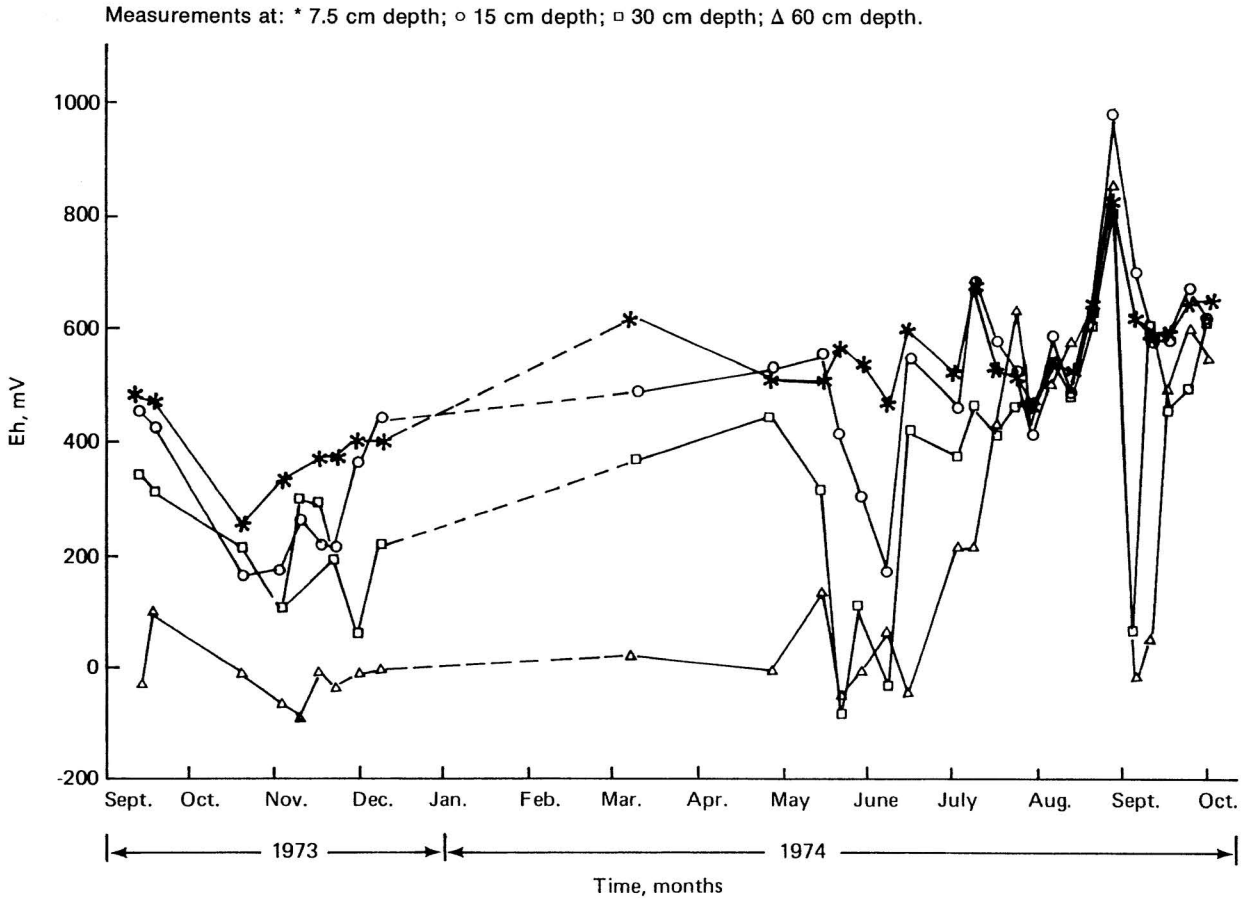

Figure 11. Yearly Eh changes in a Mexico soil with 290 kg N/ha.

