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DISTRIBUTION, MOVEMENT, AND EXTRACTION OF ARSENIC IN SELECTED FLORIDA SOILS

By

JOHN E. THOMAS

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1998

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

DISTRIBUTION, MOVEMENT, AND EXTRACTION OF ARSENIC IN SELECTED FLORIDA SOILS

By

John E. Thomas

May 1998

Chairperson: R. Dean Rhue
Major Department: Soil and Water Science

Arsenic (As), as a soil contaminant in Florida, can often be traced to the extensive use of cattle dipping vats to eradicate ticks. These vats held 5700 liters of arsenical solution, which was to be disposed of on-site yearly. With over 3400 sites in Florida, this represented a pervasive anthropogenic introduction of a potentially toxic contaminant.

Of these 3400 vats, ninety-four were located in Alachua County, Florida. Out of nine sites studied, the maximum soil As concentrations at three selected sites ranged from 100 to 767 mg/kg. The differences in As concentrations at these sites were attributed to a number of factors including variations in soil, hydrology, and vat history.

Effects of physicochemical soil properties on retention of As were investigated. Particle-size analysis suggested that soils with higher clay contents retained more arsenic. Contaminated soils with higher iron and aluminum content also exhibited higher As concentrations. Ground-penetrating radar was utilized at a Payne's Prairie vat site to locate the argillic horizon. Locating of the As plumes was effected by analysis of hand-augured soil borings. A *Fusarium* fungal culture was isolated from near this Payne's Prairie site that was capable of volatilizing As.

Soil gas collections near the surface overlying the zone of highest As concentration at two sites were shown to be essentially free of arsenic, though subsurface soil gas collections at two vat sites revealed gaseous As.

Mobilization studies were conducted on contaminated soil columns eluted with various anions under variable oxic conditions. Other studies involved surfactant extractions. A cationic surfactant, cetyl trimethyl ammonium bromide, was compared to a zwitterionic surfactant, 3-[(3-cholamidopropyl)-dimethylammonia]-1-propane sulfonate. Efficiencies of both extractants were below that of an anionic surfactant, sodium dodecyl sulfate, after arsenic has been complexed with a cationic macrocycle, [16-pyrimidium crown-4]$^{+4}$.

CHAPTER 1
INTRODUCTION

Purpose and Statement of Problem

The primary area of interest in this study was focused upon arsenic (As)- contaminated soils in Florida that resulted from the extensive long-known use of cattle dipping for the purpose of tick eradication. The investigation was divided into four objectives. First was evaluation of the extent of As contamination at selected cattle dipping vat sites. A second objective was the assessment of physical and chemical properties that affect retention and mobility of As at these sites. Third was an attempt to fit the movement of As in soil to a one-dimensional transport model that included a retardation factor. A final objective involved the examination of biotic as well as chemical extraction methods that affect the release of As from soil.

Cattle Dipping Vats

In Florida, as in many other southern states, one source of soil contamination by As can be ascribed to the extensive use of cattle dipping vats to eradicate ticks. Vats became the preferred method of eradication by virtue of the

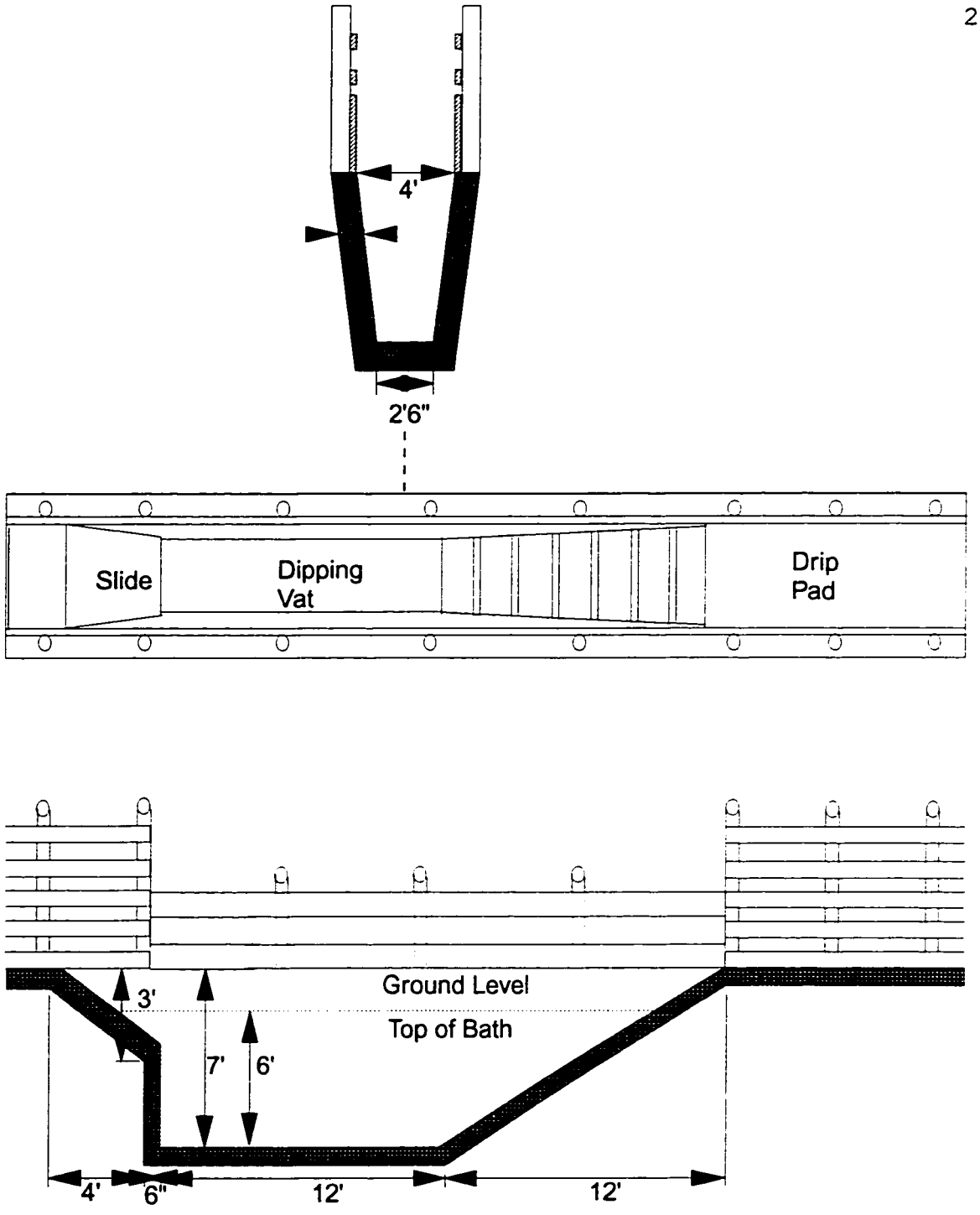


Figure 1-1. Schematic plan for the construction of concrete cattle dipping vat.

thoroughness, speed, and simplicity of the dipping operation.[1] Typically, the vats were 7.6-9.1 meters (25-30 feet) long and 0.8 to 1.1 meters (2.5-3.5 feet) wide according to plans supplied by the United States Department of Agriculture (U.S.D.A.) and the Federal Bureau of Animal Industries (Figure 1-1).[2,3,4] Florida alone had over 3400 cattle dipping vats which typically contained 5700 to 7600 liters of 0.14 to 0.22 percent total As solution.[3,4] The vats were expected to be emptied or replenished yearly. Disposal of the toxic waste was by one of two procedures. The first "approved practice is to run the waste bath into a pit properly guarded by a fence, where it will gradually seep away under the surface and do no harm, provided only that seepage cannot be carried to a well, stream or spring from which any person or domestic animal may drink".[3] This procedure was recommended in 1919 by the U.S.D.A. During the era of this recommendation, Florida had a much lower population and much less urban development, so the potential for harm was much reduced compared to today. The second method of waste disposal, proposed in 1913, was to form an insoluble precipitate. The clear liquid was to be pumped or syphoned out onto the ground, since it contained little As. The precipitate was to be "taken out and buried if so desired" and it, too, was judged to be non-poisonous.[5] The procedure to "render harmless the arsenic" called for measuring the number of gallons of solution left in the vat. For each 378 liters, 2.7 kilograms of slaked lime was to be

added. Slaked lime is made by calcining calcium carbonate from limestone, marble or seashells to form an anhydrous calcium oxide (quicklime) that can be subsequently reacted with water. After addition of the slaked lime, the vat solution was to stand for several hours. Then, for each 378 liters in the vat, 2.7 kilograms of copperas was to be added. Copperas, ferrous sulfate ($FeSO_4.7H_2O$), is a strong reducing agent. After ten to twelve hours, "the arsenic unites with the copperas (iron) and will have fallen to the bottom of the vat as an insoluble, harmless precipitate or sediment."[5] Since ferrous sulfate is quickly converted to the ferric form under basic conditions and arsenite [As (III)] is reduced to arsenate [As (V)], the precipitate would most likely be $FeAsO_4$, barring complexation with other metals and anions in the vat solution.

An interesting side note is that, at a 1992 U.S.E.P.A. workshop, the Bechtel Corporation and Artech Systems Inc. presented the "Cashman Process" in which acid leach of arsenical flue dust was treated with iron and gypsum ($CaSO_4.2H_20$) to form ferric arsenate. A long-term stability test over a period of several months was performed on a 3 meter thick pile of residues, by collecting the run-off. An estimate of 4 to 8 million years was given for all the As to leach out of such piles.[6] In this case, as in the cattle dipping precipitation/burial method, underlying assumptions were made concerning 1) low carbon input, 2) persistence of a

highly oxic environment and 3) low microbial activity. For the cattle dipping vat residues, in particular, these assumptions are suspect.

Another area of possible contamination from cattle dipping vats involves the use of pesticides other than As. From 1906 to the mid-1940s, As was the preferred tickicide by both state and federal programs. In fact, for 60 years it was the only product officially approved by the U.S.D.A. However, in 1946, an "outbreak" occurred in Florida associated with reappearance of the cattle-fever-carrying tick species Boophilus microplus. At this time, Florida officials began using 0.5% DDT with 0.03% gamma benzene hexachloride. In the cattle dipping vats, this mixture was known as "Dip 30". In 1960, dioxathion was permitted, coumaphous in 1968 and toxaphene in 1972.[1] Other contaminants found at vat sites include DDD, DDE, dieldrin, lindane, chlordane, toluene and methlyene chloride.[3]

Hindsight shows that the history of the cattle dipping vat parallels a history of As contamination of Florida soils. However, in defense of the tick eradication program, it should be emphasized that the economic devastation upon southern cattlemen by Boophilus annulatus, the cattle-fever tick, was debilitating, being on the order of $130,500,000 in 1906 dollars. In 1996, the program would have cost more than a billion dollars.[1] In light of factors such as economic impetus, sparse population, and scant chemical and

environmental knowledge (by today's standards), the tick eradication program appears justified given the historical perspective. A time table (Table 1-1)[7-15] for cattle fever, cattle ticks and cattle vats reveals a treatment period that spans more than 50 years, with variable success in pestilence control.

Table 1-1. Cattle fever, ticks and vats in the United States

Time	Description	Reference
1785	North Carolina passed a law restricting cattle movement, which was suspected to have been caused by Boophilus annulatus and piroplasmosis.	1
1796	Dr. Pease observed an outbreak of disease among Lancaster, PA, cattle following passage of South Carolina cattle.	5
1814	Virginia refused passage of South Carolina cattle suspected of being disease carriers.	7
1868	Texas cattle shipped up the Mississippi River to Cairo, IL and then by rail into Illinois and Indiana caused enormous losses in cattle.	5
1883-1885	Dr. D.E. Salmon determined the boundary line of permanently infected territory.	5
1889	Theobald Smith described the cow tick as carrier of peculiar microorganism that cause cattle fever. This was the first instance in which a disease was shown to be insect-borne.	5,7

Table 1-1. --continued

Time	Description	Reference
1889-1892	T. Smith and F.L. Kilborne confirmed the role of Boophilus annulatus in the epidemiology of Babesia bigemina.	7
1896	Dr. C. Curtice advocated cattle fever tick eradication and outlined suggested methods.	1
1897	The Interstate Association of the Livestock Sanitary Board (now known as the U.S. Animal Health Association) met in Fort Worth, TX, to discuss dipping experiments and quarantine lines.	7
1899	Dr. Curtice, State Veterinarian of North Carolina, instigated a tick eradication program in that state.	5
1903	Beaumont crude petroleum was shown to provide Twelve counties in North Carolina were released from quarantine due to a successful tick eradication program. the best tick control of any preparation tested.	7
1906	Twelve counties in North Carolina were released from quarantine due to successful tick eradication program.	5

Table 1-1. --continued

Time	Description	Reference
1906	U.S. Congress appropriated $82,500 to initiate a tick eradication program.	1
1907	≈700,000 sq. miles (1,813,000 km^2) remained under federal quarantine. Approximately, the line passed through Virginia, N. Carolina, Tennessee, Missouri, Oklahoma, Texas and California. Florida and 14 other southern states were under federal quarantine.	1
1910	Arsenic dips replaced straight crude petroleum dips.	1
1911	Four-fifths of the formerly quarantined area was released from quarantine. In general, the program was proceeding from the West and North, moving towards the Southeast.	1,5
1914	Fifty dipping vats were documented to exist in Florida.	8

Table 1-1. --continued

Time	Description	Reference
1915	Eighty-eight dipping vats were reported to be constructed state-wide, with eight in Alachua County, FL. A.L. Jackson of Payne's Prairie was listed as the owner of one vat. All vats had been built with private funds except for one vat built by the University of Florida.	8
1916	Broward and Dade counties and part of Palm Beach county were declared free of cattle tick by the federal Secretary of Agriculture. A large dipping vat and non-infectious feeding pens were established at Jacksonville, FL to facilitate shipping cattle out-of-state under a Federal certificate of dipping.	9
1917	State legislature passed a "Local Option Tick Eradication Bill" allowing counties that voted favorably to start a tick eradication program.	10
1917	Open-range policy and re-infestation from non-dipping areas, as well as a lack of public interest and funds, caused the program to fail.	10

Table 1-1. --continued

Time	Description	Reference
1923	The Florida State legislature passed a compulsory cattle-dipping law and created the State Live Stock Sanitary Board. The law allowed for partial compensation to owners for dipping their herds, as well as a one half mill levy to carry out the work.	10
1924	Dipping began in Gadsden and Escambia counties under the new law. Repercussions involved state dipmen wounded in battles with cattlemen, and 15 dipping vats in Escambia county were dynamited.	10,11
1926	Georgia built a 240 mile fence along the Florida border to prevent the movement of tick-infested cattle. This fence remained in place for 5 years and extended from the Chattacoochee River to the St. Mary's River.	10,11
1927	A more effective cattle dipping policy was initiated by the Florida Legislature. Instead of arresting cattlemen who did not dip their herds, the cattle were rounded up, dipped, and	1

Table 1-1. --continued

Time	Description	Reference
1927	held at the owner's expense. Upon refusal to pay, the cattle were sold and any unexpended balance was returned to the owners.	1
1930	Alachua county was scheduled to start dipping ≈March 1.	12
1931	The Orange county program was declared successful, yet re-infestation occurred.	1
1937	The U.S. Bureau of Entomology and Plant Quarantine and the U.S. Bureau of Biological Survey issued a report stating that: 1) The Boophilus annulatus (var. australis) tick existed in Florida 2) This tropical variety could use deer as well as cattle as a host, though no other wild animals in swamps appeared to act as hosts. 3) All deer would have to be removed if a tick program were to be successful. The Florida Legislature passed laws allowing deer removal from Orange, Osceola, Highlands, and Glades counties.	1

Table 1-1. --continued

Time	Description	Reference
1938	Overcoming a court injunction, deer removal began. Approximately 20,000 deer are slaughtered.	7
1941	Boophilus annulatus microplus, a cattle-fever tick, was found on 4 of 22 deer. Deer removal continued in Orange, Osceola, Highlands and Glades counties.	1
1943	Deer in Big Cypress Swamp, and in Collier and Hendry counties, were exempted from slaughter because they were on Seminole Indian Reservation. Forty-two of these deer were inspected and found to be tick-free. Florida was released from Federal quarantine on Dec. 1, 1943.	14
1945	A fever tick re-infestation was found in Highlands County, FL. Infested areas of Glades, Highlands, Okeechobee and parts of Osceola and Polk counties were placed under federal quarantine.	14

Table 1-1. --continued

Time	Description	Reference
1946	A Florida state official charged vats with 0.5% DDT plus 0.03% gamma benzene hexachloride (BHC). The mixture was sold as "Dip 30".	1
1948	On Oct. 1, Glades, Highlands, Okeechobee and parts of Osceola and Polk counties were released from federal quarantine. On Oct. 20, Volusia county was found to be infested, with then spread to Putnam, Flagler, Brevard, Osceola, Lake, St. John's, Alachua, Orange, Madison and Jackson counties in Florida as well as Brantley county in Georgia. All this was due to heavy movement of cattle from Volusia county.	14
1950	Florida was released from Federal quarantine on Dec. 1, but dipping continued due to a re-infestation threat associated with close proximity of Florida to tick-infested countries and islands of the West Indies.	14
1951	Florida state officials started using Toxaphene and DDT-BHC as tickicides. Arsenic dips remained the only ones	14

Table 1-1. --continued

Time	Description	Reference
	recognized by Bureau of Animal Industries for official work under Dept. of Agriculture regulations.	14
1957	On April 23, southern cattle tick (Boophilus annulatus microplus) was found on 4 ranches in southern Okeechobee county and 1 ranch in county. More than 100 ranches in 10 counties were placed under quarantine, even though the ticks were found to be non-infectious. Counties affected included Palm Beach, Hendry, Broward, St. Lucie, Glades, Highlands, Martin, Taylor, Dade and Okeechobee. An eradication program was undertaken by the Florida Livestock Board and the Agricultural Research Service.	15
1958	A limited outbreak of B. microplus apparently was successfully eradicated.	1
1960	The last reported outbreak of Boophilus microplus re-infestation occurred in Florida. No ticks of this variety have been found since 1961.	1

CHAPTER 2
OVERVIEW OF ARSENIC

Arsenic Sources and Toxicology

Arsenic occurs naturally in the atmosphere[16], water[17], sediment[18], soil[19] and various organisms[20]. It ranks 20th in abundance among the chemical elements[20] and occurs in ≈245 mineral species[6]. Arsenic is present at an average concentration of 2 to 5 mg/kg in the earth's crust and is primarily associated with igneous and sedimentary rocks.[21] Re-distribution can occur through natural means such as weathering, biological activity and volcanic activity. Anthropogenic inputs can also occur from smelting operations, fossil fuel combustion, glass and electronics manufacturing, wood preservatives and agricultural uses.[6]

Environmental contamination from As compounds introduced by man is due primarily to the use of arsenic compounds as pesticides and wood preservatives. Arsenite and arsenate, the As (III) and As (V) oxides, respectively, account for ≈ two-thirds of the arsenic compounds utilized, with organoarsenicals comprising the remainder.[22] Atmospheric contamination by As compounds has been associated with smelting operations and the burning of fossil fuels.[20]

As shown in Table 2-1, although certain areas for As usage are declining, there remains an overall increase in demand for As. With this increase in usage comes an increase in the possibility of environmental contamination. Arsenic is an element that is toxic at high levels and is considered carcinogenic at low levels.[23,24] The toxicity of As is highly dependent on its chemical formulation. Table 2-2 illustrates the toxicological variation among selected arsenical compounds as well as biological half-lives of the various species.[24] Since toxicity data are specific to individual organisms, the animal tested is listed along with the numerical value. It should be noted that the 50% lethal doses are median values. One conclusion that can be drawn from Table 2-2 is that there are no large differences in the toxicology of inorganic arsenicals. However, methylated As compounds are far less toxic than inorganic compounds. It has been hypothesized that the methylation of inorganic arsenic by organisms is a detoxification mechanism.[20] In contrast, studies on the toxicologic effects of dimethylarsinic acid (DMA) reveal damage to DNA and indicate mutagenicity.[25]

Toxicologists and nutritional experts are well aware that detrimental as well as beneficial effects are caused not by the "element" itself but by specific compounds incorporating the element. As illustrated in Table 2-2, As can be classified both as highly toxic, when in the inorganic form,

Table 2-1. Estimated U.S. demand for arsenic (metric tons)

	1971	1981	1991
Agricultural Chemicals	15,600	8,900	5,000
Glass	2,000	1,000	1,900
Industrial Chemicals	970	9,100	14,300
Nonferrous Alloys and Electronics	570	600	1,000
Other	500	400	400
Total	19,640	20,000	21,600

Table 2-2. Toxicity data of selected arsenical compounds

Arsenic Compound	LD_{50}(mg/kg)	Biological Half-Life(hours)
Arsenite (arsenic trioxide)	34.5 (mouse)	28.6 (hamster)
Arsenite (sodium arsenite)	4.5 (rat)	30 (human)
Arsenate (sodium arsenate)	14-18 (rat)	50.4 (human)
Monomethylarsonic Acid (MA)	1,800 (mouse)	7.4 (hamster)
Dimethylarsinic Acid (DMA)	1,200 (mouse)	5.6 (hamster)
Trimethylarsine (TMA)	8,000 (mouse)	3.7 (hamster)
Trimethylarsine Oxide (TMAO)	10,600 (mouse)	5.3 (hamster)
Arsenobetaine	10,000 (mouse)	6.1 (hamster)

and as innocuous to humans when present as certain organoarsenicals. Such is the case for seafood, where As is present as arsenobetaine and yet safe at 500 times the U.S.E.P.A. acceptable level for human drinking water.[20,26,27]

Arsenic and Regulatory Laws

The concept of allowable limits for As being set by regulatory agencies is based on "total concentration" rather than "species concentration". This is due to the fact that the arduous and time-consuming task of quantifying the multitude of arsenical species present is simply not economically feasible. Even though regulatory decisions concerning allowable concentrations of As may not vary based on speciation; there are regulatory variations based upon the background matrix (air, soil, water, food, etc.) and the intended usage of that matrix. There are also differing regulatory laws among various agencies setting limits on allowable arsenic concentrations. An example of the variance due to usage can be exemplified by the aqueous limits set by U.S.E.P.A. (Table 2-3).[26,27]

Currently, in the United States, there is no limit set on As contamination allowable in soil, except as a 5 ppm upper limit for the U.S.E.P.A. Toxicity Characteristic Leaching Procedure (TCLP).[28] The United Kingdom also has set a limit of 10 mg/kg for domestic gardens and 40 mg/kg for

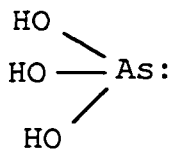
Table 2-3. U.S.E.P.A. allowable aqueous concentrations

Matrix Usage	Allowable Concentration (μg/l)
Human Drinking Water	50
Livestock Drinking Water	200
Irrigation Water for Crops	100

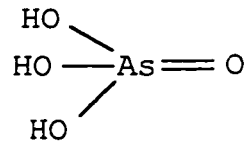
parks and playing fields.[29] The Netherlands standard for As contamination in soil is set at 30 mg/kg.[29]

Chemistry of Arsenic

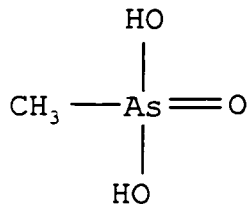
Arsenic is a member of Group Va of the periodic table. It has an atomic number of 33 and atomic weight of 74.92.[30] Arsenic exhibits properties that enable it to form alloys with metals and to form predominantly covalent bonds with hydrogen, oxygen, sulfur, and carbon.[21] Similarities between the chemical behavior of phosphorus (P) and arsenic are a result of similar electronic orbital configurations. The electronic configuration for As can be described as $[Ar]3d^{10}4s^{2}4p^{3}$. Arsenic, like phosphorus, will readily undergo catenation to form a series of cyclic compounds of formula $(RAs)_n$ where n = 3 to 6. It can also form R_2AsAsR_2 compounds. Akin to P, the stereochemistry of arsenic can be influenced by $d\pi$-$d\pi$ and $d\pi$-$p\pi$ interactions that foreshorten bond lengths as well as producing bond angles distorted by the presence of lone pairs of electrons.[31] The supposition has been made that the toxicity of arsenic arises from its similar chemical behavior to phosphorus and its ability to form covalent bonds with sulfur, which inactivates many enzymatic systems.[21] Some of the more important environmental and agricultural arsenical species are depicted in Figures 2-1 and 2-2. As illustrated by these structures, As can have coordination numbers



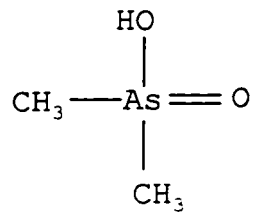
Arsenous Acid
(Arsenite Salts)



Arsenic Acid
(Arsenate Salts)

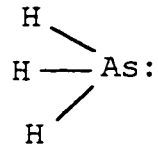


Methylarsonic Acid

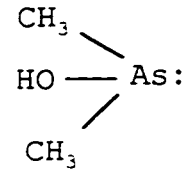


Dimethylarsinic Acid
(Cacodylic Acid)

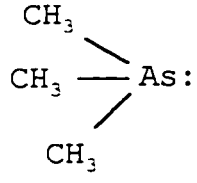
Figure 2-1. Arsenic nomenclature and structures.



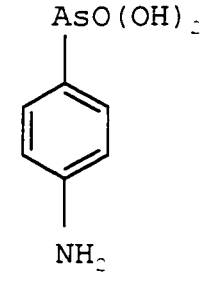
Arsine



Dimethylarsine

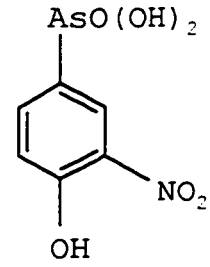


Trimethylarsine

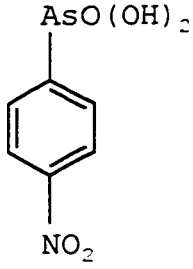


Arsanilic Acid

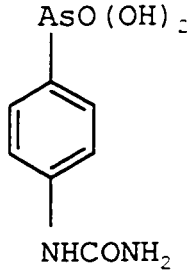
Figure 2-1. --continued



3-Nitro-4-Hydroxyphenolarsonic Acid
(Roxarsone)

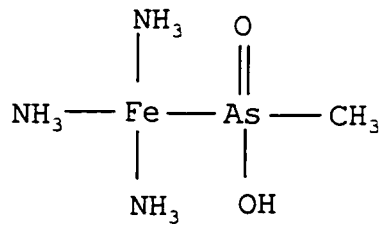


4-Nitrophenylarsonic Acid
(Nitrarsone)

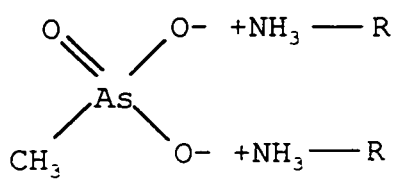


p-Ureidobenzenearsonic Acid
(Carbarsone)

Figure 2-2. Other examples of arsenic compounds.



Ferric Methanearsonate
(Neo-Arsozin)



where R = t-decyl or t-octyl

t-Octyl or t-Decyl Ammonium Methanearsonate
(AMA or Super-Dal-E-Rad)

Figure 2-2. --continued

of 3, 4 and 5. Arsenic can have coordination numbers of 2 and 6 as well.[30]

Oxidation States of Arsenic

The oxidation states of arsenic include +5, +3 and 0. Some confusion exists in the literature as to whether or not to include -3 as one of the oxidation states as well.[20] The most common method for determining oxidation states is to assign the charge distribution in chemical bonds based on the relative electronegativities of the pertinent atoms.[31] Linus Pauling first defined electronegativity as "the power of an atom in a molecule to attract electrons to itself."[32] As illustrated in Table 4, the value assigned to an atom's electronegativity is dependent on the model chosen for estimation. L. Pauling based his electronegativity scale on thermochemical data.[31] R.T. Sanderson based his scale on size and charge of the atom, to arrive at an estimation of relative electron density.[31] R.S. Milliken suggested using an average of the atom's ionization energy and electron affinity (values in Table 4 were derived from the subsequent work of H. Jaffe and co-workers).[31] A.L. Allred and E.G. Rochow derived their scale based on the electrostatic force exerted on valence electrons by the nucleus.[31] Basically, the larger electronegativity values dictate that a larger partial negative charge be assigned to that atom. Under the Pauling

Table 2-4. Different systems describing electronegativities (E.N.) of selected elements.[3]

Element	Pauling	Sanderson	Allred-Rochow	Milliken-Jaffe[a]	
	E.N.	E.N.	E.N.	E.N.	Orbital or Hybrid
As	2.18	2.53	2.20	1.59	sp
				2.58	sp^3
C	2.55	2.47	2.50	1.75	p
				2.48	sp^3
				2.75	sp^2
				3.29	sp
O	3.44	3.46	3.50	3.04	p
				4.63	20%s
				4.93	sp^3
				5.54	sp^2
S	2.58	2.66	2.44	2.28	p
				3.21	sp^3
H	2.20	2.31	2.20	2.21	s

a) Electronegativities adjusted to Pauling's scale for comparison purposes.

and Allred-Rochow scales, it is clear that As is considered to be positively charged with respect to C, O and S. However, the problem becomes muddled in the case of H. Further confusion can arise if the electronegativities are assigned using one of the two remaining systems. For the sake of consistency and simplicity, the values given by Pauling will be used throughout the remainder of this dissertation in assigning oxidation states. This necessitates that As be regarded as electropositive in relation to C, O, S and H. As such, the only oxidation states assigned to As will be +5, +3 or 0.

Reduction-Oxidation Equilibria of Arsenic

The oxidation state of aqueous As is highly dependent on the pH of the system as illustrated in Figure 2-3.[18] Typical mineral soils or sediments can have pH values in the range 5 to 9 with an Eh values of -300 (water-logged) to +900 (well-aerated) millivolts (mV). Some of the reduction potentials of As compounds are given in Table 2-5.[18] It is interesting to note that only the reduction of elemental As to arsine has a negative E^{o}; this means that reduced conditions would be required in a sterile, pure, aqueous system to produce this gas.

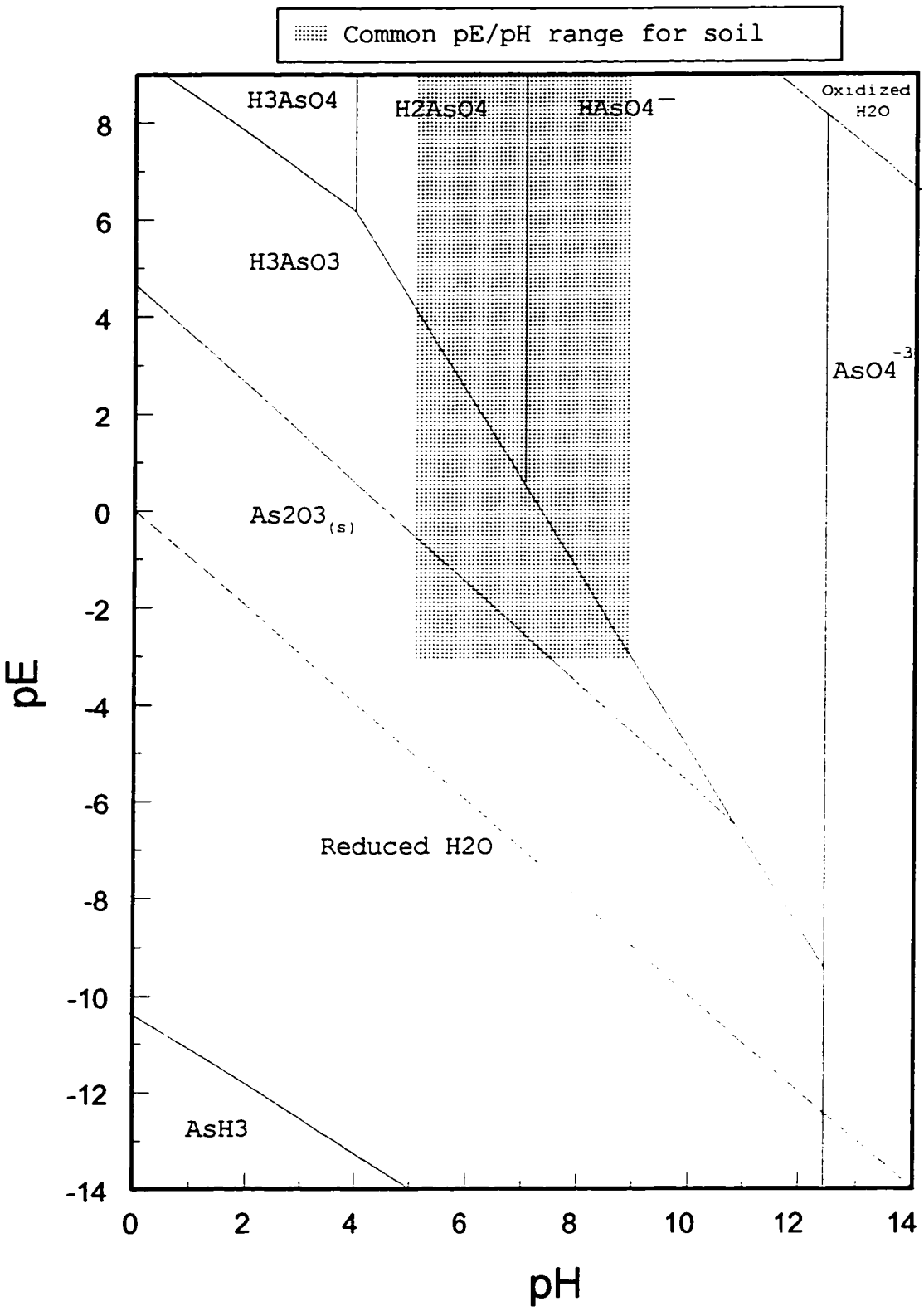


Figure 2-3. Oxidation-reduction stability diagram for As.

Table 2-5. Reduction potentials of selected As compounds.

Reaction	E°, volts (25°C)
$H_3AsO_4 + 3H^+ + 2e^- \rightleftharpoons AsO^+ + 3H_2O$	0.550
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O$	0.560
$H_2AsO_4^- + 3H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O$	0.666
$HAsO_4^= + 4H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O$	0.881
$HAsO_4^= + 3H^+ + 2e^- \rightleftharpoons AsO_2^- + 2H_2O$	0.609
$AsO_4^{-3} + 4H^+ + 2e^- \rightleftharpoons AsO_2^- + 2H_2O$	0.977
$As_2O_{3(s)} + 6H^+ + 6e^- \rightleftharpoons 2As + 3H_2O$	0.234
$As_2O_{5(s)} + 10H^+ + 10e^- \rightleftharpoons 2As + 5H_2O$	0.429
$As_2O_{5(s)} + 4H^+ + 4e^- \rightleftharpoons As_2O_{3(s)} + 2H_2O$	0.721
$AsO^+ + 2H^+ + 3e^- \rightleftharpoons As + H_2O$	0.254
$HAsO_2 + 3H^+ + 3e^- \rightleftharpoons As + 2H_2O$	0.248
$AsO_2^- + 4H^+ + 3e^- \rightleftharpoons As + 2H_2O$	0.429
$AsO_4^{-3} + 8H^+ + 5e^- \rightleftharpoons As + 2H_2O$	0.648
$2H_3AsO_4 + 4H^+ + 4e^- \rightleftharpoons As_2O_{3(s)} + 5H_2O$	0.580
$2H_2AsO_4^- + 6H^+ + 4e^- \rightleftharpoons As_2O_{3(s)} + 5H_2O$	0.687
$2HAsO_4^{-2} + 8H^+ + 4e^- \rightleftharpoons As_2O_{3(s)} + 5H_2O$	0.901
$2AsO_4^{-3} + 10H^+ + 4e^- \rightleftharpoons As_2O_3 + 5H_2O$	1.270
$As + 3H^+ + 3e^- \rightleftharpoons AsH_{3(g)}$	-0.608

Precipitation Reactions of Arsenic

Pure systems are rarely, if ever, encountered in a natural environmental setting, but the effect of precipitation reactions as well as sorption-desorption equilibria must be considered when determining the fate and transport of As. A compilation of the negative log of the solubility product equilibrium constants (pK_{sp}) are given in Table 2-6 for selected metal arsenical complexes.[18,34] The relatively high values for pK_{sp} indicate that arsenate can form practically insoluble metallic salts. Other practically insoluble compounds bearing As may be formed as well; for instance, under conditions where sulfides are stable, As will precipitate with sulfur. One example is the formation of orpiment (As_2S_3) under conditions when the pH=4 and -3<pE<0. Another example is the formation of realgar (As_4S_4) at pH=4 and -4<pE<0. Stability diagrams have been reported in the literature for these systems.[35]

Arsenic Compounds in Soil

As mentioned previously, As is ranked 20th among the chemical elements in abundance[20] and can be found in more than 245 minerals.[6] Although arsenite and arsenate are considered to be the most common forms of As compounds in the environment, organo-arsenicals can be found in soil pore waters as well. The presence of many arsenical compounds in

Table 2-6. Metal-arsenate solubility product constants.

Compound	pK_{sp}[a]	Reference
$AlAsO_4$	15.80	18
$Ba_3(AsO_4)_2$	21.62	34
$BaHAsO_4 \cdot H_2O$	24.64	34
$Ca_3(AsO_4)_2$	18.48	34
$Cd_3(AsO_4)_2$	32.66	18
$Co_3(AsO_4)_2$	28.11	18
$Cu_3(AsO_4)_2$	35.12	18
$CrAsO_4$	20.11	18
$FeAsO_4$	20.24	18
$Mg_3(AsO_4)_2$	30.32	34
$Mn_3(AsO_4)_2$	28.72	18
$Ni_3(AsO_4)_2$	25.51	18
$Pb_3(AsO_4)_2$	35.39	18
$Sr_3(AsO_4)_2$	18.79	34
$Zn_3(AsO_4)_2$	27.40	18

a) pK_{sp} represents the negative log of the solubility product equilibrium constant.

soil is due to the intervention of various organisms. Man introduces organo-arsenicals as feed additives (arsanilic acid, 3-nitro-4-hydroxyphenol arsenic acid and 4-nitrophenylarsenic acids), as post-emergence grass herbicides (mono- and disodium salts of methanearsonic acids), as insecticides (calcium and lead salts of arsenate), as fungicides (sodium arsenite, ferric methanearsonate and 10,10-oxybisphenoxarsine), and as desiccants/defoliants (dimethylarsinic acid and t-octyl or t-decyl ammonium methanearsonate).[21, 38-41] Molds, yeasts, fungi, algae and bacteria have all been reported in various reviews to produce organo-arsenicals, predominantly by methylation of arsenic oxides and hydroxides.[18,20,21,37] Volatile species of dimethyl- and trimethylarsine, as well as AsH_3, have been formed under both aerobic and anaerobic conditions in soils.[18,20,21,37] Most of these compounds are depicted in Figures 2-1 and 2-2.

Abiotic Interactions of Arsenic

As amply demonstrated in the preceding paragraphs, arsenic can be found in a multitude of compounds, all of which will interact with soil to various degrees. Some generalities can be drawn in regards to the interactions of As with soil. Autoradiography, electron microscopy, and electron probe microanalysis have each been used to measure the location of added arsenate on soil components. Sorption is a function of interlayer spacing in a clay lattice in conjunction with the

amount of hydroxyaluminum on the surface of the clay.[19] Arsenic retention has also been reported to be proportional to soil sesquioxide content and to decrease as amorphous iron and aluminum are removed. Organo-arsenicals, similar to inorganic As and P, will sorb to iron hydroxides in clay with increasing sorption in the order cacodylate < arsenate = methylarsonate. Adsorption has been shown to be a function of arsenical species concentration, iron content and clay type. For methanearsonate, the sorptive capacity of clays is given as kaolinite > vermiculite > montmorillonite. The greater adsorptive capacity of 1:1 type clays (kaolinite) was attributed to greater number of exposed hydroxyl groups of these minerals.[42]

Another study revealed that this generalization holds for arsenate only in the pH range of 1 to 9. At pH >9, the adsorptive capacity of montmorillonite exhibited a minima and subsequently increased while that for kaolinite continued to decrease. The increase in sorptive capacity was explained by noting that the montmorillonite contained calcite as a small impurity. Calcite has been shown to reach a maxima of sorptive capacity for arsenate at pH = 11.43. This study reached the conclusion that, the finer the soil texture, the higher the clay and/or the iron content, the more the sorption of arsenicals will occur.[19]

Interaction of humic acid with As has been reported as well as the conclusion that, at certain pH values, these

interactions may outweigh the sorption of As to hydrous oxides.[20] Other investigators concluded that sorption of As to metals may be a greater influence on immobilization than organic matter.[21]

Accumulation of As by metal hydrous oxides in "rhizosphere soil" has been suggested as possible by the oxidative effect of wetland plant roots. Oxidation of the rhizosphere could cause iron oxyhydroxides to precipitate, and the oxyhydroxides, in turn, would sorb As.[44]

Manganese oxide/hydroxides will also form complexes with various As species. Studies of pore water in sediments and flooded soils have shown that the As concentration correlates better to dissolved Fe than to Mn. The conclusion was that, as Mn(IV) is reduced to Mn(II), the released As is resorbed by the iron oxides/hydroxides. As such, iron content can still be considered to be the controlling factor in the release of As.[20,45]

Arsenic can also be released from soil through competitive reactions for sorption sites by P. Seventy-seven percent of As present in a soil was displaced by KH_2PO_4 in an experiment designed to simulate phosphate additions to an orchard soil.[46] Another study involving fourteen different extracting solvents on four different soils concluded that the order of effectiveness was: deionized distilled water ≈ 1 N NH_4Cl ≈ 0.5 M CH_3COONH_4 ≈ 0.5 M NH_4NO_3 < 0.5 M $(NH_4)_2SO_4$ < 0.5 M NH_4F ≈ 0.5 M $NaHCO_3$ ≈ 0.5 M $(NH_4)_2CO_3$ < 0.5 M KH_2PO_4 < 0.5 N

H_2SO_4 = 0.1 N NaOH. No solvent removed more than 80% of the total As from any of the four soils, even after 18 hours of shaking.[47]

One soil washing procedure that has been reported to remove more As involved use of a surfactant and a chelating agent. Four surrogate contaminated soils with average pH of 8.5 were washed with chelating agent (ethylene diaminetetra-acetic acid) - water and surfactant-water solutions. This system was effective in removing 93% of the spiked As.[48]

The removal efficiency of As by leaching with water through soil is highly dependent on the soil type with an order of sand < silt loam < clay. Organoarsenicals tend to leach in much the same manner as arsenate. However, one study has indicated, that in sandy loam and clay columns, the leaching of cacodylic acid was more rapid than for the sodium salts of methylarsonate.[19]

The rate of leaching for inorganic As is dependent on its oxidation state. During laboratory elution of a sandy column under oxidizing conditions, As (III) eluted at five to six times greater rate and at about eight times greater quantity than As (V). These differences were considered to be related to the weaker interaction of As (III) to Fe (III) in comparison to As (V) and Fe (III). In reducing conditions, As (V) and As (III) leached at similar rates. This behavior was attributed to the reduction of iron, the reduction of arsenic, or both.[20]

Biotic Interactions of Arsenic

Redox reactions, as well as methylation/demethylation reactions, are often facilitated by micro-organisms in the soil. Several review articles have been published dealing with microbial transformations of As.[18,19,20,21]

One of the major transformations of As is through bacterial oxidation. Microbial-mediated oxidation of arsenite to arsenate in cattle dipping fluids was suggested in a 1909 Australian article.[20] It remained a matter of dispute whether this change was brought about biotically or abiotically. In 1911, an agent for the United States Bureau of Animal Industry reported independently finding the same phenomenon and showed the change occurred through the growth of microorganisms in the dipping baths, with other factors being of little importance.[49] Confirmation of bacterial oxidation of arsenite was obtained by a South African group that isolated a pure culture capable of bringing about such change. The bacteria, named *Bacillus arsenoxyduns*, was eventually lost.[20]

The oxidation of arsenite to arsenate has been suggested as a detoxification mechanism, since bacteria are about ten times more sensitive to arsenite than arsenate.[21] Even in the early 1900's, it was recognized that the cattle fever tick was approximately two times more susceptible to arsenite than arsenate.[49] In fact, a simple field test for arsenite concentration in cattle dipping fluids was developed based on

titrating with iodine until the starch indicator changed color.[50] Knowing the amount of arsenite in the dip was extremely important in light of the fact that it is more toxic to cattle than arsenate.

Conversely, the concentration of arsenite may be increased, rather than decreased, in the dipping vats by evaporation or by biotic reduction of arsenate. The influence of bacterial reduction of arsenate in cattle dipping fluids was described in 1915 as a development that occurred after the rapid growth of oxidizing bacteria, but only if dipping was done in sufficient amounts and over short intervals. It was conjectured that the bath became so rich in nutrients that it finally formed a favorable medium for the growth of reducing organisms, which could flourish and counteract the action of oxidizing microorganisms. It was hypothesized that the oxidizing organisms worked slowly, but steadily; whereas the reducing organisms worked sporadically, briefly, and only during sufficiently rich nutrient conditions.[49] Although there seems to be no literature reporting the isolation of such a reducing bacterium from cattle dipping fluids, an anaerobic (also microaerophilic) bacteria has been isolated from a freshwater marsh sediment that is capable of using As (V) as an electron acceptor and lactate as the electron donor.[51] This particular strain showed a time lag before growth was evident that was dependent on the amount of O_2 present. Oxygen at 1, 3 and 5% induced a lag time of 40

hours, while a culture kept at 15% O_2 required 95 hours. This bacterial growth pattern leads to the speculation that, as the aforementioned cattle dipping fluids became enriched with nutrients, the oxidizing bacteria would flourish to the point of depleting the oxygen level in the bath. Then, the reducing bacteria could quickly grow and, subsequently, the rapid rise in arsenite concentration would be observed.

Reduction of arsenate to arsenite may also lead to biotic methylation and subsequent formation of a volatile arsine species. In anaerobic conditions, a *Methanobacterium* strain produced dimethylarsine and fungal strains of *Penicillium* and *Aspergillus* converted sodium methylarsonate, sodium cacodylate and arsenous acids to trimethylarsine. A wood rotting fungus, *Lenzites trabea*, produced a garlic-smelling volatile As compound (probably trimethylarsine) from a medium containing arsenic trioxide.[21] The volatile arsenic compounds are stable in anaerobic conditions, but rapidly oxidize in the presence of oxygen if the concentration of methylarsines is above 0.05 - 0.10 milligram per liter. At lower concentrations, these volatile arsenical species are stable enough to migrate from the area.[18]

Demethylation of methylated As species has also been shown to occur. Some of the same species that form volatile alkylarsines are also capable of using methane arsonic acid as a carbon source for growth. Species that can do both include *Flavorbacterium*, *Aeromona*, and *Norcardia*.[20] Other species

that can utilize methanearsonate as a carbon source include *Achromobacter*, *Pseudomonas*, *Alcaligenes* and *Enterobacter*.[21] An *Alcaligenes* species that was isolated from soil produced only arsenate. Another study showed that dimethylarsinic acid degraded to arsenate in soil in aerobic conditions, but not in anaerobic conditions.[18]

The general rule is that biomethylation is favored in anaerobic or reducing conditions and that carbon cleavage of organo-arsenicals occurs predominantly with aerobic or oxidizing conditions. Like most general rules, exceptions can be found. For example, one study showed that a mixed bacterial fungal population could release trimethylarsine in aerobic or anaerobic conditions.[18] Another organism, *Aspergillus fumigatus*, was reported to produce a volatile form of arsenic from As(III) in aerobic conditions.[44]

Methylation and volatilization have been suggested as possible means to remediate As contaminated sites. This combination is, by no means the only procedure capable of cleaning a site.[44]

Remediation Techniques for Arsenic-Contaminated Soil

There is a plethora of remedial treatments for contaminated sites. These remedial methods can be placed within the three headings of in-situ, prepared-bed and in-tank reactors. In each of these categories the processes may be physical[29], chemical[29], biological[44] or any combination of

these approaches. The aim is to achieve separation, volume reduction, immobilization, and detoxification, if possible. Not all remediation techniques apply to As-contaminated sites; however, a brief summary of the techniques that apply follows:

Physical remediation techniques

Excavation. Excavation is a simple prepared-bed method that aims to transfer contaminants elsewhere or to prepare them for further treatment. Disadvantages include determining the volume of contamination, the requiring of large amounts of clean fill material, and an increase in groundwater pollution due to disturbing of the soil column. There are also problems involving traffic, noise, dust and surface water pollution.

Entombment. Entombment is another prepared-bed method, wherein a collection is made of one or more contaminants that are placed on a single site and a tomb is then constructed to avoid dispersion. Disadvantages include the associated contamination of the collection area, the need to physically move the contaminants with its concurrent problems, and the need for construction of an effective structure.

Cover. This technique is widely used in the United Kingdom and applies to both *in situ* and prepared-bed methods. The cover material can be anything from asphalt, or concrete, to clean soil. Disadvantages are that the area under the cover is still contaminated and lateral migration can occur with the influence of surface and ground water.

Soil Washing. Separation and volume reduction can be accomplished using this in-tank method. It is particularly well suited for remediation of non-volatile organics and metals. The washing procedure does not work as well with soil that contains an appreciable amount of clay or organic matter; however, the main disadvantage is that the washing fluid becomes highly toxic and usually hard to treat.

Soil Flushing. While soil washing is an in-tank procedure, soil flushing does not require excavation. It is an *in situ* method that also aims to separate and reduce the volume of contaminants. Solutions used to flush the soil include water, acidic and basic solutions, surfactants, and various solvents. The same problems exist for soil flushing as for soil washing.

Soil Vacuum Extraction. This is an air-stripping technique that applies to both *in situ* and prepared-bed methods. This method extracts contaminants by moving clean air through unsaturated soil. This air movement causes mass migration from soil water into the soil air. Disadvantages are the need for a volatile or semi-volatile contaminant, and the air-movement restriction problems inherent with non-homogeneous and/or saturated soils.

Electro-kinetic Reclamation. This is an *in situ* method which requires that the soil be electrically charged using direct current along with the insertion of a water-circulation

system at one or both electrodes. Charged contaminants in such a system cause water movement to the oppositely charged electrode. The moving water also carries non-charged contaminants, usually to the cathode. Drawbacks include a strong dependence on soil composition and moisture content as well as limits on the amount of electric charge and the length of time required to complete the process.