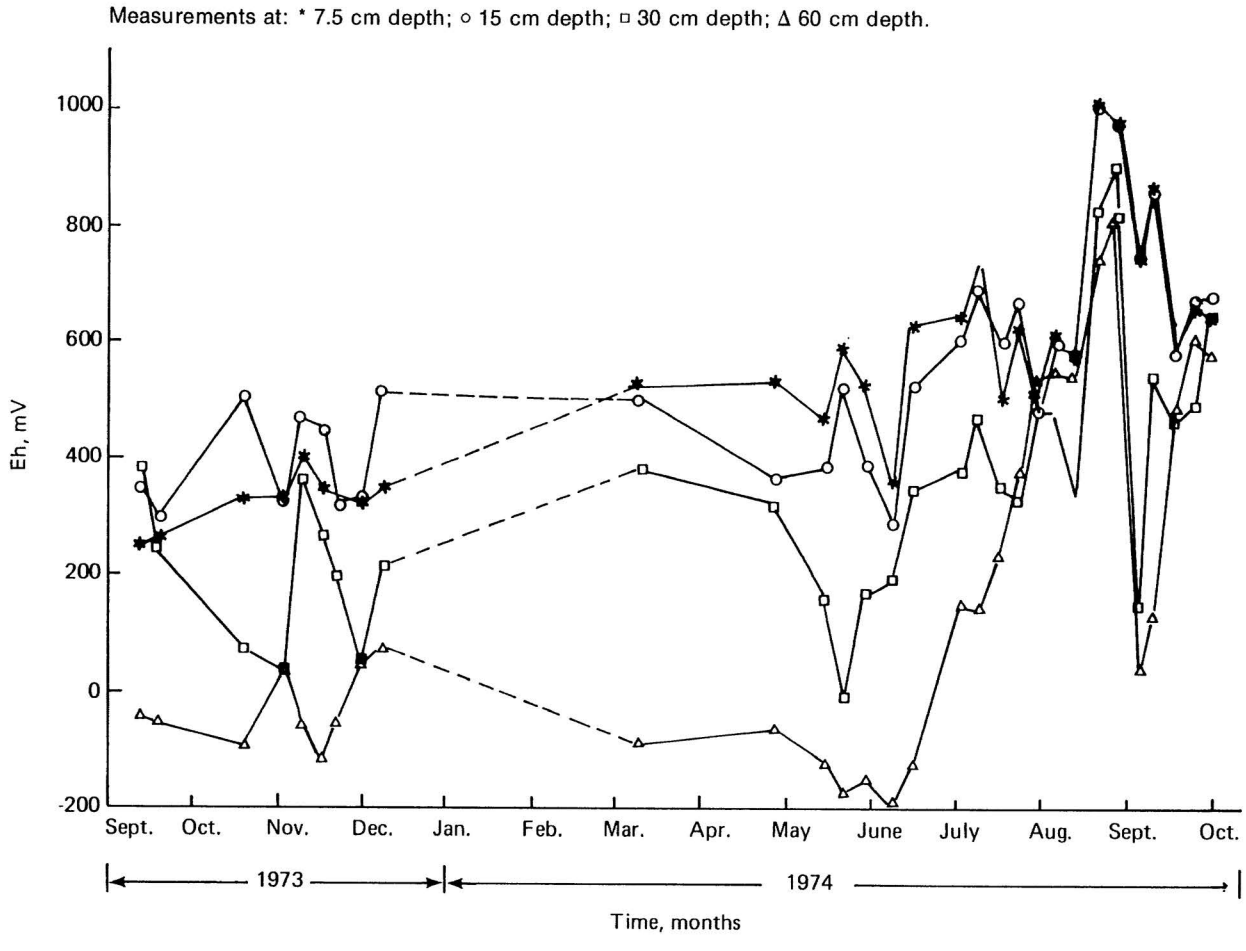

Figure 12. Yearly Eh changes in a Mexico soil with 145 kg N/ha.