Particle Size Separation. With this method, size separation is carried out by gravity via an in-tank method. It requires that the contaminants, such as arsenic, are associated with the finest soil particles. Drawbacks include the complexity of the operation and problems with subsequently treating the fine particles.

Rotary Kiln. This is an in-tank process that is successful in volume reduction and detoxification. Disadvantages are that it produces fly ash, a highly particulate emission that can be as toxic, or more so, than the original material. It also is limited to small particles and thus usually needs to have prior size reduction done on the contaminated material.

Pyrolysis. This is an in-tank process that is utilized for volume reduction and detoxification of contaminated soil that cannot undergo regular incineration in a rotary kiln. The principal disadvantage is that it can only handle small quantities at a time.

Cement Solidification. This is an *in situ* or in-tank method of storage and immobilization. It is accomplished by mixing Portland cement with the contaminated soil. Disadvantages include incompatibility with large amounts of dissolved sulphate salt or metallic anions such as arsenate, along with difficulty in hardening over a short time if the soil has a high amount of organic matter, silt or clay. Long-term effects of this method have not been adequately studied.

Vitrification. This is an *in situ* or in-tank method that is used to immobilize and store contaminants by fusing them into a glass-like substance. The main disadvantage is the high energy requirement, particularly with soils of high water content.

Chemical remediation techniques

Precipitation. This technique can be done as an *in situ*, prepared-bed or in-tank method. The premise is separation, possible volume reduction and/or immobilization by the formation of insoluble precipitates. This method was recommended by the Florida State Board of Health, Veterinary Division, for the As dipping-vat program. The arsenic was to be precipitated as a ferric salt in basic conditions, and then buried. Unfortunately, subsequent microbial action reduces the iron and frees the As species for migration. The main drawback to this method is a lack of testing on long-term stability of the precipitates.

Carbon Adsorption. This procedure can be used as an *in situ* or a prepared-bed technique, or as a complimentary technique in conjunction with other methods such as pyrolysis. It is most effective with contaminants of high molecular weight, high boiling point, low solubility, and low polarity. The primary drawback is the lack of knowledge of long-term stability.

Ion Exchange. This is an *in situ* or prepared-bed method emphasizing separation and immobilization of contaminants. Disadvantages include the limitation of applicable inorganic contaminants in suitable soils and the requirement of convenient pH control.

Biological remediation techniques

Bioleaching. This technique can be performed as *in situ*, in-tank or in prepared beds. Bioleaching may affect arsenical compounds directly by increasing mobility of As through reduction to inorganic As (III) or through reduction of associated ions (i.e., iron or sulfur). Bioleaching may occur indirectly by microbial production of organic acids, such as malic acid, or by microbial production of inorganic acids, such as sulfuric acid. These acids could in turn mobilize As via dissolution or ionic displacement mechanisms. Impediments to bioleaching may derive from soil composition, soil pH, nutrient requirements, bioavailability of the As compounds, and competition by indigenous microorganisms. Another

drawback is the need to remediate large volumes of contaminated liquid resulting from the bioleaching process.

Volatilization. This remediation method occurs naturally *in situ*. It may also be carried out in a prepared bed or in-tank. Volatilization of As can be mediated by bacteria, algae, actinomycetes or fungi or by a mixture of organisms. This technique exhibits all of the drawbacks exemplified by the bioleaching process, except that the large volume of contaminated liquid is replaced by a large volume of highly toxic gas.

Bioaccumulation and Biosorption. This technique involves the sorption of As onto microbial biomass or direct accumulation of As within soil microorganisms. The remediation may occur *in situ*, in-tank or in prepared beds. Drawbacks include soil composition, pH, nutrient requirements, microbial competition, and bioavailability of the contaminant. Additional problems arise in regards to biosorption stability and subsequent separation of bioaccumulated As.

CHAPTER 3
CATTLE DIPPING VAT SITES

Introduction

A number of difficulties arose during the process of selecting which cattle dipping vat sites were to be investigated. Among the problems encountered was the fact that there is no public record of vat locations. The vats have been unused for cattle dipping for over thirty years. During this time period, Florida has been developed extensively and many vats are no longer even in existence. Often the vats have been buried, paved or constructed over, so that physical evidence of their presence has been virtually obliterated. In addition, there was initially a problem involving liability for the cost of remediating these sites, if contamination were found. During the 1996 legislative session, the State of Florida passed a bill (House Bill #1073 and Senate Bill #956) releasing property owners whose land contained a cattle dipping vat from liability for costs, damages or penalties associated with the discharge, evaluation, containment, assessment or remediation of any substances that were used in the cattle-fever tick eradication program, retroactive to 1909.[52] However, at the onset of this

research project in 1992, the liability for remediation costs rested solely with the owner of the property. With estimates of such costs ranging from $130,000 to $800,000 per site (not including cost of annual operation and maintenance),[4] private property owners were not willing to admit even having a vat, much less allow an investigation of the site. One of the first criteria for site selection thus became the need for vats to be located on state property. Other factors included proximity to the University of Florida in Gainesville, accessibility to the vat and to the surrounding land and, if possible, availability of anecdotal accounts of the location and the history of use for the vat site. The latter criterion is, in fact, the key to locating many of these vats. It must be remembered that cattlemen who utilized these vats when they were in their thirties would now be in their sixties. They thus constitute a location resource that is steadily disappearing. Some other assumptions and facts also can aid in locating vats; for instance:

a) a water source was needed (each vat held ≈5700 liters);

b) vats needed to be drained; therefore, the location would be at higher elevation in relation to surrounding terrain, although in some cases only by a matter of centimeters;

c) the Florida sun is an extreme condition that could be alleviated if the vat were located under tree cover;

d) no cow was expected to travel more than 1.6 kilometers

(three miles) to the nearest vat; hence, it can be assumed that vats are no farther than 3.2 kilometers apart;

e) the number of vats per Florida county were recorded, often with the original owner's name;

f) tax rolls should also reveal the original owner of the cattle, since the taxman was invariably present at major dipping operations; and

g) holding areas such as auction houses and railway heads invariably had vats nearby.

All of these assumptions can be utilized to find cattle dipping vat sites. Clearly, the easiest way to locate a vat is still through anecdotes from the people involved in using them.

Materials and Methods

Those vats that were located during the course of this study usually came from anecdotal accounts, primarily by the Payne's Prairie park staff (Butch Hunt, Jack Gillem, Jim Weimer, and Howard Adams). Other sources included previous vat surveys by Woodward-Clyde, Inc., and sources located on the University of Florida campus.[19]

All vat sites near the University of Florida were visually confirmed and the surrounding soil was sampled for As contamination, if the site was accessible. Only one confirmed vat site for this study was not in Alachua County. This site

was located in adjacent Marion County with the owner amenable to a cursory examination of the vat, which had been filled with soil. A total of nine vats were investigated at least to the extent of 1) obtaining latitude and longitude using global positioning satellite technology, 2) placement on topographical and soil survey maps and 3) if permitted by the landowner, selected soil sampling and analysis for As contamination. Ten other vat sites were investigated by the Woodward-Clyde consulting firm and the results were reported to the Florida Department of Environmental Protection.[4]

The global positioning survey was accomplished using a Magellan Model GPS 2000 unit (Magellan Systems Corp., San Diego, CA). Topographical maps were supplied by the U.S. Geological Survey, Denver, CO. Soil map units, taxonomic classes, and soil survey maps were obtained from the U.S.D.A. Natural Resource Conservation Service.[53-62] Vat locations were superimposed on a road map using latitudes and longitudes by the program "ArcView GIS version 3.0".[63]

Soil samples were selected on the basis of topography and tested on-site for As. The on-site As soil test was a modification of water analysis procedure for the "EM Quant Arsenic Test Kit" (EM Science, Gibbstown, NJ). The test was rapid, though more qualitative than quantitative. The kit came with zinc dust, 30% HCl and 100 indicator strips as well as a graduated color chart to estimate the concentration of As.

The original procedure called for placing 5 mL of water into a 50 mL tube. This procedure was modified to substitute a 0.5 g soil sample (delivered via scoop) and 5 mL of a 500 mg/L P solution (from KH_2PO_4). A few drops of isopropanol were added to suppress foaming, if required. A small scoop of zinc dust (≈0.4 g) was added and the contents thoroughly mixed. An indicator strip containing mercuric (II) bromide was inserted into a septa cap and the cap was attached to the culture tube after 0.2 mL 30% HCl was added. A syringe needle (18 gauge) was put through the cap to relieve excess pressure. The arsine gas generated would react with the indicator strip turning it from light yellow to orange-tan to dark chocolate brown, depending on the amount of As in the soil.

The pH of the soil was measured by mixing 2:1 water:soil, stirring, and then allowing the slurry to equilibrate for ten minutes. The pH was measured using a combination electrode and an Accumet pH meter model #910 from Fisher Scientific, Inc., Norwalk, CT.[64]

Percent moisture in the soil samples was determined by drying a known weight of field-moist soil for 24 hours at 105°C. The dried sample was weighed and percent moisture calculated on a dry weight basis.[65]

Soil organic matter was measured using a modified Walkley-Black method. This involved a sulfuric/chromic acid digestion followed by sodium hydroxide titration using diphenylamine as an indicator.[66]

Particle size distribution of the soil samples was determined using sodium metaphosphate solution to suspend the clay. An aliquot of the suspension was taken at a prescribed depth, dried and determined by weighed to measure the amount of clay. Sand was separated from silt by wet sieving, dried and determined by weighing. Percent silt in the soil was determined by difference [100-(% sand + % clay)].[67]

Soils were digested for metal analysis using U.S.E.P.A. method #3050 or #3051. The former is a $HNO_3/HCl/H_2O_2$ digestion on a hot plate, while the latter is a HNO_3 digestion using pressurized teflon bombs and a microwave oven as a heating source. Both methods yield results termed "Total Recoverable" metals, although method #3050 yields slightly higher results than method #3051.[68,69] All reagents were analytical grade and obtained from Fisher Scientific Supply Co. (Orlando, FL). The digestion instrumentation for method # 3051 was a CEM MDS-2000 microwave unit.

The digestates were analyzed for aluminum (Al), iron (Fe), manganese (Mn) and arsenic (As) by one of four methods. Al, Fe and Mn were either determined by inductively coupled argon plasma spectrometry (ICAP) or by flame atomic absorption spectrophotometry. The As was determined by either a cold vapor hydride method according to instructions supplied by the Perkin-Elmer Corporation or by graphite furnace as in U.S.E.P.A. method #SW846-7060.[70] The instrumentation used for

these analyses included a multi-channel Jarrell-Ash Inductively Coupled Argon Plasma unit model 161-E, a Perkin-Elmer (Franklin, MA) Atomic Absorption Spectrometer (AAS) model #2380, a Perkin-Elmer Graphite Furnace (GF) model HGA-400 and a Perkin-Elmer Hydride System MHS-10 (Norwalk, CT). Spectrophotometer conditions for the flame and hydride vapor atomic adsorption analysis are given in Table 3-1. Operational parameters for the graphite furnace are shown in Table 3-2.

Background correction for the graphite furnace utilized a deuterium lamp. This type of correction compensates for smoke; however, it is inadequate for spectral interference. A spectral interference "occurs when an absorbing wavelength of an element present in the sample but not being determined falls within the bandwidth of the adsorption line of the element of interest".[71] For As analysis by graphite furnace using deuterium lamp background correction, the spectral interference is caused by aluminum.[72] Fortunately, the spectral interference caused by aluminum absorption exhibits a strong linear correlation (R^2=0.996) with the apparent As concentration (Table 3-3). Since the aluminum can be measured by nitrous oxide flame AAS, the contribution of aluminum to the apparent As signal can be calculated and subtracted from the measured As concentration to obtain the true, or the corrected As concentration. After correction for aluminum

Table 3-1. Operational parameters for metal analysis by flame or hydride generation.

Perkin-Elmer 2380 Atomic Absorption Spectrometer			
Element	Slit Width (nm)	Wavelength (nm)	Standard Range (mg/L)
Arsenic	0.7	193.6	0.002-0.02
Aluminum	0.7	309.3	5-100
Iron	0.2	248.3	0.3-10
Manganese	0.2	279.5	0.1-10

Table 3-2. Operational parameters for arsenic analysis by graphite furnace.

Perkin-Elmer 2380 Atomic Absorption Spectrometer					
Wavelength = 193.7 nm					
Slit Width = 0.7 nm					
Integration Time = 5 s					
Absorption Mode = Peak Height					
Background Correction = Deuterium Lamp					
Pyrolyzed Graphite Tube with L'vov Platform					
Perkin Elmer HGA-400 Graphite Furnace					
Program:	Step	Temp. (°C)	Ramp (s)	Hold (s)	Other
	1	100	20	30	
	2	1300	10	10	
	3	2300	0	5	Stop Flow Read
	4	2500	1	3	
Perkin-Elmer AS-40 Autosampler					
Sample Injection Volume = 10 μl					
Modifier Injection Volume = 10 μl					
Matrix Modifier = 5% $Ni(NO_3)_2$ in 0.1 N HNO_3					

Table 3-3. Spectral interference by aluminum in the analysis of arsenic at wavelength 193.6 nm using a graphite furnace atomic absorption spectrometer with deuterium background correction.

Aluminum Concentration (mg/L)	Apparent Arsenic Concentration (μg/L)
10	2.59
25	13.7
50	39.5
100	84.1
250	189.
500	349.

interference, the As concentration as measured by graphite furnace agreed well with the values obtained by hydride generation, which was free from this particular interference.

The cold vapor hydride system was operated in accordance with the Perkin-Elmer MHS-10 mercury/hydride system manual.[73] In general, 10 mL of acidic sample solution was placed in a reaction flask and the flask was purged with argon. The reductant, 3% $NaBH_4$ in 1% NaOH, was added for no more than 15 seconds. The resulting gas, AsH_3, was swept from the reaction vessel into a heated T-shaped quartz cell and the maximum peak height for absorbance at a wavelength of 193.6 nm was measured and recorded. All reagents were of analytical grade and purchased from Fisher Scientific Supply Co. (Orlando, FL).

For sites where the arsenic contaminant plume was delineated in the soil, soil samples were collected using either a 2.5 cm soil probe or a 10 cm bucket auger (Forestry Suppliers, Inc., Jackson, MS). The soil samples were transferred to plastic bags, labeled and stored in the laboratory at 8°C until digestion and analysis. All soil samples for this phase were digested and analyzed for As within two weeks of collection.

The contaminant plumes were plotted using "Geo-Eas 1.0.1"[66] and/or "Surfer v.5".[74] Depths to the argillic horizons were determined by soil probe and measuring tape. Topographical measurements were performed using a

Lietz/Sokkisha C3a Automatic Level from Florida Level and Transit Co., Jacksonville, FL.

To better determine the subsurface topography of the argillic horizon at one of the sites, ground-penetrating radar (GPR) was employed. The GPR unit, a Geophysical Systems model 3102, was run at 400 nm/s with attenuation of 100 and with a frequency of 500 MHZ at 16 scans/s. Output was interpreted using the Radan III program.[75]

All photographs of the vats were taken using a Ricoh RDC-2E digital camera from Ricoh Corporation, Sparks, NV. Color prints were produced by an Epson Stylus Color 800 printer.

Results and Discussion

This discussion section of the vat site studies was broken into two major sections, confirmed (personally investigated) and reported (investigated by state-contracted consultants). In order to facilitate future investigations of the confirmed vat sites, the locations were overlayed by GIS on road maps (Figures 3-1 and 3-2). A summary of confirmed vat sites with the soil map units and taxonomic class revealed that seven out of nine sites were located on Ultisols (Table 3-4). The only two vat sites not on an Ultisol were located at the Payne's Prairie State Preserve South Rim location and

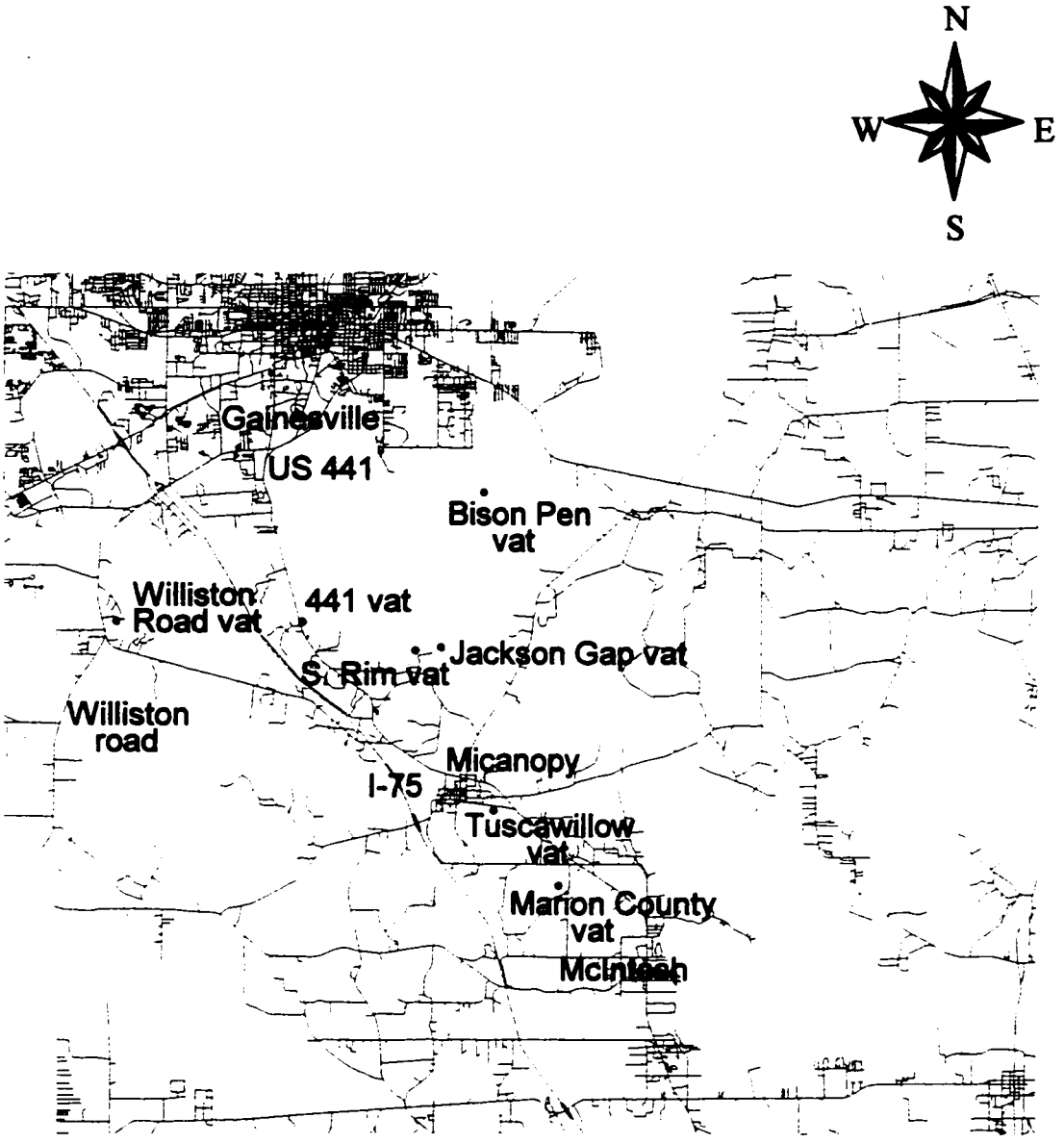


Figure 3-1. Map of roads and vats south of Gainesville, FL.

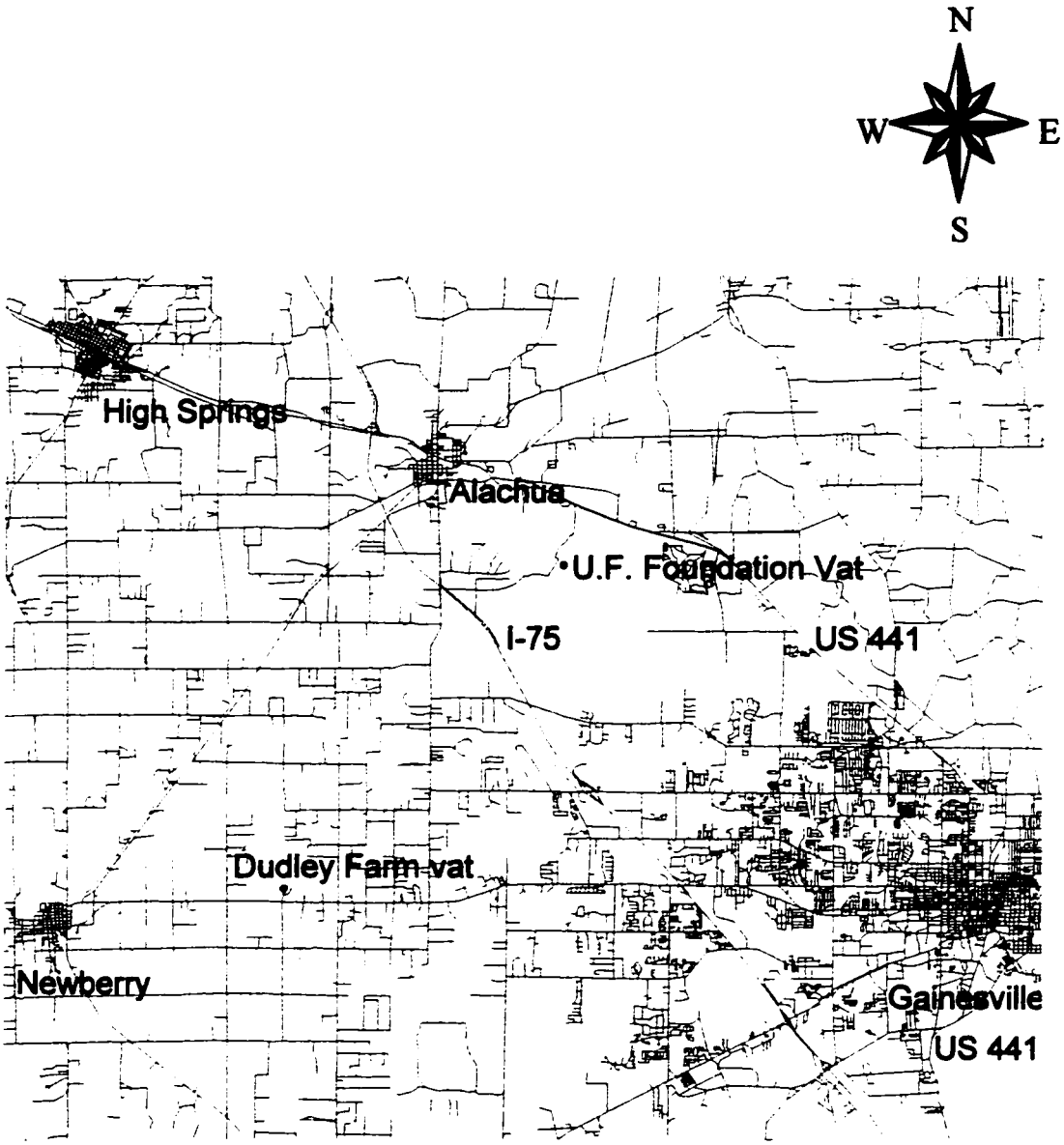


Figure 3-2. Map of roads and vats west of Gainesville, FL.

Table 3-4. Soil map units and taxonomic classes for confirmed cattle dipping vat sites.

Site	Soil Map Unit	Taxonomic Class
Bison Pen vat	Millhopper sand	Loamy, siliceous, hyperthermic Grossarenic Paleudults
US 441 vat	Lochloosa fine sand	Loamy, siliceous, hyperthermic Aquic Arenic Paleudults
Marion County vat	Blichton sand	Loamy, siliceous, hyperthermic Arenic Plinthic Paleaquults
Dudley Farm vat	Bonneau fine sand	Loamy, siliceous, thermic Arenic Paleudults
UF Foundation vat	Lochloosa fine sand	Loamy, siliceous, hyperthermic Aquic Arenic Paleudults
Tuscawillow vat	Kanapaha sand	Loamy, siliceous, hyperthermic Grossarenic Paleaquults
Jackson Gap vat	Millhopper sand	Loamy, siliceous, hyperthermic Grossarenic Paleudults
South Rim vat	Tavares sand	Hyperthermic, uncoated Typic Quartzipsamments
Williston Road vat	Pottsburg sand	Sandy, siliceous, thermic Grossarenic Haplaquods
	Monteocha loamy sand	Sandy, siliceous, hyperthermic Ultic Haplaquods
	Wauberg sand	Loamy, siliceous, hyperthermic Arenic Albaqualfs

bordered by Williston Road. All raw data for the confirmed sites that had transects were tabulated in Appendix A.

Confirmed Vat Sites

Payne's Prairie Bison Pen Vat Site

The first site that was investigated was located on the Payne's Prairie State Preserve ≈46 meters from the Gainesville-Hawthorne railway. The vat was largely intact, although partially filled with loose concrete, branches, decomposing leaves and other detritus (Figure 3-3). The topographical map shows that the vat was located on the side of a hill (Figure 3-4). The soil survey map, which is superimposed on an aerial photograph (Figure 3-5), reveals that the site is wooded and heavily shaded. The name for this site was derived from the holding pens for bison and cattle that were once located nearby. The train rails and the holding pens have since been removed from this site, but the vat itself is still largely intact. The soil immediately to the south (downhill) of the vat was mapped as a Millhopper sand.[53] Selected soil characteristics, including particle size distribution, organic matter content, pH and As concentrations are given in Table 3-5. The argillic horizon that is common to the Millhopper sand played an important part in delineation of the contaminant plume at this site. The As contaminant plume was found on the southern side of the vat with the

Figure 3-3. Photograph of the Payne's Prairie Bison Pen vat.

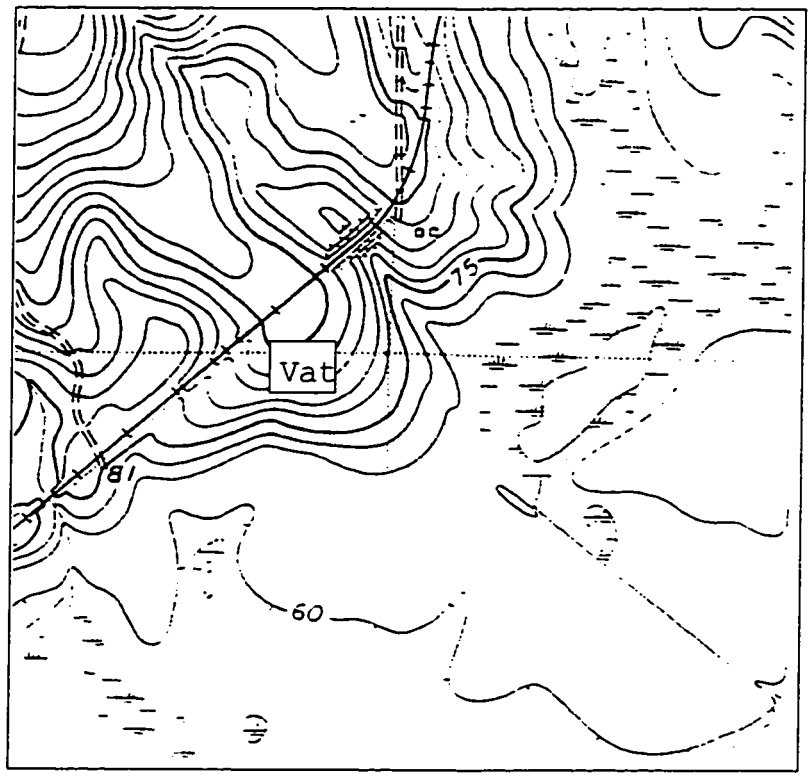


Figure 3-4. U.S.G.S. topographical map of the Payne's Prairie Bison Pen vat site.

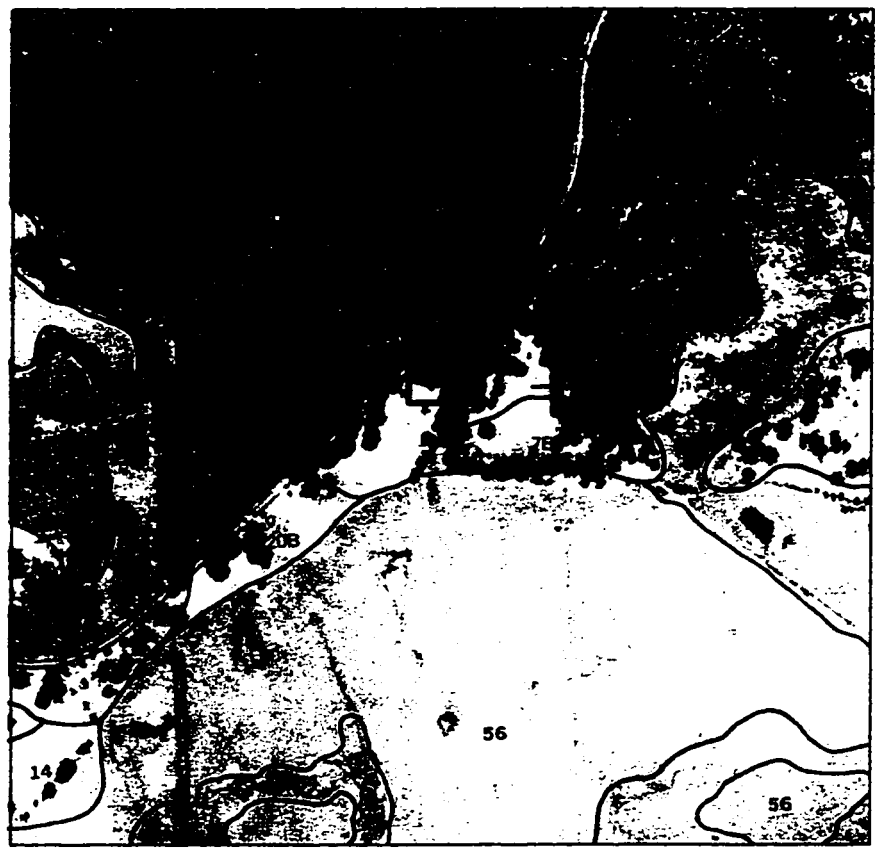


Figure 3-5. Soil survey map of the Payne's Prairie Bison Pen vat site. Map unit designations: 8B Millhopper sand, 20B Tavares sand, 25 Pomona sand, 31B Blichton sand, 54 Emeralda fine sandy loam, and 56 Wauberg sand.

Table 3-5. Selected characteristics of soil 10 meters south of the Bison Pen vat.

Soil Taxonomic Class	Depth (cm)	Horizon	Dominant Munsell Color	Particle Size Distribution (%)			Organic Matter (%)	pH	Arsenic (mg As/ kg soil)
				Silt	Sand	Clay			
Udult	0-30	Ap	10YR 4/1	4.3	95.0	0.7	0.8	5.7	---
	30-91	E1	10YR 7/1	3.3	95.8	0.9	0.6	5.8	---
	91-122	E2	10YR 7/2	4.0	95.3	0.7	0.4	5.4	0.8
	122-152	E3	10YR 6/4	3.4	95.8	0.8	0.3	5.6	21.5
	152-178	Bt	10YR 5/3	2.3	84.4	13.3	0.2	5.3	72.2
	178-	Btg	10YR 4/2	1.4	78.4	20.2	0.1	5.3	1.8

highest concentration of As in this plume being found 12.2 meters south of the center of the vat. This particular soil sample from the Bt horizon contained 110 mg As/kg dry soil. The location of the contaminant plume in relation to the vat was expected, since anyone who had to empty the vat would naturally do so to the downhill side of the vat. Transects were laid out at 4.6 meter intervals east-west and at 6.1 meter intervals north-south. The north-south transects extended to 12.2 meters uphill from the vat and 61.0 meters downhill from the vat. The east-west transects measured a maximum of 13.7 meters in east or west direction from the center of the vat, though not all transects were of equal total length. Transect length was determined by taking soil samples from the top of the argillic horizon, which were analyzed for As. Vertical soil sampling showed that the As concentration is greatest on and directly above the Bt horizon (Table 3-6). At this vat site, the arsenic did not penetrate down to the lower, gleyed argillic horizon (Btg). It is important to note that this soil sits directly on top of the Hawthorn formation, which is almost impermeable to water. Since the upper argillic was readily distinguished from the E horizons by texture as well as by As content, it was chosen as the diagnostic horizon for delineating this contaminant plume.

To delineate the contaminant plume, thirty-six samples were taken from the top of the argillic horizon using a ten centimeter soil auger and analyzed for metals (Figure 3-6).

Table 3-6. Selected metal concentrations in soil 10 meters south of the Bison Pen vat.

Horizon	Arsenic (mg As/kg soil)	Iron (mg Fe/kg soil)	Aluminum (mg Al/kg soil)	Manganese (mg Mn/kg soil)
Ap	---	365	960	9.4
E1	---	238	690	7.5
E2	0.8	203	660	6.3
E3	21.5	170	560	4.1
Bt	72.2	129	770	1.7
Btg	1.8	183	970	2.0

Data for the depth, and for the northing and easting coordinates as well as the As concentrations, were used as input to the U.S.E.P.A. program "Geo-EAS". The "Geo-EAS" program correctly stopped the contaminant contour at the edge of the vat (Figure 3-7). However, it is interesting to note that the U.S.E.P.A. program also generated a single point at 100 northing and 45 easting outside the plume contour. Since it was set to draw contours at increments of 20 μg As/g soil, it ignored a point at 120 northing and 45 easting that yielded an arsenic concentration of 12.2 μg As/g soil. When the plume contour was generated using "Surfer - version 5.0" a dumbbell shape was shown using contour levels of 20 mg As/kg soil (Figure 3-8). The biggest obvious drawback of the "Surfer" program was closure of the contours nearest to the vat where it actually had no data to confirm this depiction. On the other hand, the "Surfer" program has the advantage of allowing the user to superimpose the contour map of the contaminant plume on top of a three-dimensional grid representing the argillic horizon (Figure 3-9). In addition, the topographic map of the surface may be superimposed over the argillic horizon and plume depictions (Figure 3-10).

The argillic horizon's three-dimensional representation was generated using ground-penetrating radar (GPR). A ten-cm bucket auger was used to "ground-truth" the GPR readings at thirty-six locations. The depths measured by GPR and by soil probe were linearly correlated, with a regression coefficient of R^2 = 0.989. One source of error in these measurements was that the

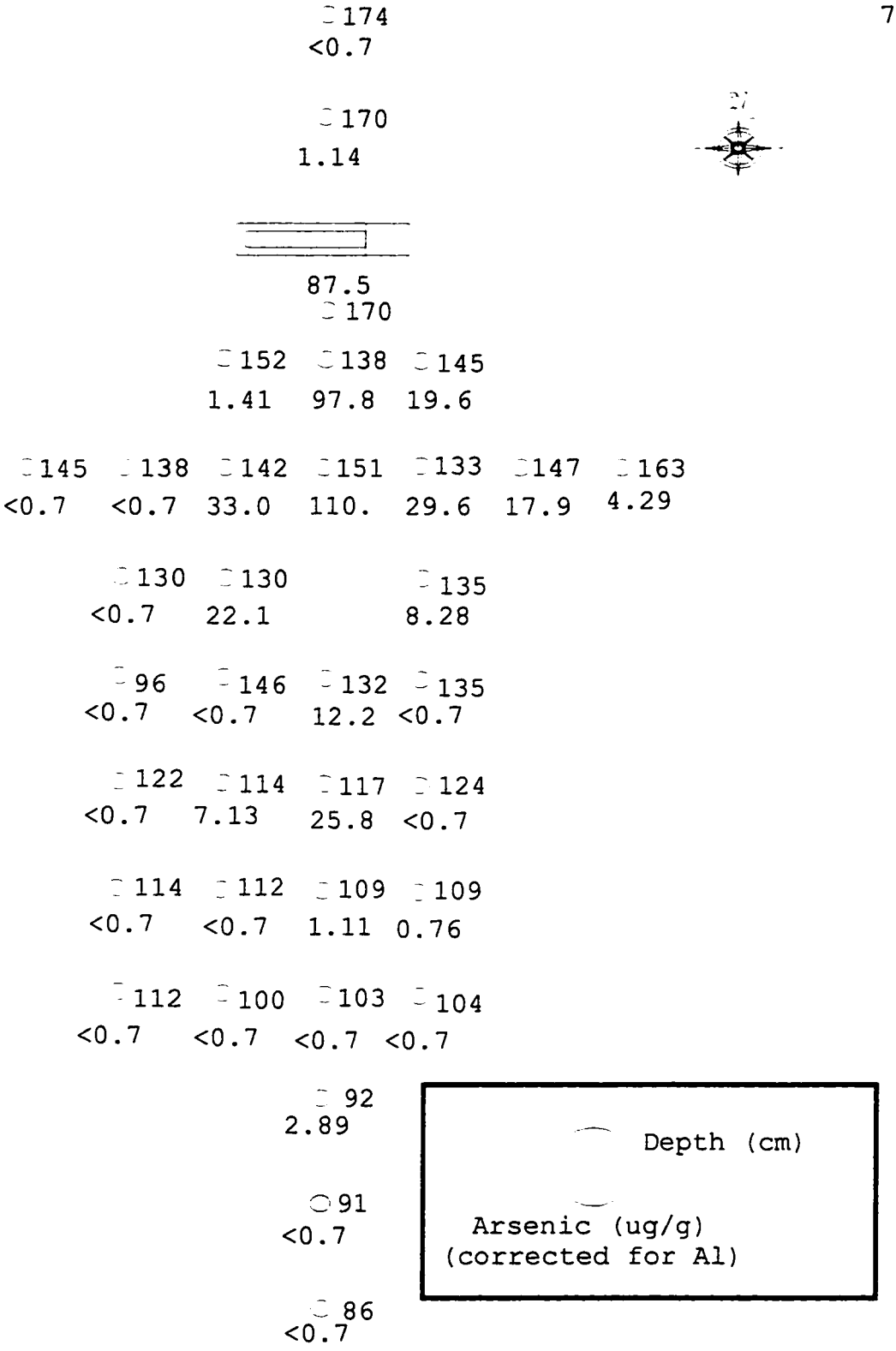


Figure 3-6. Argillic horizon depth and associated As concentrations at the Payne's Prairie Bison Pen vat.

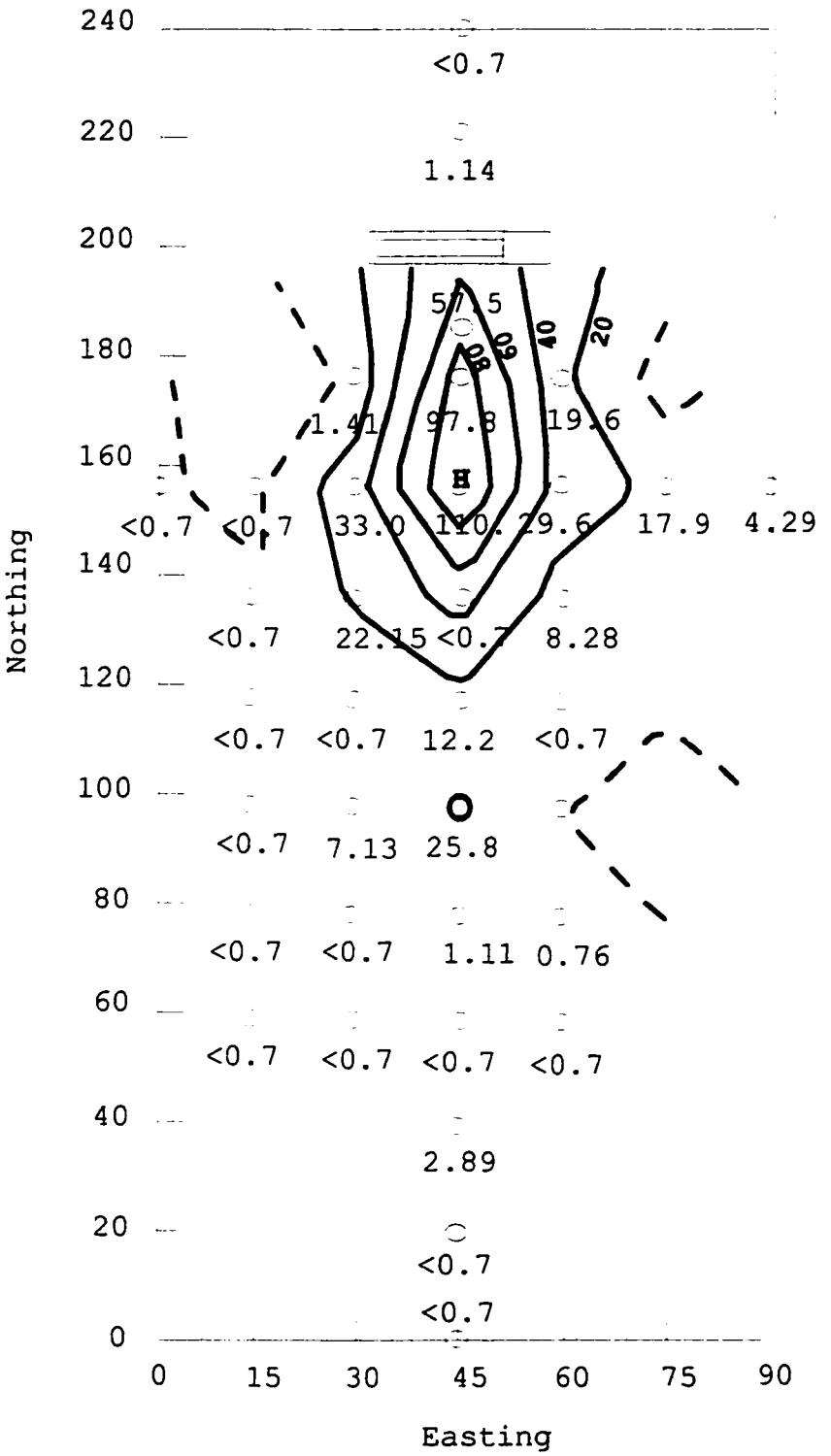


Figure 3-7. "Geo-Eas" contour map of As plume at the Payne's Prairie Bison Pen vat site.

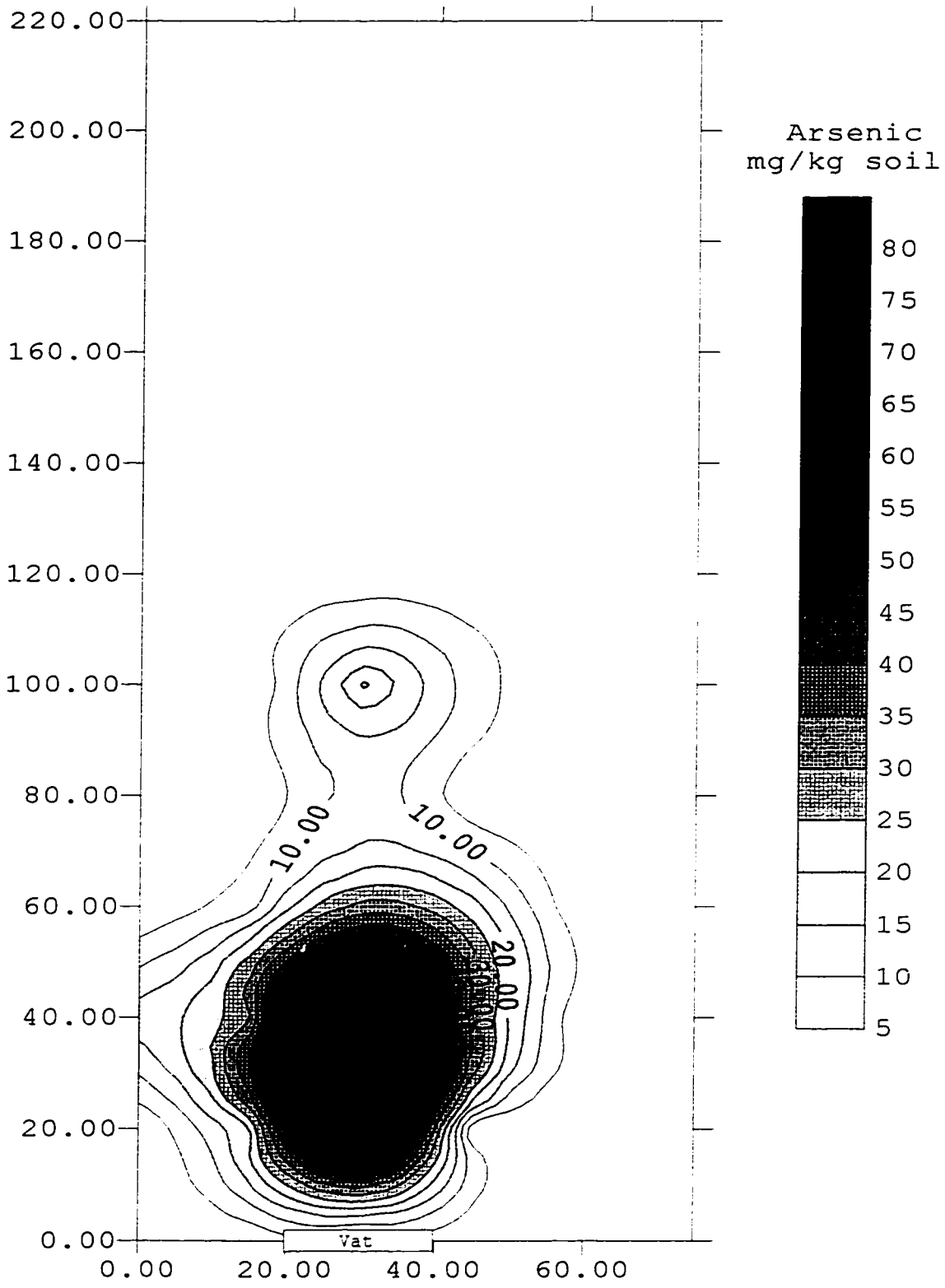


Figure 3-8. Two-dimensional "Surfer" contour map of As plume at the Payne's Prairie Bison Pen vat site. All distances measured in meters.

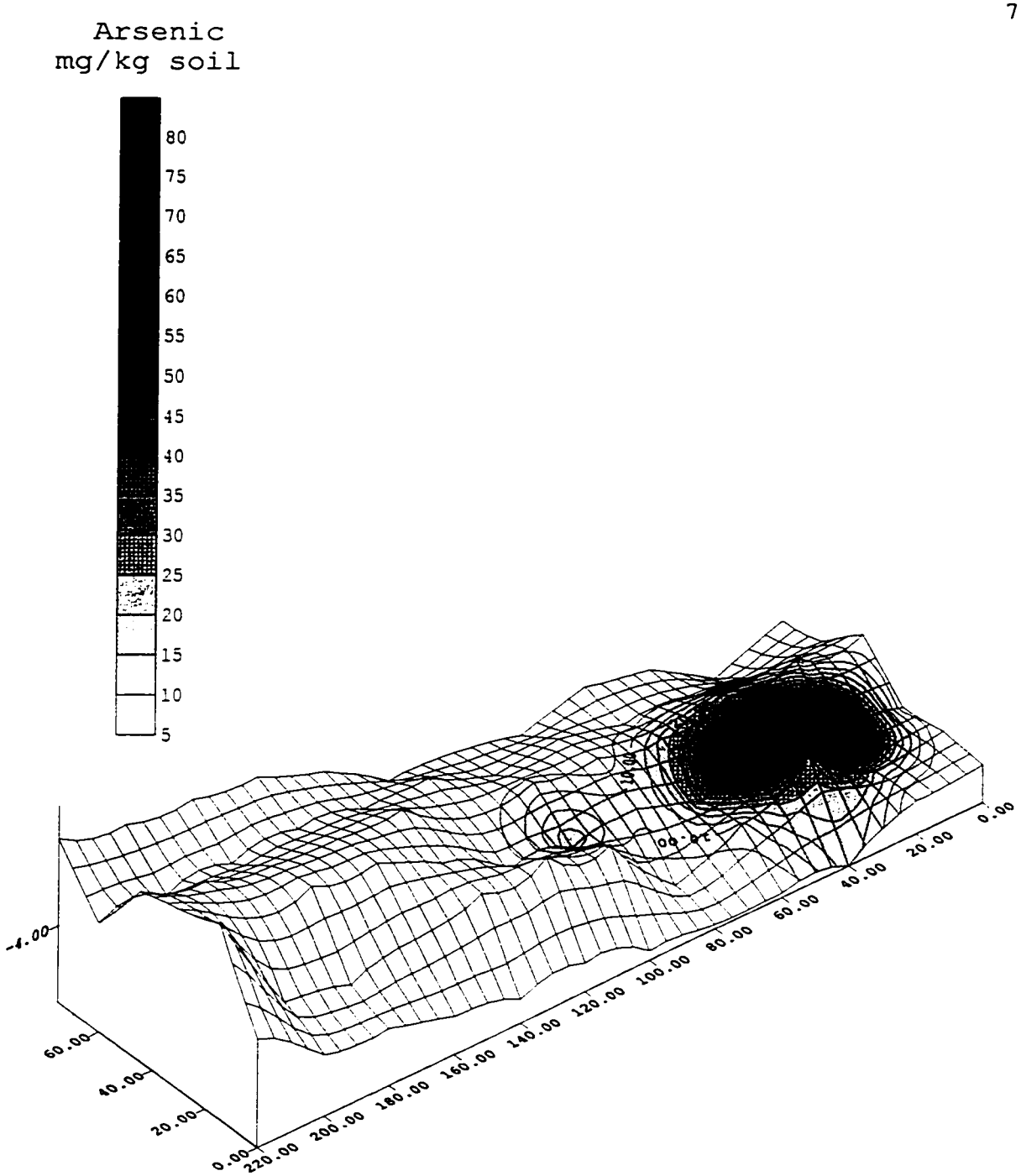


Figure 3-9. Three-dimensional "Surfer" map of the As plume across the argillic horizon at the Payne's Prairie Bison Pen vat site. All distances shown in meters.