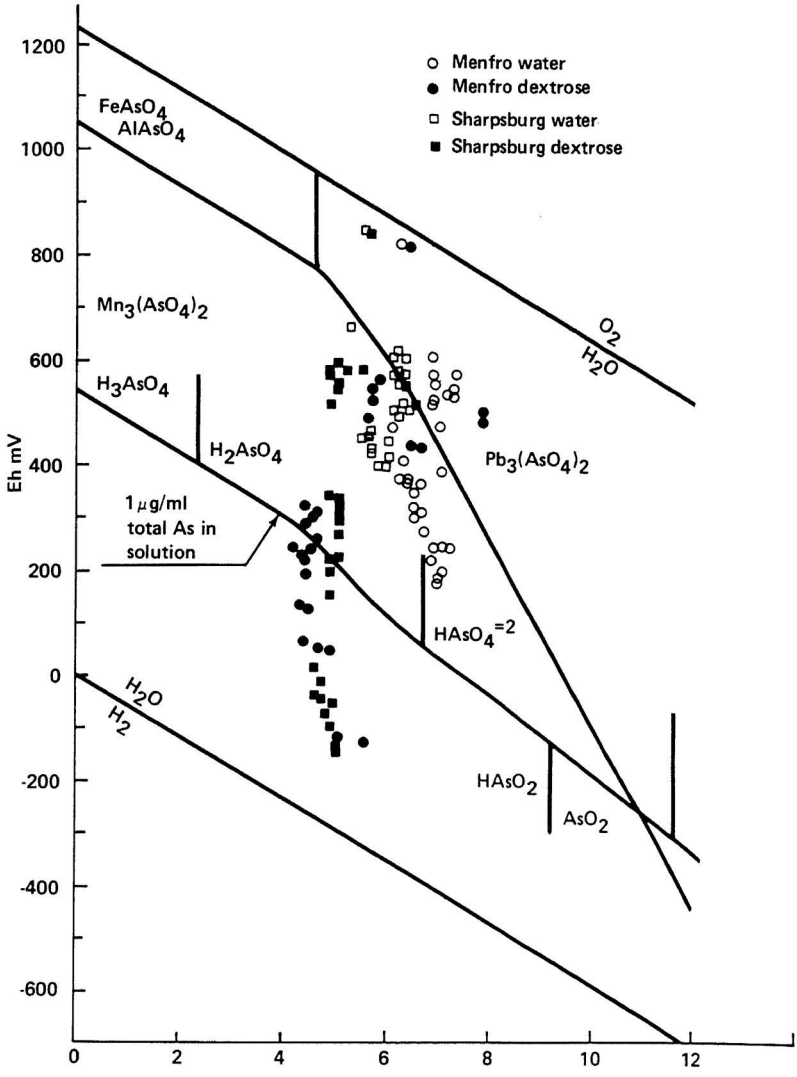

Figure 13. Eh-pH diagram showing the relative stability of aluminum, iron, manganese, and lead arsenates and the range of Eh-pH values for Menro and Sharpsburg soils.

Table 9 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 to 6 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 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 10 lists the dry weight and As content of the Reed 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.

Impact of Arsenic on the Soil Test for Available Phosphorus: In order to determine the effect of As on soils highly contaminated with As on the Bray tests for available phosphorus, both Bray tests (P_1,0.1N HCl + 0.25N NH_4F : P_2,0.03N HCl + 0.025N NH_4F) were performed on the soils in the survey. The Bray extract was divided and arsine evolved and absorbed in iodine solution from one part and phosphorus determined on the second fraction. Table 11 shows that a small, but 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 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.

CONCLUSION

It was shown 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.

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 of As and Pb accumulation appears to be a function of how long the lead arsenate was used, and how long since the use was discontinued, although neither As nor 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. Low available phosphorus levels could be masked because As is quantitatively indicated by the available Phosphorus test.

The oxidation-reduction potential and the pH of the Mexico soil show seasonal fluctuations. When the soil is watered heavily, but not flooded, the Eh at depths below 50

Table 9. 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
15.0-22.5	5	23	6	22	4	7	4	6
22.5-30	4	14	4	9	4	4	4	6

Table 10. 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			

Table 11. Comparison of Bray 1 and 2 tests in extracting arsenic and phosphorus from soils.

		Bray Test				P Error	
	Depth	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	1.69	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

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.

Practical Implications of this Study: Before land use changes are implemented on old orchard soils the levels of lead and arsenic in the soil should be checked. Samples of the soil to a 10 cm depth (4 inch depth) should be taken from the area as described in the sampling section of this report. If the levels of lead and arsenic are low, no problem exists. But if high levels are found, care should be taken in the use to which the soil is put.

Arsenic toxicity:

Changes in soil environment which restrict aeration and result in low Eh (reduced systems) will increase the toxicity of arsenic to plants and animals.

1) *Plowing* should be considered as having possible deleterious effects if the arsenic and high amounts of organic matter are layered far enough below the surface to be waterlogged (without air) for long periods of time. Most orchards are on well-aerated sites and this may not be a problem. However, this factor should be considered where waterlogging is a possibility.
2) *Irrigation* on soils contaminated with arsenic should be done carefully to insure that too much water is not applied.
3) *Gardening* with additions of water and organic matter should not be done on these

soils. However, if it is known that the soil is contaminated with arsenic, the upper 4 inches could be removed and garden plots established.

4) *Sewage disposal* by overland flow systems on these soils are not recommended. The data presented in this report suggest that arsenic would be solubulized and removed in the renovated water. Subsurface septic systems which do not saturate the soil's surface should be satisfactory in terms of arsenic problems.
5) *Crops* grown on these soils under well-aerated conditions should not have elevated arsenic contents and yields should not be reduced. However, crops grown when the soils are over-watered and anaerobic may be damaged and may have elevated arsenic contents.

Lead Toxicity:

Lead present in these soils is relatively unreactive and probably will have little effect on plant growth. However, any uses for this soil where ingestion of soil by animals may occur should be avoided.

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 remained low in the summer months if excess water was applied to the soil. This indicated that in flooded soils, the potential may become low enough for the arsenate to be reduced to arsenite, and possible toxic affects may be observed.

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

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