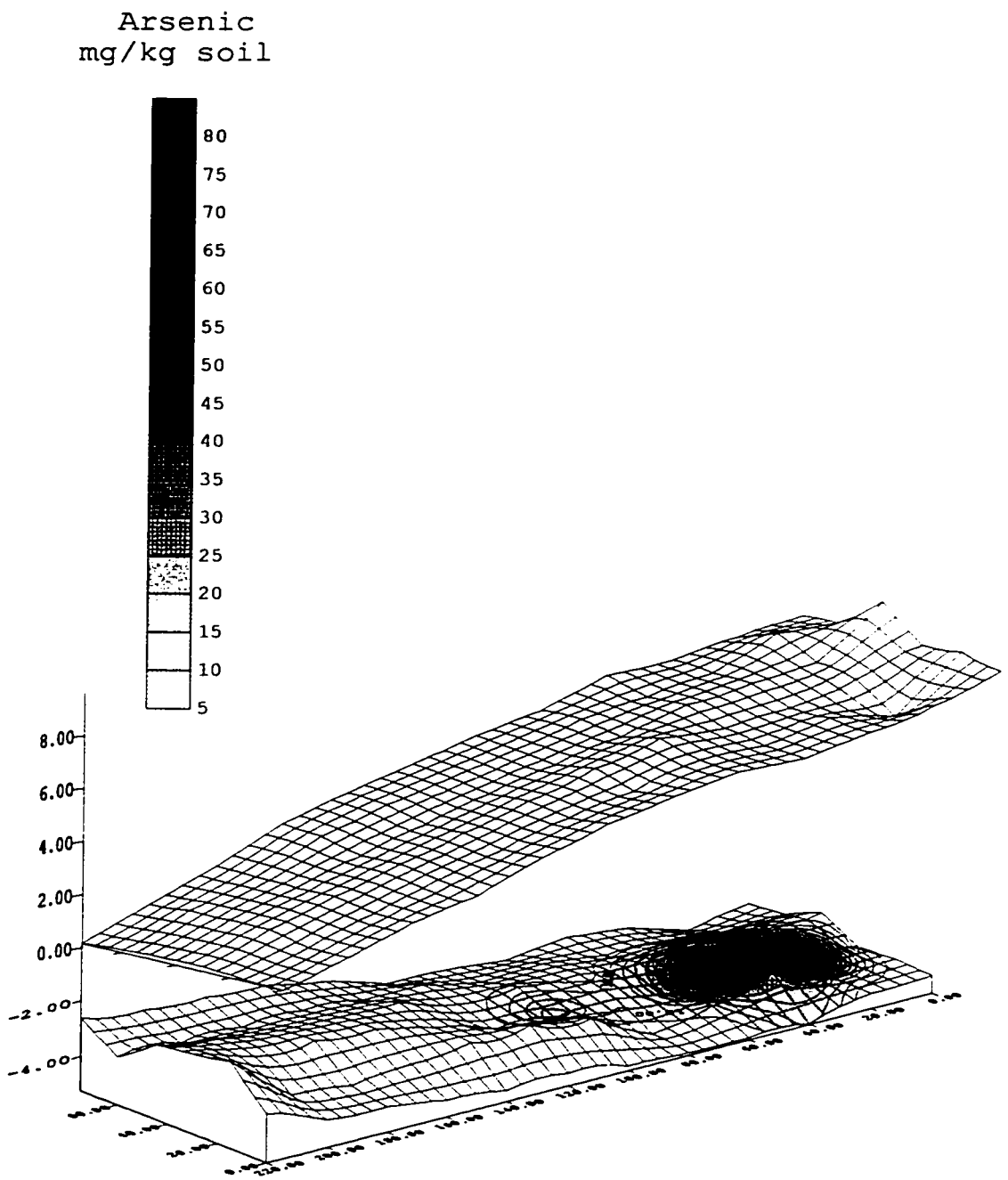


Figure 3-10. Three-dimensional map of As plume on the argillic horizon along with surface topography at the Payne's Prairie Bison Pen vat site. All distances measured in meters.

heavy brush on-site made surface contact with the radar unit difficult to maintain. Overall, the GPR allowed the argillic horizon to be mapped to a three-dimensional grid. Once the "dumbbell"-shaped contaminant plume was overlayed on this grid, it was easy to see that the "crests" and "valleys" of the argillic horizon actually determined the shape of the plume.

Payne's Prairie Williston Road Vat

Another vat at Payne's Prairie State Preserve that had its contaminant plume shape heavily influenced by the argillic horizon was located at 10205 S.W. Williston Road, Gainesville, FL. This vat was 90% intact, although there is currently a tree growing through the side of the vat (Figure 3-11). The soil survey map[53] (Figure 3-12) shows an area that is wooded; however, there is evidence (small or missing trees) that at one time it was at least partially clear-cut. Presently, the area has heavy (< 1 meter height) brush to dense thickets (>3 meter height). The heavy undergrowth prevented use of ground penetrating radar at this location, since good contact with the surface could not have been maintained. The contaminant As plume was mapped solely by soil sampling with either a 10-cm bucket auger or a 2.5 cm soil probe (Forestry Suppliers, Inc., Jackson, MS). The first 50 m were "bush-hogged" to allow for easy access. The soils found at this site were actually similar inclusions to those mapped, but did not match
the taxonomy rigorously. This area near the vat was mapped as

Figure 3-11. Photograph of the S.W. 10205 Williston Road vat.

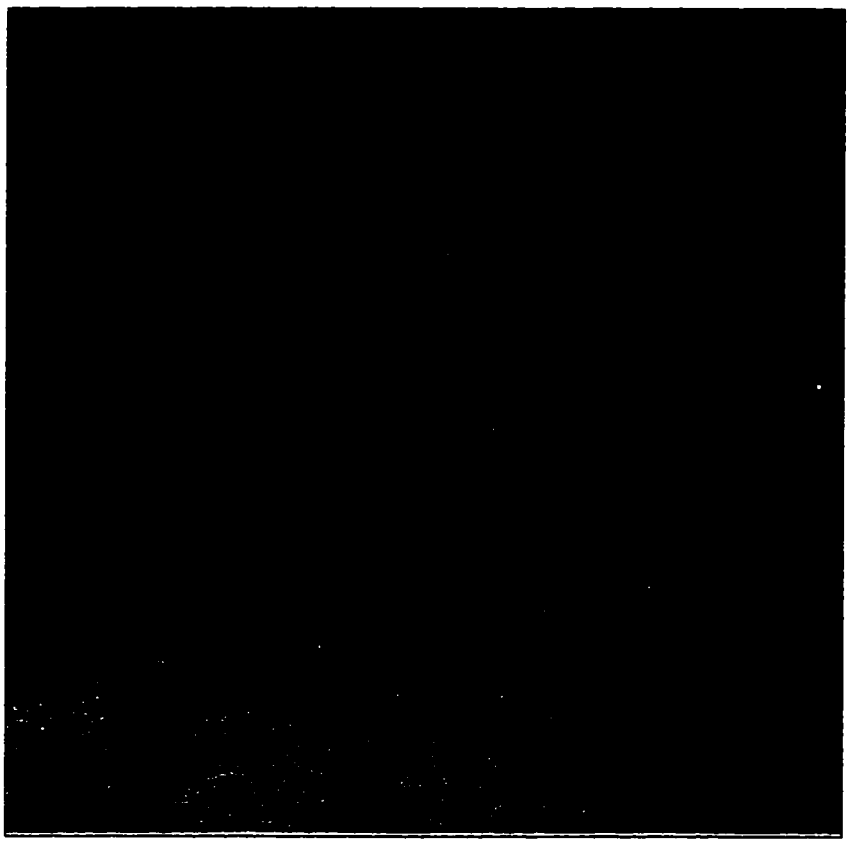


Figure 3-12. Soil survey map of the S.W. 10205 Williston Road vat site. Map unit designations: 3B Arredondo fine sand, 7B Kanapaha sand, 8B Millhopper sand, 19 Monteocha loamy sand, 20B Tavares sand, 28 Chipley sand, 50 Sparr fine sand, 52 Ledwith muck, and 59 Pottsburg sand.

Pottsburg sand.[53] Between 60 and 70 meters, the soil was described in the soil survey report as a Monteocha loamy sand.[53] The transects then extended into an area mapped as Wauberg sand. The soil actually found at this site did not match the taxonomy given for the map units. Inclusions of similar soil were identified. The soil mapped as Pottsburg sand was taxonomically an Aquod and the soil mapped as Wauberg sand was an Aqualf. The transects for the Aqualf had to be performed along lanes cut by machete, since this was where the dense thicket began (Figure 3-13). The particle size distribution for the Aquod and Aqualf soils as well as organic matter content, pH and As concentrations are given in Table 3-7. The surface, spodic and argillic horizons of all three soils were plotted in a three-dimensional grid (Figure 3-14A). What is not clearly shown in this area plot is how the Pottsburg and Monteocha soil map units overlap. In this transitional phase, the two spodic horizons do not intersect each other as one would surmise from the plot. The spodic horizon of the Aquod actually overlaid the Bh horizon of the soil mapped as Monteocha sand, and was separated from it by an E horizon located between the organic horizons. In fact, the Monteocha soil was never clearly identified as a separate soil in the field, although it is delineated on the soil survey map. The As contaminant plume's shape was influenced not only by the soil horizons composition, but also by the contours of these soil horizons. This is similar to the situation found at the Payne's Prairie Bison Pen Vat site. The maximum concentration

Figure 3-13. Photograph of the Williston Road vat's transect lane. Flag marks soil with greatest As concentration at this site.

Table 3-7. Selected characteristics of soils sampled at Williston Road vat site. These soils were located within the Pottsburg sand and Wauberg sand map units in the Alachua county soil survey and represent inclusions of similar soils.

Soil Taxonomic Class	Depth (cm)	Horizon	Dominant Munsell Color	Particle Size Distribution (%)			Organic Matter (%)	pH	Arsenic (mg As/ kg soil)
				Silt	Sand	Clay			
Aquod	0-15	Ap	10YR 5/1	0.6	98.0	1.4	0.75	4.8	---
	15-79	E	10YR 6/1	0.7	97.6	1.7	0.18	5.2	1.24
	79-113	Bh1	10YR 2.5/2	3.5	94.2	2.3	1.01	5.4	11.8
	113-135	Bh2	10YR 3/2	2.9	95.6	1.5	0.84	6.0	12.9
	135-147	Bt	10YR 4/2	8.3	84.4	7.3	0.49	6.4	12.4
	147-	Btg	10YR 4/1	1.7	82.2	16.1	0.24	7.2	---
Aqualf	0-30	A1	10YR 2.5/1	8.0	87.8	4.2	3.38	5.9	51.2
	30-46	A2	10YR 2.5/2	2.7	95.6	1.7	1.02	6.2	75.1
	46-114	Bw	10YR 3/3	3.3	95.6	1.1	0.45	6.4	60.1
	114-	Bt	10YR 4/2	2.8	75.0	22.2	0.37	6.4	99.6

[a] Soil sample was taken 12 meters northeast of vat.
[b] Soil sample was taken 68 meters northeast of vat.

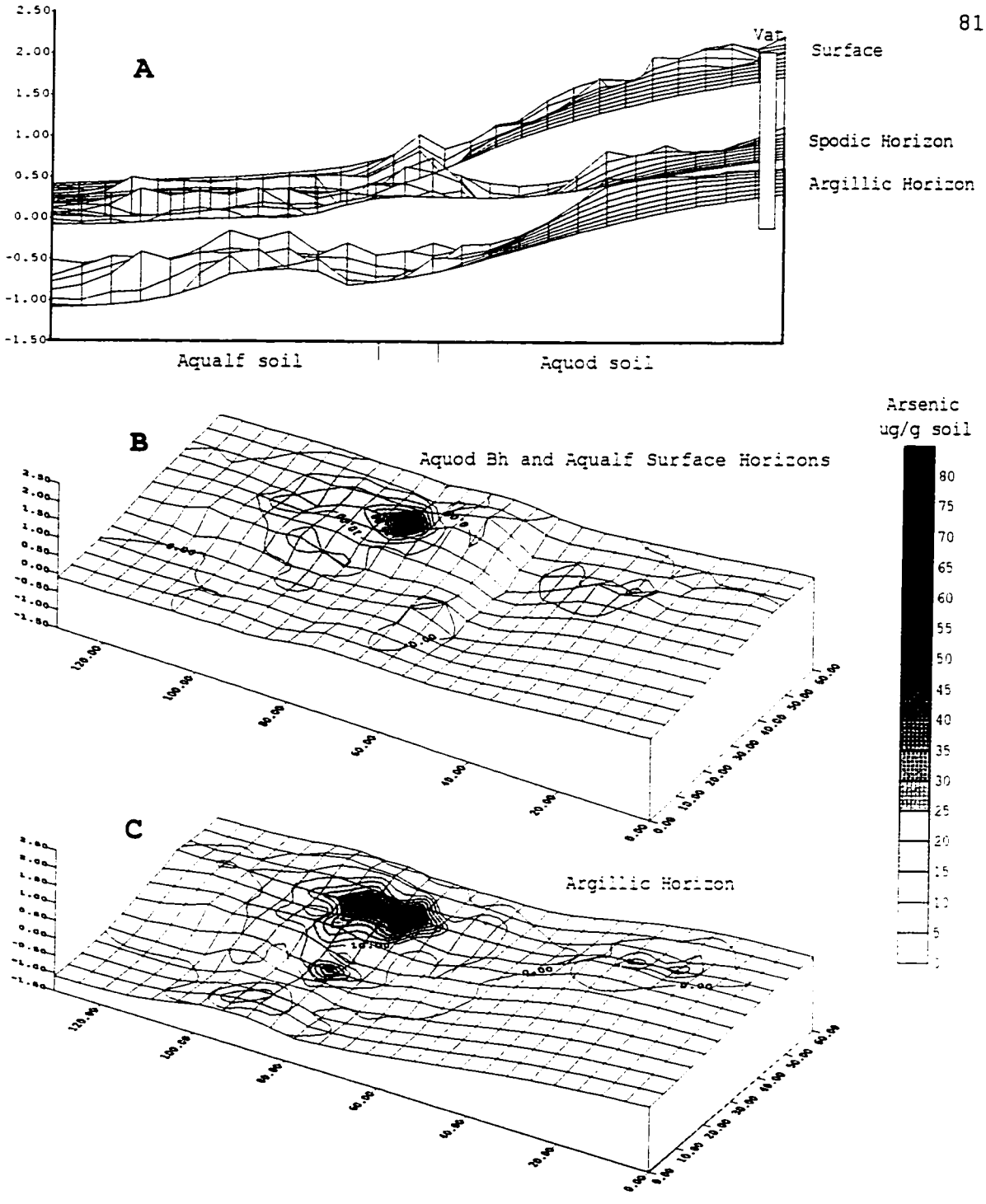


Figure 3-14. Soil horizons at the Williston Road vat site in terms of: a) a two-dimensional map of three horizons, b) the Aquod Bh horizon and Aqualf surface horizon with the As plume, and c) the argillic horizon with its As plume. All As concentrations were based on laboratory analysis. All distances are in meters.

of arsenic (Table 3-8) was found on top of the argillic horizon for the Aqualf soil; however, at this site, the arsenic had moved a greater distance from the vat (Figure 3-14C). The greatest amount of arsenic was located 80 m from the vat, almost twice as far as found at the Bison Pen vat site. The vat was located at coordinates of 15 by 40-50 on the grid map of Figure 3-14. The highest concentration of arsenic found in the Bh horizon was located directly above the spot on the argillic horizon that had the maximum amount of arsenic. The maximum concentration of As (99.6 mg/kg dry soil) in the argillic horizon was higher than the maximum concentration (30.1 mg As/kg soil) found in the spodic horizon. It was at this site that the As field test was first used extensively to delineate the contaminant plume. A typical scenario involved one person using a machete to blaze a transect, a second person measuring distance, sampling soil and keeping the transect straight (as well as parallel to the other transects), and a third person conducting the field test for arsenic. The transects were made only as long as absolutely necessary according to the field test results. This site required seven days for the three-man team to delineate the arsenic plume. The soil was sampled at the blackest section of the surface or spodic horizon and at the top of the argillic horizon. Only the upper Bh horizon was sampled in the area where overlaying spodic horizons were found. For comparison, the contour map of the field test was

Table 3-8. Selected metal concentrations in soil from Williston Road vat site.

Aquod soil				
Horizon[a]	Arsenic (mg As/kg soil)	Iron (mg Fe/kg soil)	Aluminum (mg Al/kg soil)	Manganese (mg Mn/kg soil)
Ap	---	111.2	1854.	6.55
E	1.24	169.8	2488.	---
Bh1	11.8	658.6	11103.	5.24
Bh2	12.9	412.7	7230.	---
Bt	12.4	2060.	2864.	2.62
Aqualf soil				
Horizon[b]	Arsenic (mg As/kg soil)	Iron (mg Fe/kg soil)	Aluminum (mg Al/kg soil)	Manganese (mg Mn/kg soil)
A	51.2	372.	2863.	7.86
A2	75.1	500.	1761.	7.86
Bw	60.1	336.	1455.	2.62
Btg	99.6	1191.	9507.	2.62

[a] Soil sample was taken 12 meters northeast of vat.
[b] Soil sample was taken 68 meters northeast of vat.

placed adjacent to the contour map of the laboratory analysis for Aquod Bh and Aqualf surface horizons as well as for the argillic horizon (Figures 3-15 and 3-16, respectively). The field test had an upper limit of 37.5 mg As/kg soil. Any soil containing As above this level would yield a colorimetric response (black) that gave no indication of the actual As concentration. Since the field test was based on a crude colorimetric comparison, the concentrations found were somewhat rough estimates. However, the field test was performed on a 1:10 dilution while the laboratory analysis involved a 1:100 dilution during the digestion procedure. Because of this, the overall shape of the plume as shown by the field test may be a more accurate depiction; whereas, the concentrations given by the laboratory analysis would certainly be more accurate.

The greater movement of the As plume at this site, compared to the Bison Pen Vat site, is probably due to the presence of the Bh horizons, which were absent at the first site. The greater migration of the arsenic plume at the second site might be due to the spodic horizon inhibiting the downward flux of arsenic by causing a perched watertable which would have allowed the arsenic to travel laterally. Alternatively, the influx of organic compounds down to the argillic horizon may have facilitated volatilization of the As by stimulating microorganism growth and thus, allowed lateral

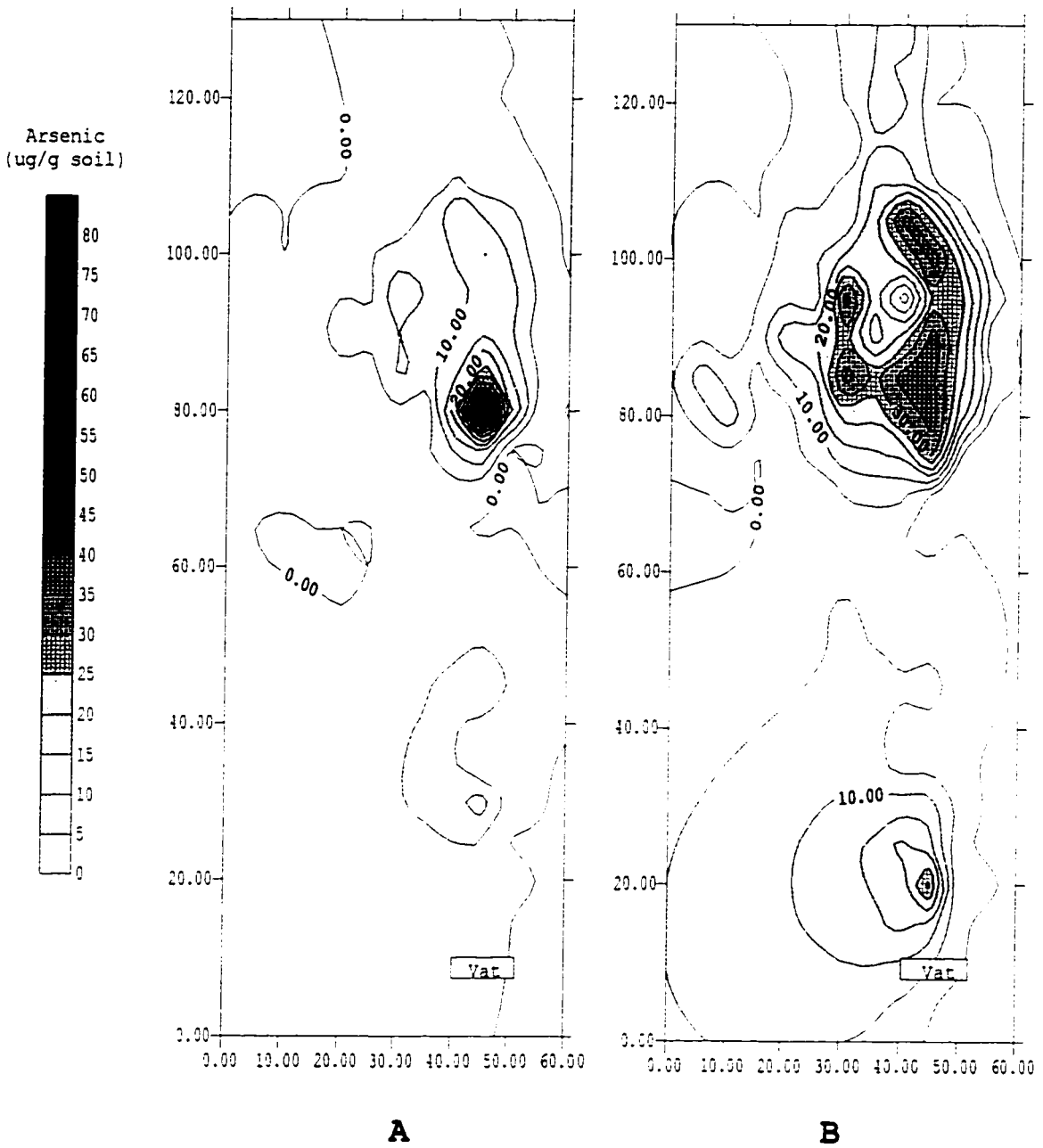


Figure 3-15. Contour maps of As on Aquod's Bh horizon and Aqualf's surface horizon of the Williston Road vat using: a) the laboratory analysis versus b) the field test. All distances are in meters.

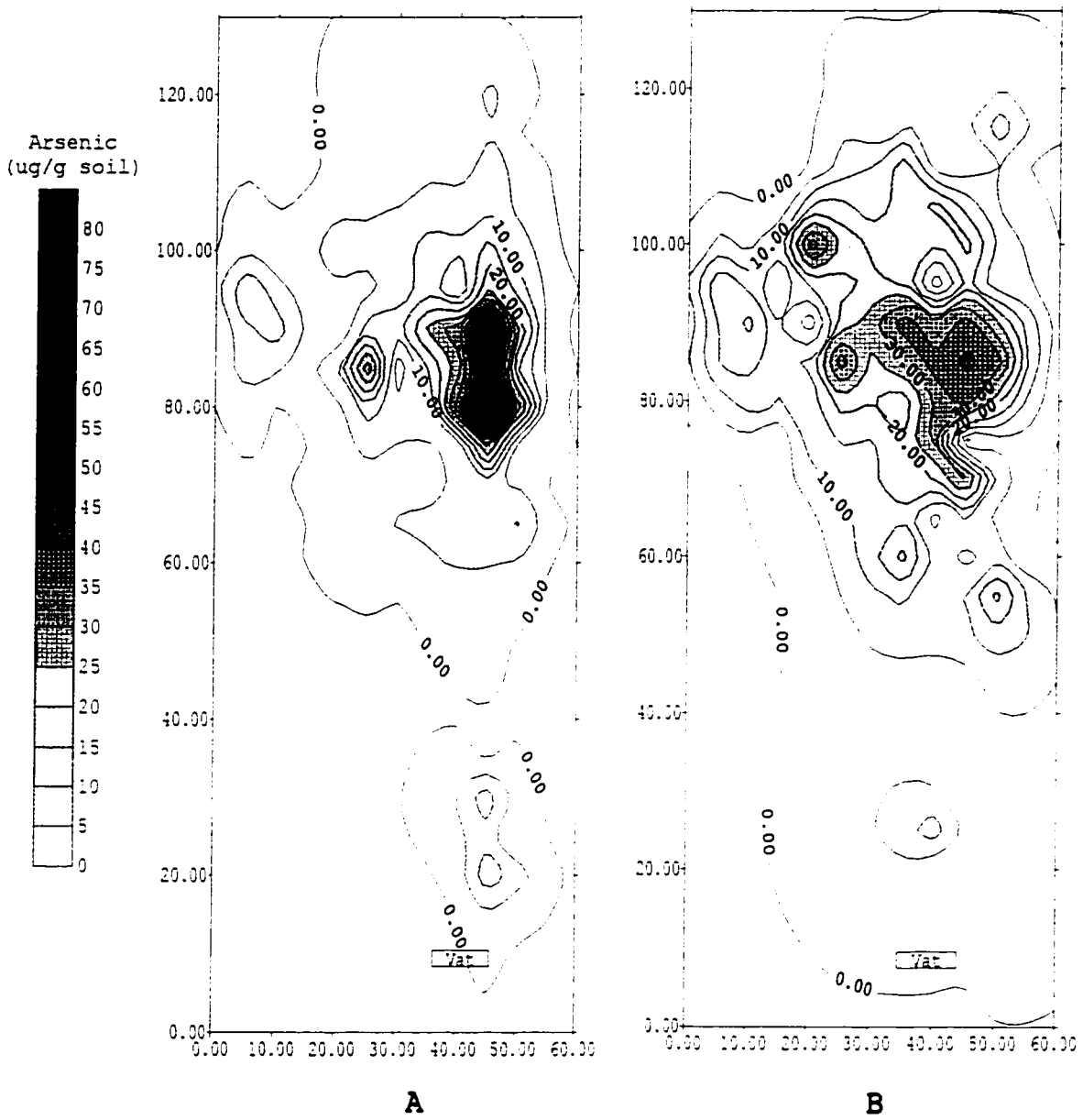


Figure 3-16. Arsenic on argillic horizon's contour maps of the Williston Road vat using: a) laboratory analysis versus b) the field test. All distances are in meters.

movement of arsenic in gaseous form to occur; hence, the plume migrated further. It will be demonstrated later in this dissertation that subsurface volatilization of As did occur at both of these sites. As such, it may be a contributing factor in the movement of arsenic through the soil.

Dudley Farm Vat

In contrast to the Williston Road Vat site, the Dudley Farm Vat site had a plume which was laterally confined on one side by a large limestone formation. However, this vat site had a plume depth that was significantly greater than found at the two other sites previously discussed. Lateral dimensions of the plume had been previously mapped by the firm of Woodward-Clyde Consultants (Tallahassee, FL).[4] This vat remained in good shape, with the most damage occurring from the collapse of the splash wall (Figure 3-17). The in-ground walls were intact and the vat still contained water. This water was tested for As, but concentrations were below the analytical detection limit of 8.0 μg As/mL solution. Water from a well located 46 meters east of the vat was sampled and analyzed, but no As was detected. The Woodward-Clyde Consultants had already delineated the arsenic plume at this site for the Florida Department of Environmental Protection.[19] The surface and subsurface data for this site were depicted on site maps in Appendix B. The soil around the vat was mapped

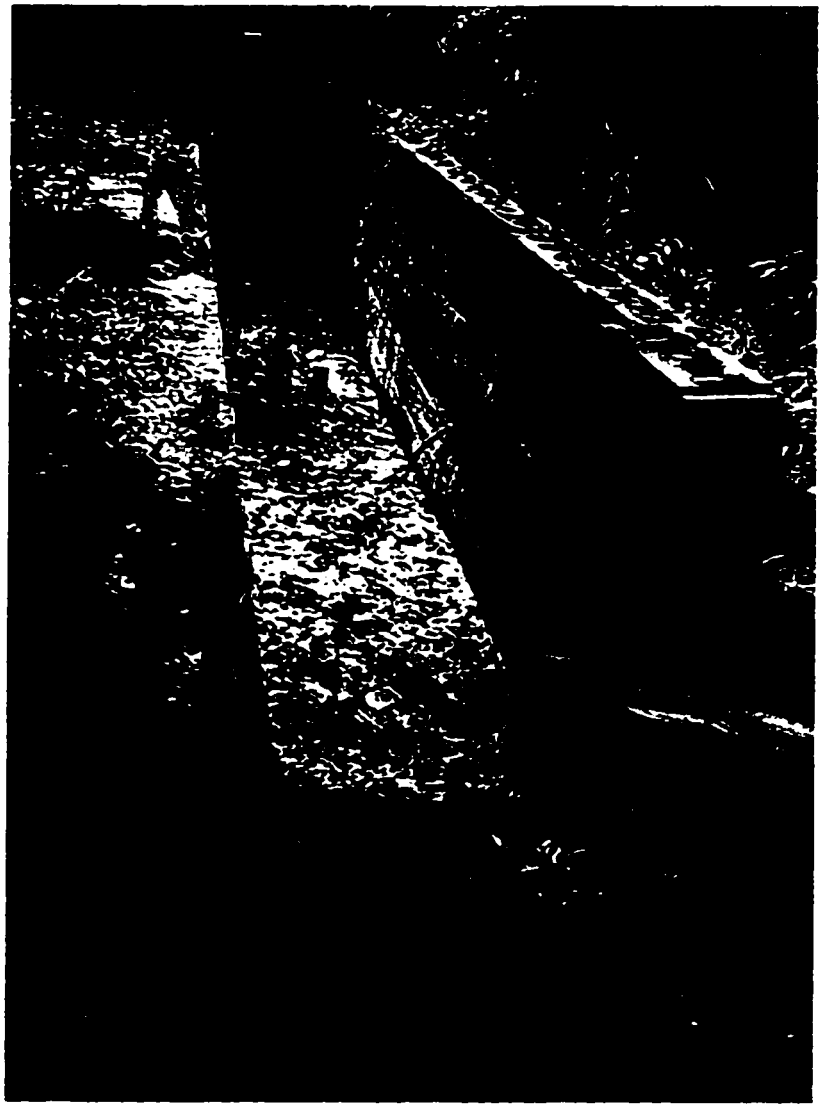


Figure 3-17. Photograph of the Dudley Farm vat.

as a Bonneau fine sand (Figure 3-18). As shown in Table 3-9, these soils tend to be slightly acidic, with organic matter content greatest for the surface (0-36 cm) soil. The soils from the lower depth contained redoxymorphic features and red concretions. The surface topography was mapped (Figure 3-19) and As was analyzed to a 5 cm depth. To the south of the vat there is a sinkhole (Figure 3-20) that might have constituted a problem if the arsenic contaminant plume had reached it. Some As (0.8 μg/g soil) was detected on the road outside the gate leading from the vat towards the sinkhole. This was probably tracked there by humans or cattle, although transport by erosion could not be excluded. More As (1.9 μg/g soil) was found approximately 30 meters south of the vat. The probable source of this contamination was from the copper-chromate-arsenate (CCA) pressure-treated fence posts that were stacked in a pile at this location. In general, the Woodward-Clyde data and the surface soil analysis indicate that the arsenic contaminant plume is moving to the west towards the undeveloped pasture rather than towards the homestead to the east or towards the sinkhole to the south. Vertical movement of the As was investigated by utilizing a truck-mounted drill unit. It was generously supplied by the Florida Department of Environmental Protection test(D.E.P.) and operated by Mr. Lee Booth of D.E.P.'s Waste Management Division. All holes were back-filled with "Dolomite" mixed with soil taken from the

Figure 3-18. Soil survey map of the Dudley Farm vat site. Map unit designations: 3B Arredondo fine sand, 8B Millhopper sand, 29B Lochloosa sand, 33B Norfolk loamy fine sand, and 39B Bonneau fine sand.

Table 3-9. Selected characteristics of soil 2.3 meters east of the Dudley Farm vat.

Soil Taxonomic Class	Depth (cm)	Horizon	Dominant Munsell Color	Particle Size Distribution (%)			Organic Matter (%)	pH	Arsenic (mg As/ kg soil)
				Silt	Sand	Clay			
Udult	0-36	Ap	10YR 3/2	5.4	91.2	3.4	1.79	5.4	74.5
	36-66	E	10YR 5/2	4.2	91.2	4.6	0.63	7.1	108.
	66-112	Bt1	10YR 6/3	5.2	82.2	12.6	0.36	7.1	73.7
	112-147	Bt2	10YR 6/2	5.4	78.4	16.2	0.23	7.0	356.
	147-197	Bt3	10YR 6/2	3.9	68.4	27.7	0.25	5.4	525.
	197-	Btg	10YR 6/1	4.3	68.4	27.3	0.22	5.3	767.

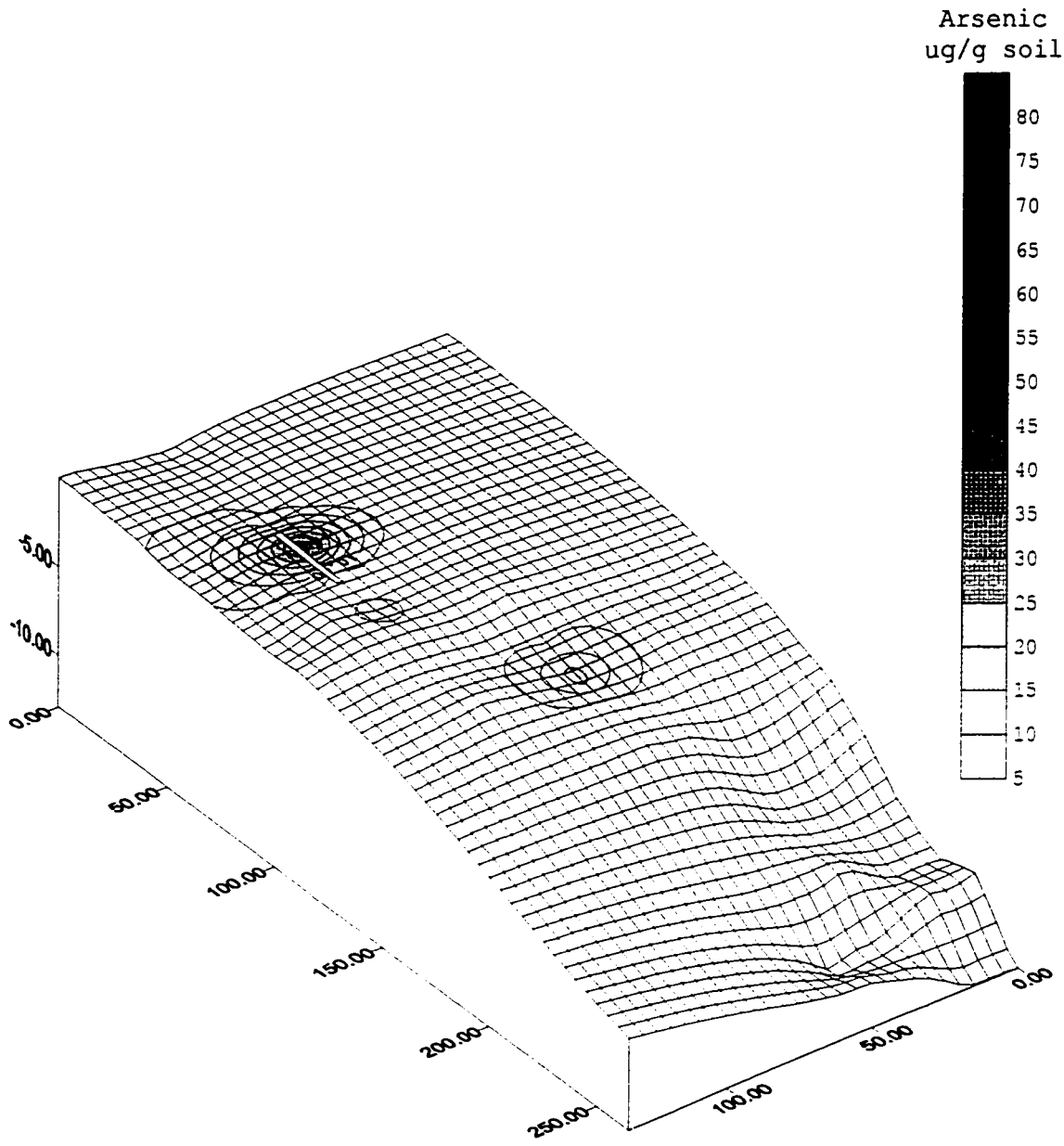


Figure 3-19. Surface map of the Dudley Farm site with arsenic plume. All distances are measured in meters.

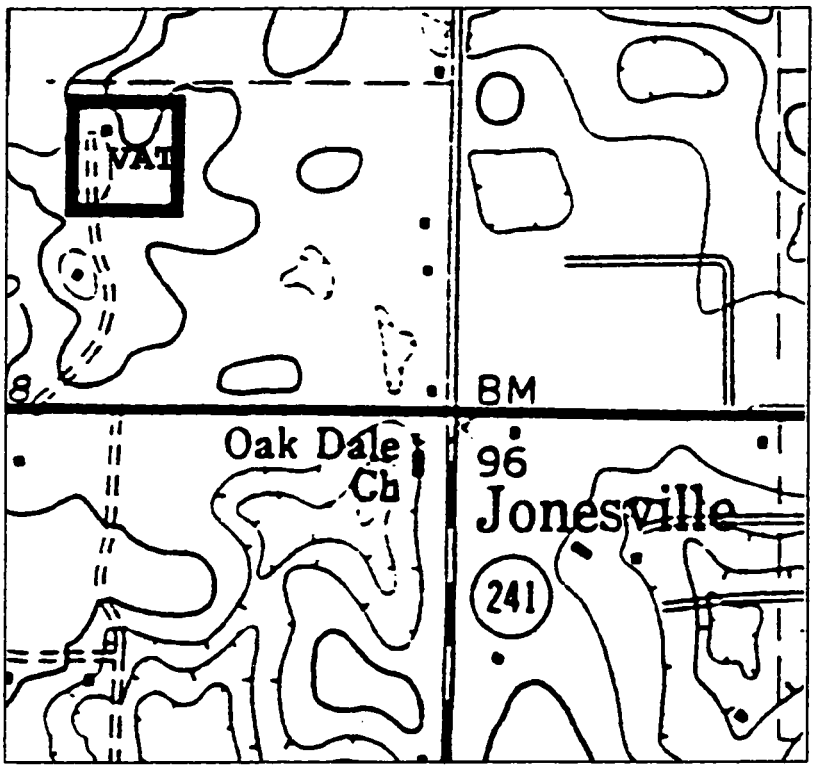


Figure 3-20. Topographical map of the Dudley Farm vat site.

holes, minus the soil samples (≈10 g each), which were kept for laboratory analysis. Lateral movement exceeded vertical movement of the contaminant. The As field test was done on samples taken 1.8 meters east of the vat. Results of the laboratory analysis and the field test are presented graphically in Figure 3-21. The greatest As concentration was 356 μg As/g soil at a depth of 1.2 meters. This is the depth where soil clay content noticeably increases. It is interesting to note that As concentration tended to increase and decrease in "waves" as the depth increases. One hypothesis that would explain this finding invokes the idea that the vats were to be emptied on an annual basis and that the "waves" provide physical evidence of the dumping pattern. Since no records were kept on the vat's operation, such hypotheses cannot be tested. Drilling verified the presence of As to a depth of 6.8 meters. The depth increments used in Figure 3-21 do not represent all of the soil horizons sampled at this site. If As is analyzed by soil horizon (Table 3-10) then it is apparent that, similar to the previous vats investigated, presence of the argillic horizon is associated with an increase in the amount of As detected in the soil. Unlike the previous vat sites, the Dudley Farm's argillic horizon did not appear to constitute a barrier to the downward migration of As.

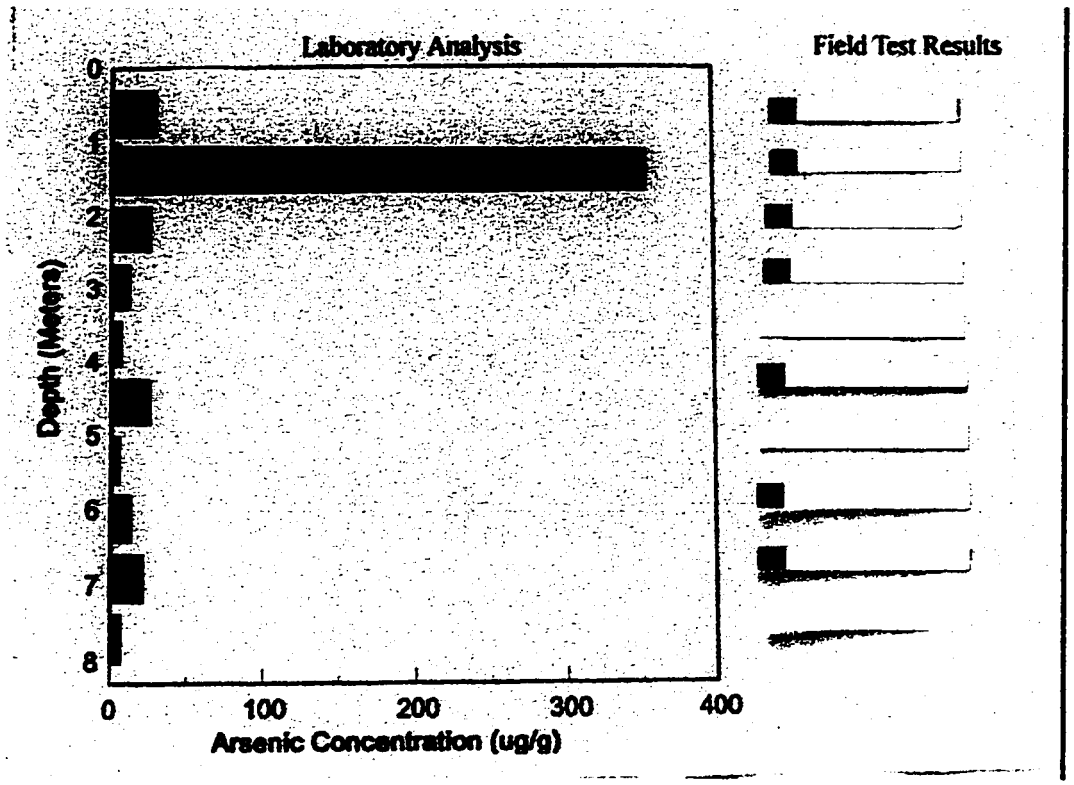


Figure 3-21. Field test strips and laboratory analysis results for Dudley Farm vat soil by depth.

Table 3-10. Selected metal concentrations in soil 2.3 meters east of the Dudley Farm vat.

Horizon	Arsenic (mg As/kg soil)	Iron (mg Fe/kg soil)	Aluminum (mg Al/kg soil)	Manganese (mg Mn/kg soil)
Ap	74.5	119.1	333.3	5.2
A	108.	170.6	356.8	2.8
Bw	73.7	109.4	507.0	2.1
Bt1	356.	231.8	650.2	0.7
Bt2	525.	299.4	1704.2	0.5
Btg	767.	766.3	1239.4	0.2

University of Florida Foundation Vat

In contrast to the Dudley Farm site, the U.F. Foundation vat is highly disturbed to the point of virtual non-existence. The vat itself, as well as a nearby barn, have been removed from the site. The hole where the vat was located has been back-filled with soil. Occasional pieces of concrete rubble and a report prepared for the U.F. Foundation by CH_2M Hill Engineering (Gainesville, FL) are the only gross physical evidence of where the vat was located.[76] On the other hand, chemical analysis of the soil revealed the presence of organic contaminants such as Toxaphene and DDT along with its associated degradation products. Arsenic was also found by CH_2M Hill up to a maximum of 37.6 mg As/kg soil. The concrete rubble, along with the CH_2M Hill report, place the vat at the top of a hillside (Figure 3-22). The soil survey map (Figure 3-23) and actual soil sampling with a 10-cm bucket auger indicated that the soil classification was actually a similar soil inclusion to Lochloosa fine sand. The soil physical characteristics showed that the clay content increases sharply at a depth of 149 centimeters (Table 3-11). Similar to the previous vat sites, the increase in clay content was reflected by an increase in the As concentration (Table 3-12). The argillic horizon at this site exhibited strong redoximorphic features. A red mottle was separated from the surrounding Bt soil and acid digested. Subsequent metal analysis revealed

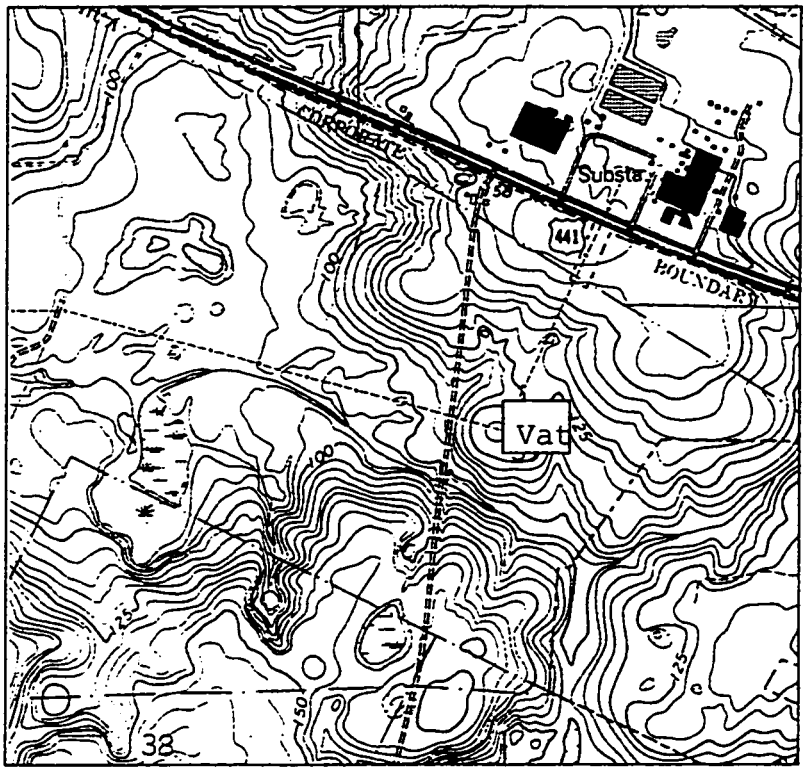


Figure 3-22. U.S.G.S. topographical map of the U.F. Foundation excavated vat site.

Figure 3-23. Soil survey map of the U.F. Foundation excavated vat site. Map unit designations: 5B Fort Meade fine sand, 7B Kanapaha sand, 8B Millhopper sand, 13 Pelham sand, 14 Pomona sand, 29B Lochloosa fine sand, and 31C Blichton sand.

Table 3-11. Selected characteristics of soil 0.9 meters north of the excavated U.F. vat. These soils were located within the Lochloosa fine sand map units in the Alachua county soil survey and represent inclusions of similar soils.

Soil Taxonomic Class	Depth (cm)	Horizon	Dominant Munsell Color	Particle Size Distribution (%)			Organic Matter (%)	pH	Arsenic (mg As/ kg soil)
				Silt	Sand	Clay			
Udult	0-23	Ap	10YR 4/4	3.7	89.4	6.9	0.3	6.2	26.9
	23-121	E1	10YR 5/4	4.0	92.6	3.4	0.1	6.2	7.7
	121-149	E2	10YR 4/3	3.5	93.8	2.7	0.0	6.3	2.7
	149-170	Bt	10YR 5/3	4.4	80.8	14.8	0.0	6.6	33.8
	170-	Btg	10YR 4/2	4.0	77.8	18.2	0.0	6.7	24.3

Table 3-12. Selected metal concentrations in soil 0.9 meters north of U.F. vat.

Horizon	Arsenic (mg As/kg soil)	Iron (mg Fe/kg soil)	Aluminum (mg Al/kg soil)	Manganese (mg Mn/kg soil)
A	26.9	261.	711.	3.0
E1	7.7	173.	505.	2.0
E2	2.7	116.	255.	1.0
Bt	33.8	412.	1037.	1.0
Btg	24.3	320.	1197.	1.0

that aluminum (1577 mg/kg) and iron (1697 mg/kg) were higher than for the surrounding soil. Of particular interest is the fact that the As analysis detected 68.2 mg As/kg, which is more than double the amount found in the Bt soil matrix. This was a strong indication that the arsenic was associated with the ferric and aluminum oxides/hydroxides evident in these redoximorphic features.

Jackson's Gap Vat

This vat was located in the Payne's Prairie State Preserve. It was similar to the previous (U.F. Foundation) vat in that the only gross physical evidence of its prior existence was the concrete rubble and a report from a consulting firm. The consulting firm of Woodward-Clyde, Inc. evaluated the contamination at this site in 1994 and published its findings in a report for the Florida Department of Environmental Protection.[4] Based on their prioritization scheme, this site was rated last in terms of relative hazard out of the twelve sites that they investigated. The rationale for this rating was based on restricted access, a low level of contamination, and other risk assessment factors. The location relative to Gainesville is shown in Figure 3-6. The soil map (Figure 3-24) and the topographical map (Figure 3-25) are the only additional data supplied in this dissertation. The soil was mapped as a Millhopper sand, with no further study being done at this site.

Figure 3-24. Soil survey map of the Payne's Prairie Jackson's Gap vat site. Map unit designations: 3B Arredondo fine sand, 8B Millhopper sand, 14 Pomona sand, 16 Surrency sand, 19 Monteocha loamy sand, 20B Tavares sand, 21 Newnan sand, 31B,C,D Blichton sand, and 50 Sparr fine sand.

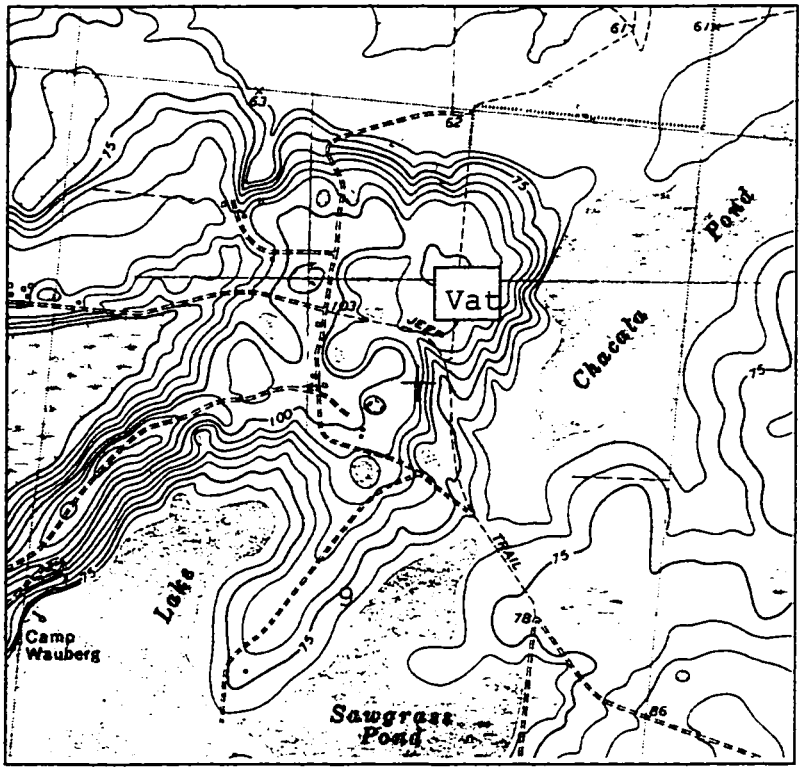


Figure 3-25. U.S.G.S. topographical map of the Payne's Prairie Jackson's Gap vat site.

Payne's Prairie South Rim Vat

This site is located within Payne's Prairie on Tavares sand. The As field test was used to analyze soil down to a depth of 249 cm. At no point along this soil core was arsenic detected above background soil levels. Although some small redoxymorphic features were present, no elevated As concentrations were detected within these red mottles. This vat remains in relatively good shape, although when it was investigated there was no standing water in it. The bottom of the vat contained plant detritus; hence, no visible cracks in the vat could be discerned. The soil map (Figure 3-26) shows the area to be heavily wooded. There is a depression located within a hundred meters of the vat, although this is not clearly depicted on the topographical map (Figure 3-27).

Payne's Prairie US 441 Vat

The last vat located inside Payne's Prairie State Preserve to be included in this dissertation is located along U.S. Highway 441. The soil map (Figure 3-28) listed the soil as Sparr fine sand. The topographic map (Figure 3-29) depicts the vat as being located on the edge of a sharp slope. There was a dry well located halfway down this slope and, at the bottom of the slope, some very old pier pilings. It was conjectured that this site might have been a docking area before Lake Alachua (Payne's Prairie) was drained. The vat structure remains in good shape, with murky water containing

Figure 3-26. Soil survey map of the Payne's Prairie South Rim vat site. Map unit designations: 3B Arredondo fine sand, 8B Millhopper sand, 14 Pomona sand, 16 Surrency sand, 19 Monteocha loamy sand, 20B Tavares sand, 21 Newnan sand, 31B,C,D Blichton sand, and 50 Sparr fine sand.

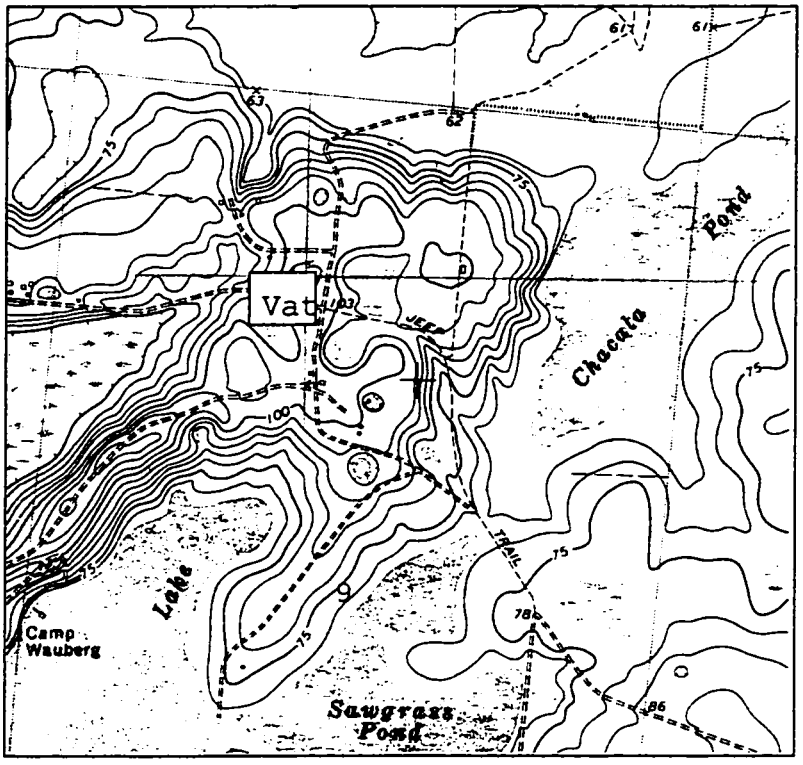


Figure 3-27. U.S.G.S. topographical map of the Payne's Prairie South Rim vat site.

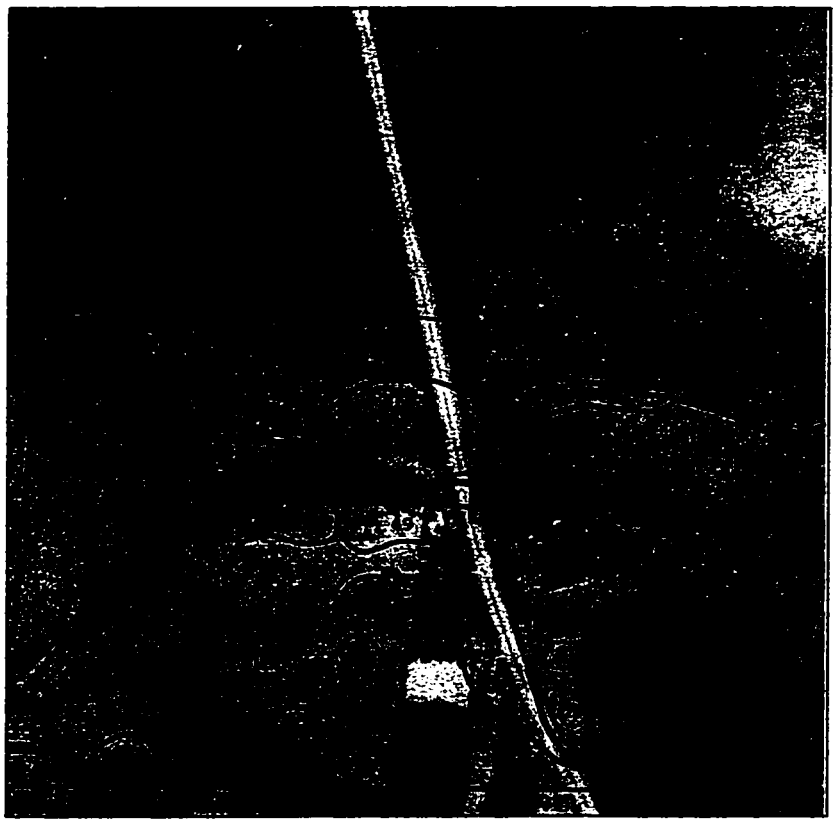


Figure 3-28. Soil survey map of the Payne's Prairie U.S. 441 vat site. Map unit designations: 16 Surrency sand, 17 Wauchula sand, 19 Monteocha loamy sand, 29c Lochloosa sand, 31c Blichton sand, 49 Lochloosa fine sand, 50 Sparr fine sand and 52 Ledwith muck.

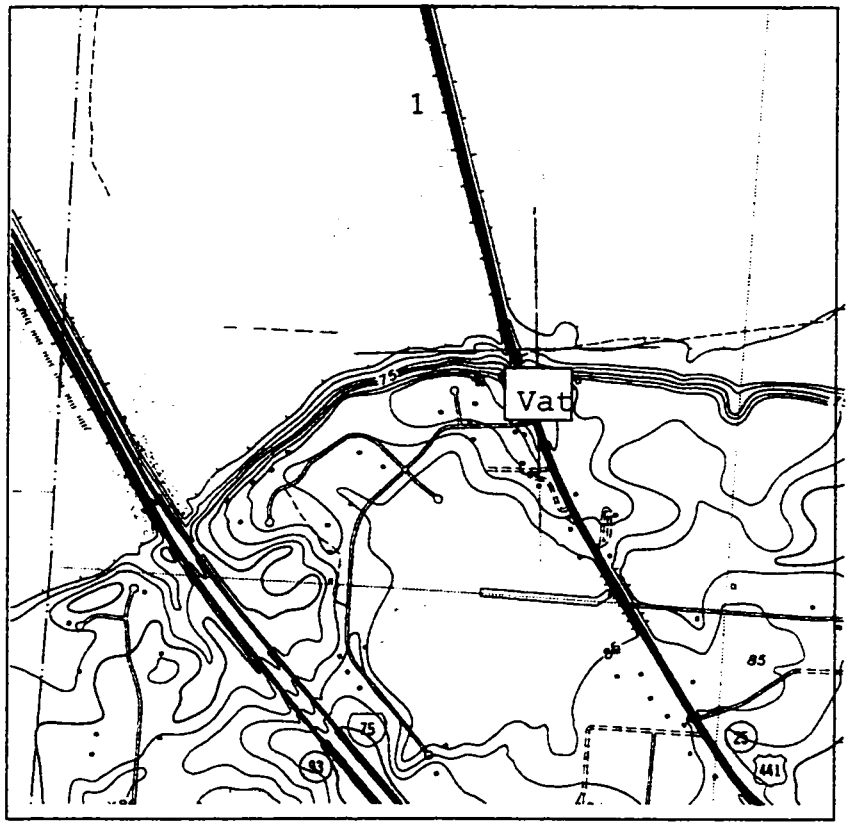


Figure 3-29. U.S.G.S. topographical map of the Payne's Prairie U.S. 441 vat site.

plants and algae. Five mL of water were tested using the As field test. The As concentration was at the lowest colorimetric detection limit of 0.1 mg As/L water. Soil samples taken at the 60 cm depth for both 0.99 m west and 0.58 m east of the vat exceeded the limits (>37.5 mg As/kg soil) of the colorimetric test. Soil samples 3.7 meters west of the vat and at depths of 30 and 43 cm tested at 17.5 mg As/kg soil. No further assessment was made on the soil at this site.

Tuscawillow Vat

This site had a vat which remained in good structural shape with standing water. It was located outside the Micanopy city limits, adjacent to the Tuscawillow Prairie. This vat was fenced and on private property, so only the location and condition of the vat could be confirmed from the public roadside. The soil map (Figure 3-30) shows a small stand of trees that surround the vat. The soil map gives the location as occupied by soil belonging to the Kanapaha series. Topography around the vat is low-lying and nearly level (Figure 3-31).

Marion County Vat

The final vat investigated was located in nearby Marion County. This vat was privately owned. The owner was gracious in allowing us to complete a cursory examination of

Figure 3-30. Soil survey map of the Tuscawillow vat site. Map unit designations: 7B Kanapaha sand, 8B Millhopper sand, 14 Pomona sand, 18 Wauchula-Urban land complex, 21 Newnan sand, 23 Mulat sand, 29B Lochloosa fine sand, 31B Blichton sand, and 56 Wauberg sand.

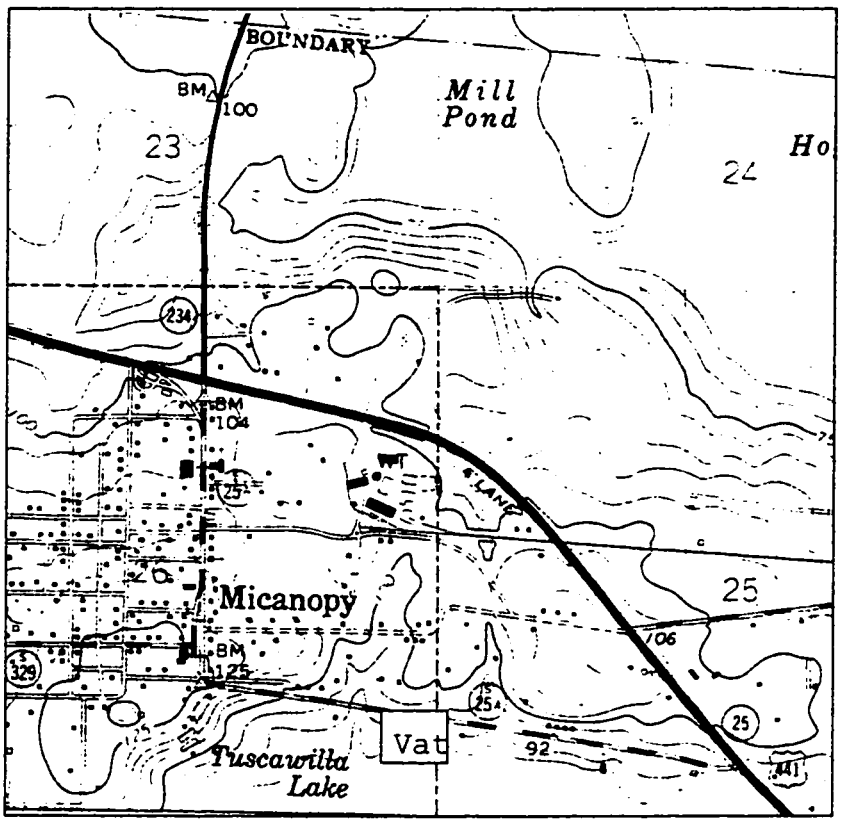


Figure 3-31. U.S.G.S. topographical map of the Tuscawillow vat site.

the vat. The vat had been constructed using material apparently garnered from a nearby railway bed. It was filled with soil and only the tops of two sides could be seen. The owner of the property gave anecdotal evidence that the vat had been constructed by black cowboys who worked for one of his ancestors. The soil survey map (Figure 3-32) depicted this soil as a Blichton sand and hand-augured soil samples supported this listing. Soil samples taken 1 m east of the vat and at a depth of 64 cm contained at least 37.5 mg As/kg soil. Four meters to the east of the vat only the upper 15 centimeters of soil contained this much As and, at a depth of 50 cm, the As concentration had fallen to 18.7 mg As/kg soil according to the As field test. A well was located ≈60 meters away from the vat and reportedly drawing water from 22 meters deep. No As was detected in the water from this well by the arsenic field test. The topographical map (Figure 3-33) shows that the vat is located on the slope of a hill. The zone of As contamination was apparently moving downhill and parallel to the well.

Reported Vat Sites

A summary of the vat sites reported by state-contracted consultants[4], along with each vat location's county, possible soil map units and their taxonomic families are given in Table 3-13. Raw data for these sites are given on site maps in Appendix B.

Figure 3-32. Soil survey map of the Marion County vat site. Map unit designations: ArB Arredondo sand, BcB Blichton sand, BoC Boardman loamy sand, FeC Fellowship loamy sand, FgC Fellowship gravelly loamy sand, FmB Flemington loamy sand, KeB Kendrick loamy sand, LoB Lochloosa fine sand, SpB Sparr fine sand, WgB Wacahoota gravelly sand, and ZuC Zuber loamy sand.

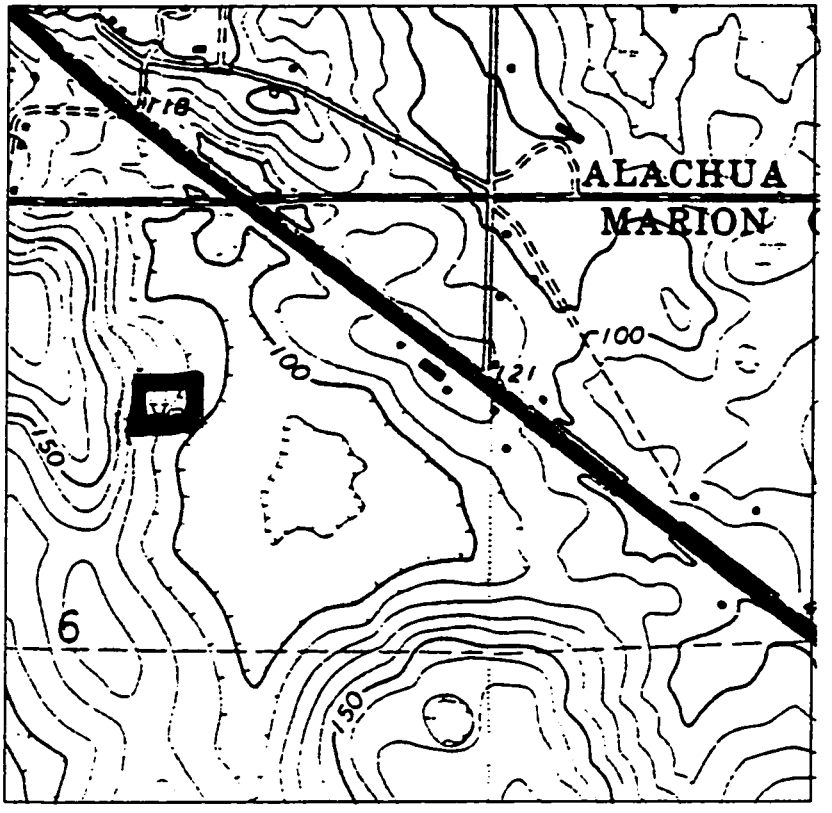


Figure 3-33. U.S.G.S. topographical map of the Marion County vat site.

Blackwater River State Forest Vat

The Blackwater River vat is located in Santa Rosa County, Florida. Due to the scale of the topographical map (Figure 3-34), it is not possible to accurately place the vat on the soil survey map (Figure 3-35).[55] The possible soil series are mapped as Orangeburg, Bonifay or Troup. All of these soils are Paleudults. The argillic horizon depth may vary from 36 cm (Orangeburg) to 119 cm (Bonifay) to 140 cm (Troup). An actual sampling of the soil at this site is the only way to confirm the soil series. Regardless of which of these three soil series is found, the highest As concentration will be found in or on the "Bt" horizon. The sampling plan executed by the consulting firm was performed at pre-set depth intervals determined prior to visiting the site. It is quite likely that the highest concentration in the soil profile was missed, since the soil structure at the site was ignored in favor of simplicity and consistency. The highest As concentrations found at this site were 340, 370 and 320 mg As/kg soil. The general movement of the plume appears to be southwest from the drip pad.

Cecil Webb Vat

The Cecil Webb vat was located in Charlotte County, FL. The topographical map showed the vat site as level with a preponderance of wet areas surrounding it (Figure 3-36).

Table 3-13. Soil map units and taxonomic classes for reported cattle dipping vat sites.

Site/County	Mapped Soil Name	Taxonomic Class
Blackwater River /Santa Rosa	Bonifay	Loamy, siliceous, thermic Grossarenic Plinthic Paleudults
	Orangeburg	Fine-loamy, siliceous, thermic Typic Paleudults
	Troup	Loamy, siliceous, hyperthermic Arenic Paleudults
Cecil Webb /Charlotte	Pineda	Loamy, siliceous, hyperthermic Arenic Glossaqualfs
Jay Livestock Market /Santa Rosa	Red Bay	Fine-loamy, siliceous, thermic Rhodic Paleudults
Lake Arbuckle /Polk	Astatula	Hyperthermic, uncoated Typic Quartzipsamments
	Immokalee	Loamy, siliceous, thermic Arenic Paleudults
Lake Kissimmee /Polk	Myakka	Sandy, siliceous, hyperthermic Aeric Haplaquods
	Smyrna	Sandy, siliceous, hyperthermic Aeric Haplaquods
Myakka River /Manatee	EauGallie	Sandy, siliceous, hyperthermic Grossarenic Argiaulls
Okaloosa-Walton Community College /Walton	Lakeland	Thermic, coated Typic Quartzipsamments
	Troup	Loamy, siliceous, hyperthermic Arenic Paleudults

Table 3-13. – continued

Site/County	Mapped Soil Name	Taxonomic Class
Tosohatchee /Orange	Malabar	Loamy, siliceous, hyperthermic Arenic Ochraqualfs
	Pineda	Loamy, siliceous, hyperthermic Arenic Glossaqualfs
St. Marks Wildlife Refuge /Wakulla	Otela	Loamy, siliceous, thermic Grossarenic Paleudalfs
	Seaboard	Thermic, coated Lithic Quartzipsamments
	Shadeville	Loamy, siliceous, thermic Arenic Hapludalfs
Walker Ranch	Immokalee	Loamy, siliceous, thermic Arenic Paleudults

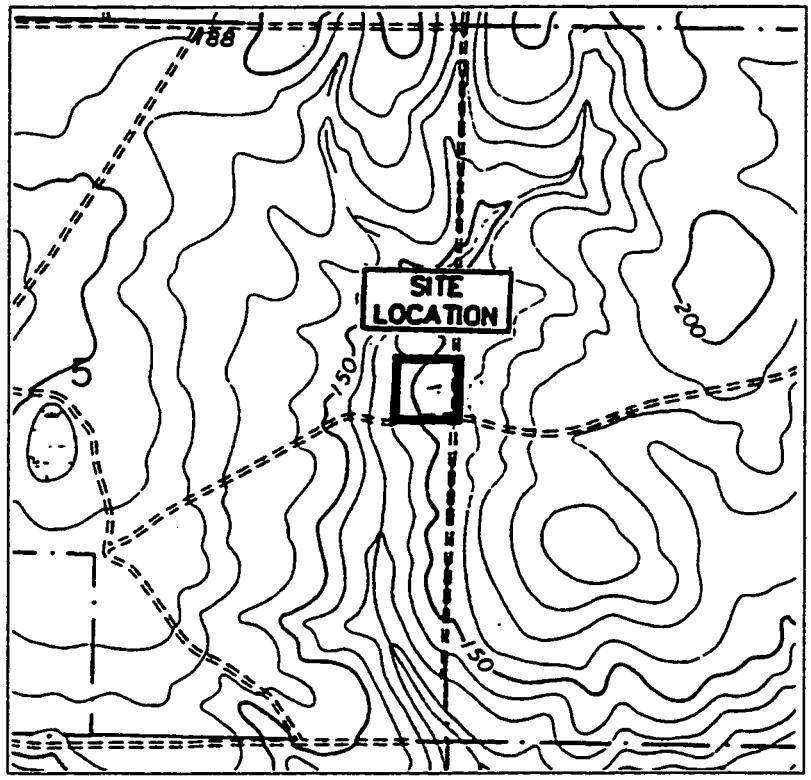


Figure 3-34. Topographical map of the Blackwater River State Forest vat site.

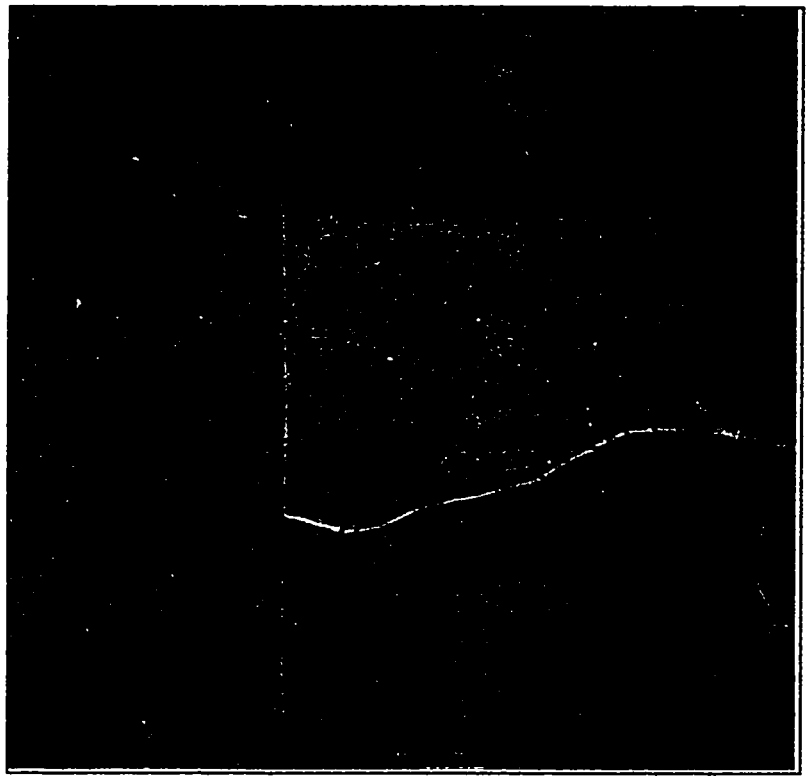


Figure 3-35. Soil survey map of the Blackwater River State Forest vat site. Map unit designations: 5 Bonifay loamy sand, 9,10 Dothan fine sandy loam, 25 Lucy loamy sand, 31,32 Orangeburg sandy loam, 43 Tifton sandy loam, and 47 Troup-Orangeburg-Cowarts complex.

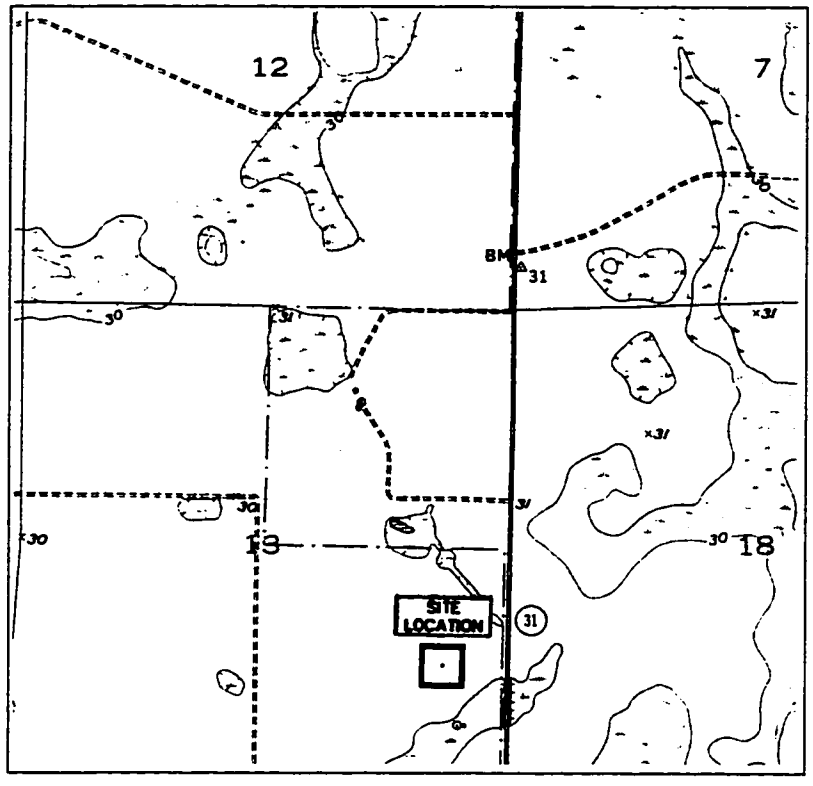


Figure 3-36. Topographical map of the Cecil Webb vat site.

The soil survey report has the soil mapped as Pineda series (Figure 3-37).[56] These soils are deep, poorly drained Alfisols with an arenic horizon in the subsurface. Based on the study done at the Williston Road vat, it would be expected that the As plume has traveled ≈100 meters from the vat. The hydrology at this site would largely determine the distance the contaminant plume has migrated. The mixed horizon of "B2tg" & "A'2" would contain the highest concentration of arsenic. Although the sandy intrusions into this horizon may allow the arsenic to pass through it, the slightly sticky, sandy loam should retain enough arsenic to allow a plume to be delineated. The typical depth for this horizon is given as 91 to 137 cm. The consulting firm that did the preliminary survey did found 140 mg As/kg soil in the only sample taken, at the 122 cm depth. All other samples ranged from <0.7 to 7.0 mg/kg at the pre-determined sampling depths of 15 and 76 cm.

Jay Livestock Market Vat

The Jay Livestock Market vat, located in Santa Rosa County, Florida, was described as nearly level to gently sloping (Figure 3-38) and well-drained. This soil series was mapped as Red Bay sandy loam soil (Figure 3-39).[55] The soil at this site was highly disturbed and the vat had been removed. Its reported position was in front of a metal building. The direction of drainage would cause the plume to

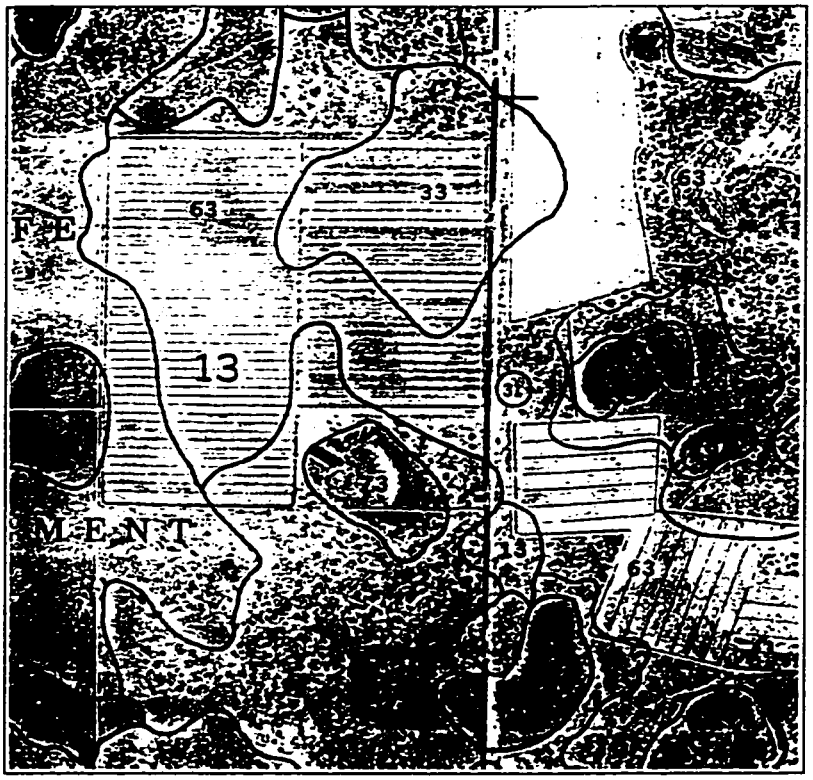


Figure 3-37. Soil survey map of the Cecil Webb vat site. Map unit designations: 13 Boca fine sand, 33 Oldsmar sand, 44, 63 Malabar fine sand, 49 Felda fine sand, 53 Myakka fine sand, and 73 Pineda fine sand.

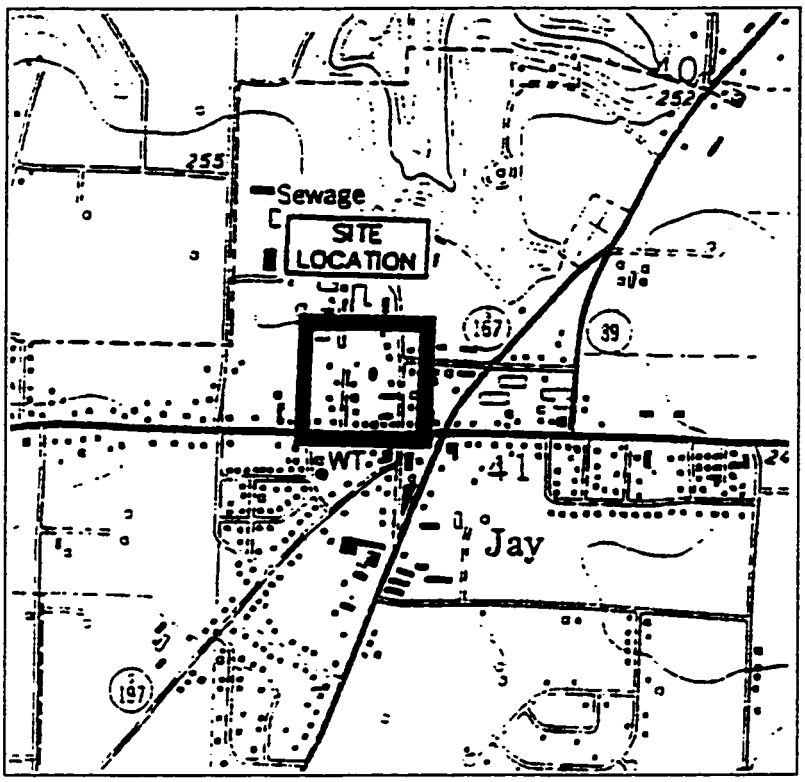


Figure 3-38. Topographical map of the Jay Livestock Market vat site.

Figure 3-39. Soil survey map of the Jay Livestock market vat site. Map unit designations:
5 Bonifay loamy sand, 9,10 Dothan fine sandy loam,
25 Lucy loamy sand, 31,32 Orangeburg sandy loam,
43 Tifton sandy loam, and 47 Troup-Orangeburg-Cowarts complex.

migrate beneath this building. The consulting firm did not report arsenic levels above 9 mg/kg. This soil series typically has reddish sandy clay loam starting at 20 cm and extending to 200 cm. Although the area is considered to be well-drained, the sandy clay loam has sand particles coated and bridged with clay which would inhibit the movement of arsenic. It is quite possible that the maximum arsenic concentration at this site lies under a metal building and was inaccessible to sampling by the consulting firm.

Lake Arbuckle Vat

The Lake Arbuckle vat site was located in Polk County, Florida, in an area bordering the Blue Jordan Swamp (Figure 3-40). The soil series are mapped as Immokalee or Astatula (Figure 3-41).[57] The Astatula series consists of uncoated Typic Quartzipsamments. The only confirmed site mapped as this soil series was located at the south rim of the Payne's Prairie State Preserve. It was determined at this site that the uncoated Typic Quartzipsamments were not capable of retaining arsenic. On the other hand, the Immokalee soil series has several spodic horizons. Based on prior experience at the Williston Road vat, it has been shown that the "Bh" horizon can retain arsenic. Since the range of As in the consulting firm's survey extended from 0.73 to 73 mg/kg, it can be assumed that the soil series is more likely to be similar to Immokalee than Astatula.

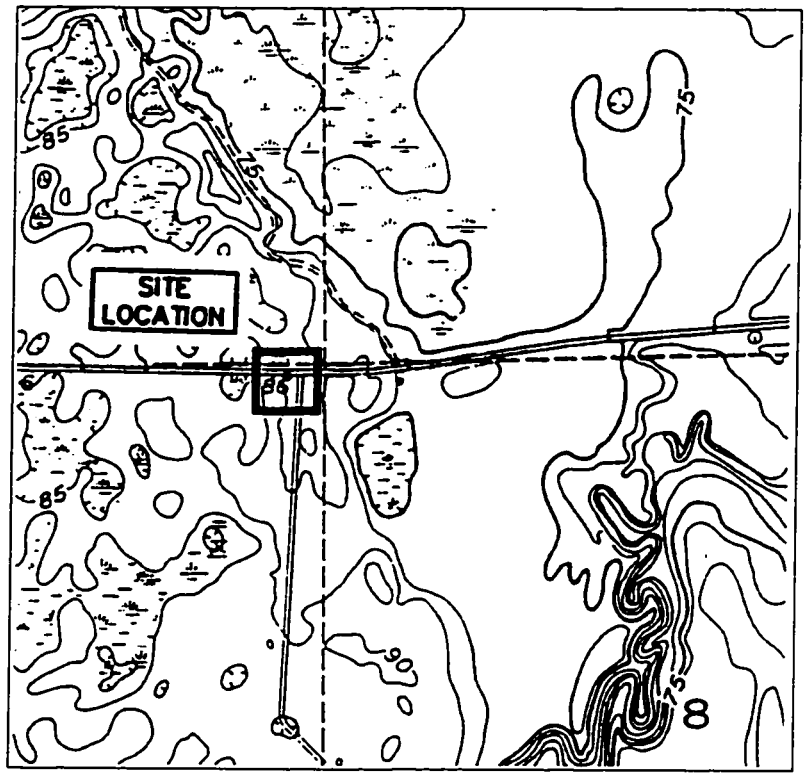


Figure 3-40. Topographical map of the Lake Arbuckle vat site.

Figure 3-41. Soil survey map of the Lake Arbuckle vat site. Map unit designations: 15 Tavares fine sand, 21 Immokalee fine sand, 25 Placid and Myakka fine sands, 30 Pompano fine sand, 35 Hontoon muck, 36 Basinger mucky fine sand, 77 Satellite sand, and 83 Archbold sand.

Lake Kissimmee Vat

The Lake Kissimmee vat was located in the Kissimmee State Park in Polk County, Florida. The topographical map revealed the surrounding area to be marshy, although the vat site itself is on slightly higher ground (Figure 3-42). The soil survey report has the vat site mapped as Smyrna and Myakka fine sands (Figure 3-43).[57] The main difference between these two soil series is depth to the spodic horizon. The Myakka typically has the spodic horizon starting at 64 cm, whereas the Smyrna has a shallow spodic horizon at 30 cm. In either case, the maximum arsenic concentration would probably be found in these spodic horizons. The lowest horizon in both of these soil series was given as "C" with single grained sand, loose and very strongly acidic. This implied that As would not be retained once it had migrated through the spodic horizons. The shallow water table, indicated by the prevalence of marsh on the topographical map, probably has dispersed the arsenic contamination over a large area. The preliminary survey showed a range of <0.7 to 76 mg As/kg soil. The latter value was at 73 cm depth, which corresponded to within the spodic horizons of these soil series.

Myakka River Vat

This vat was located near a camp ground in Manatee County, Florida (Figure 3-44). The soil series was mapped as

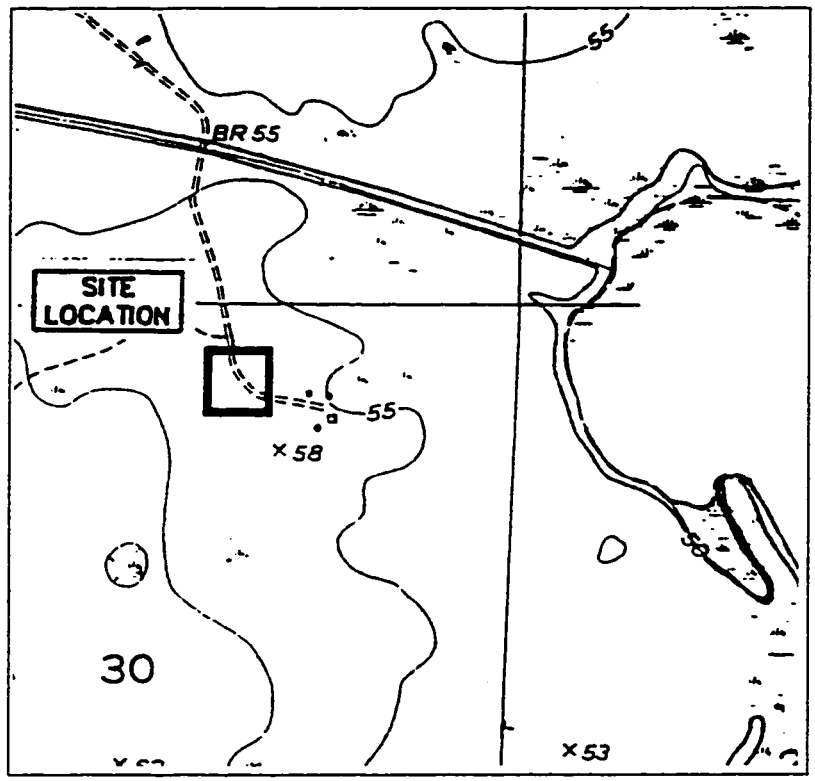


Figure 3-42. Topographical map of the Lake Kissimmee vat site.

Figure 3-43. Soil survey map of the Lake Kissimmee vat site. Map unit designations: 13 Samsula muck, 17 Smyrna and Myakka fine sands, 21 Immokalee sand, 25 Placid and Myakka fine sands, 74 Narcoossee sand, and 87 Basinger fine sand.

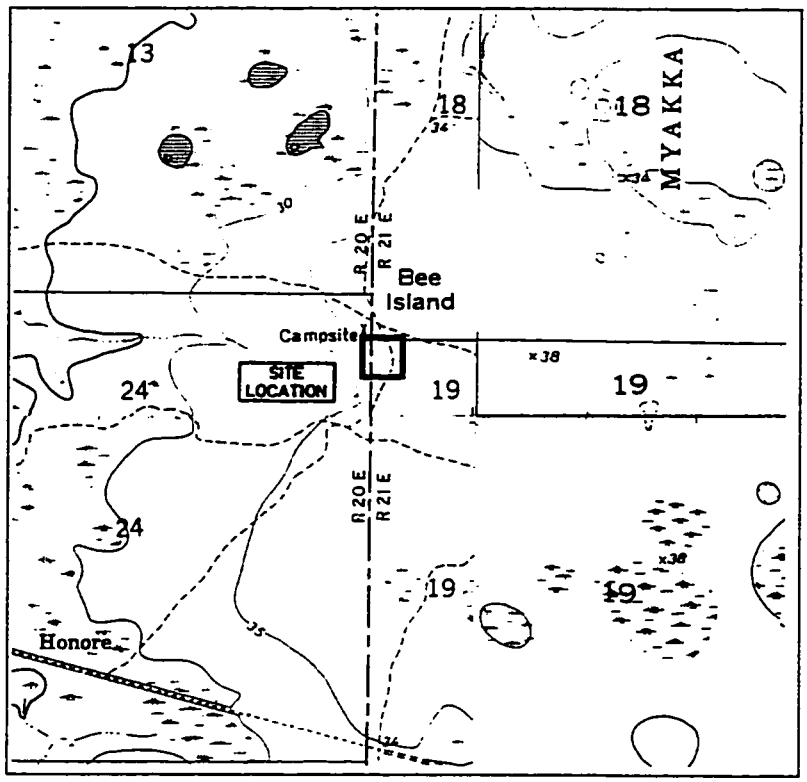


Figure 3-44. Topographical map of the Myakka River vat site.

EauGallie fine sand, an Alfic Haplaquod (Figure 3-45).[58] Arsenic would be expected to be found in the spodic horizon and, at its maximum concentration, in the top of the "Bt2g" horizon. However, the preliminary survey gave a maximum arsenic concentration of 880 mg/kg in the "A" horizon at only one sampling point. Whether this value came from disturbed soil or typographical error, it is clearly anomalous. Excluding this one point, the range of As for this site was <0.7 to 52 mg/kg. However, it should be noted that at sampling depths of 15 cm and 45 cm, neither the spodic (expected at 71 cm) nor the "Bt2g" (mapped at 127 cm) horizons would have been analyzed for arsenic.

Okaloosa-Walton Community College Vat

Near the town of Defuniak Springs in Walton County, Florida, the Okaloosa-Walton Community College has a vat site. The vat structure has been removed and the site fenced off from the rest of the campus. The area is highly developed (Figure 3-46). The soil survey report has the area mapped as either Lakeland or Troup sand (Figure 3-47).[59] The Troup soil series consists of well-drained moderately permeable Grossarenic Paleudults. Some arsenic should be retained in the "Bt2" horizon where the sand particles are coated and bridged with clay. On the other hand, the Lakeland series is described as excessively drained, with rapidly permeable soils containing 5 to 10 percent silt plus clay in the 2.5 to 101-cm

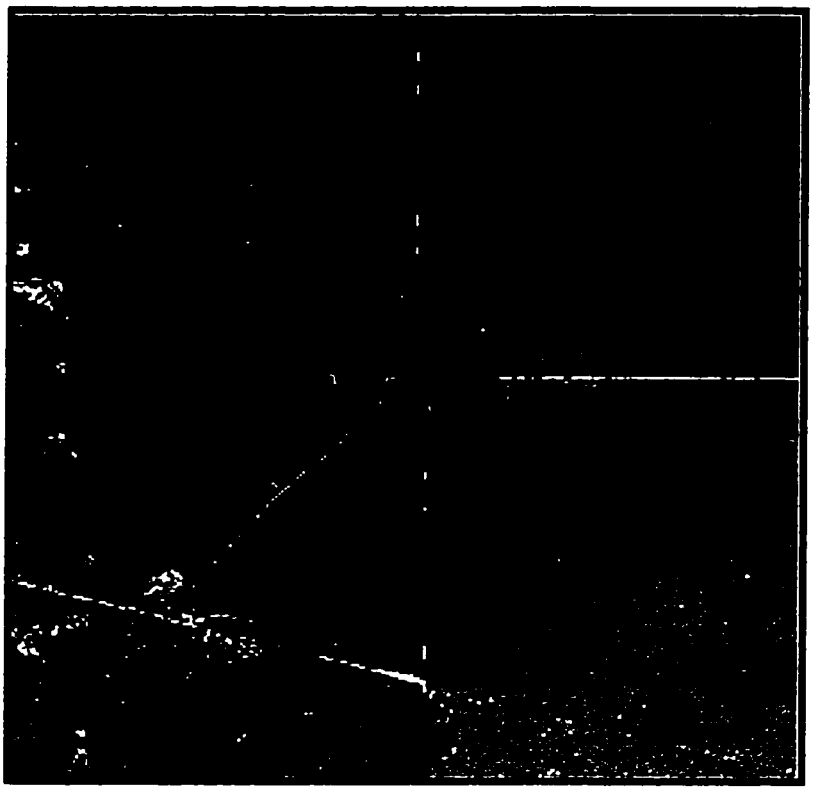


Figure 3-45. Soil survey map of the Myakka River vat site. Lower right quadrant map unit designations: 16 Delray complex 20 EauGallie fine sand, 26 Floridans-Immokalee-Okeelanta association, and 22 Felda fine sand.

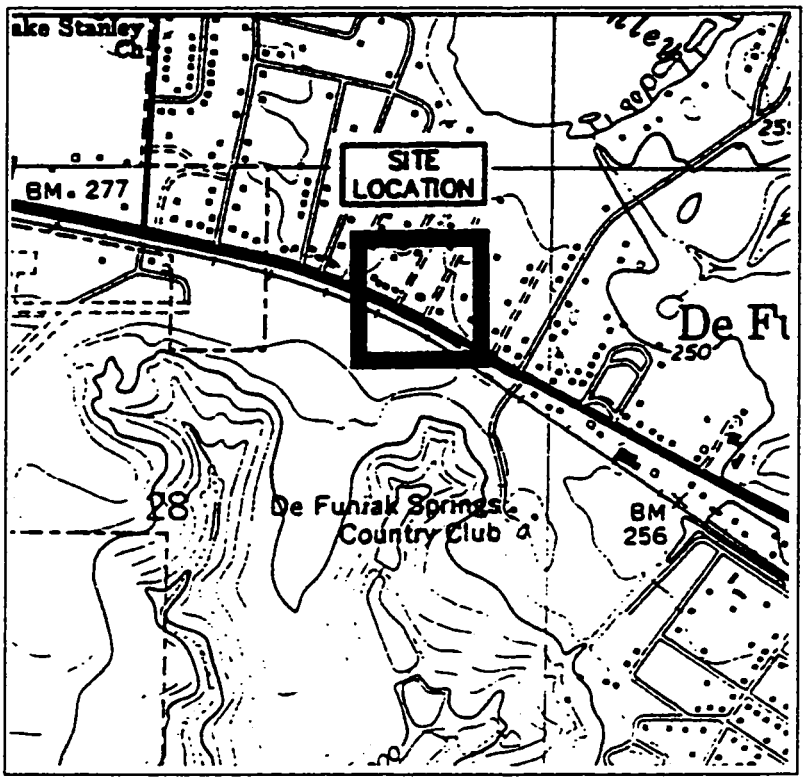


Figure 3-46. Topographical map of the Okaloosa-Walton Community College vat site.

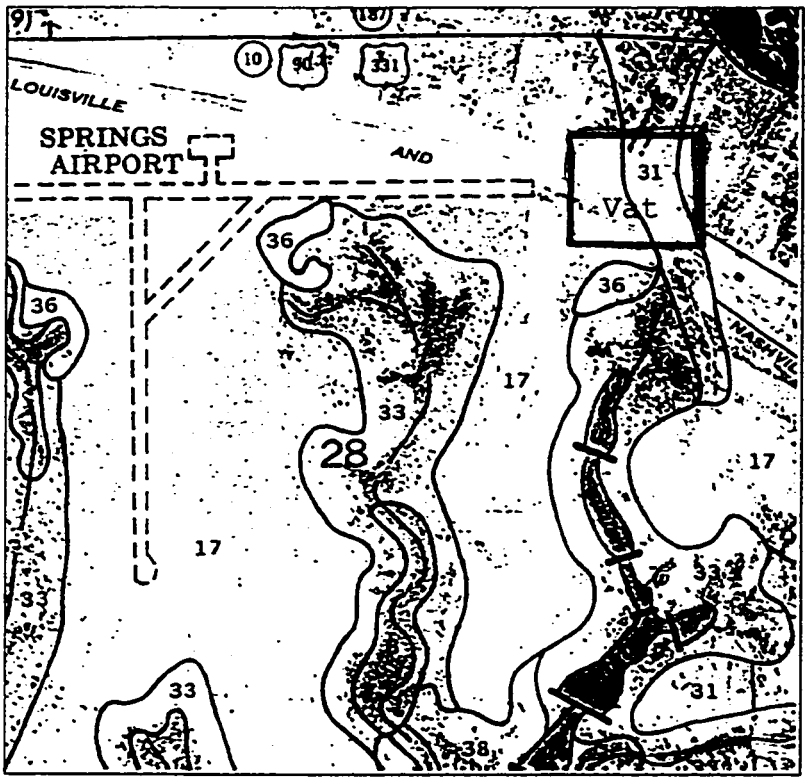


Figure 3-47. Soil survey map of the Okaloosa-Walton Community College vat site. Map unit designations: 17 Lakeland snad, 31,33 Troup sand, and 36 Pits.

control section. This type of soil would not be expected to retain arsenic in any appreciable amounts. Indeed, the consulting firm's survey revealed a range of <0.7 to 4.90 mg As/kg soil, although it should be noted that no samples were taken within the fenced-off area.

Tosohatchee Vat

The Tosohatchee vat in Orange County, Florida, was found on nearly level topography (Figure 3-48). The site was mapped as either Pineda or Malabar soil series (Figure 3-49).[60] The main difference in these soils is the depth of the typical argillic horizon. The Malabar soils have an argillic horizon depth of 102-147 cm, in contrast to the Pineda soils having it at 94-147 cm. In either case, the maximum concentration of arsenic would be expected to be found in the argillic horizon. The arsenic sampling survey reported that the maximum concentration of arsenic (100 mg/kg) was found at 152 cm. Given that the error in sampling depth was given as ±15 cm and that this soil may not be a typical example of the soil series mapped, it is quite probable that the maximum concentration was found in the argillic horizon.

St. Marks Wildlife Refuge Vat

The St. Marks Wildlife Refuge was located in Wakulla County, FL. The vat site was situated along the Seaboard railway (Figure 3-50). The soil survey report revealed the

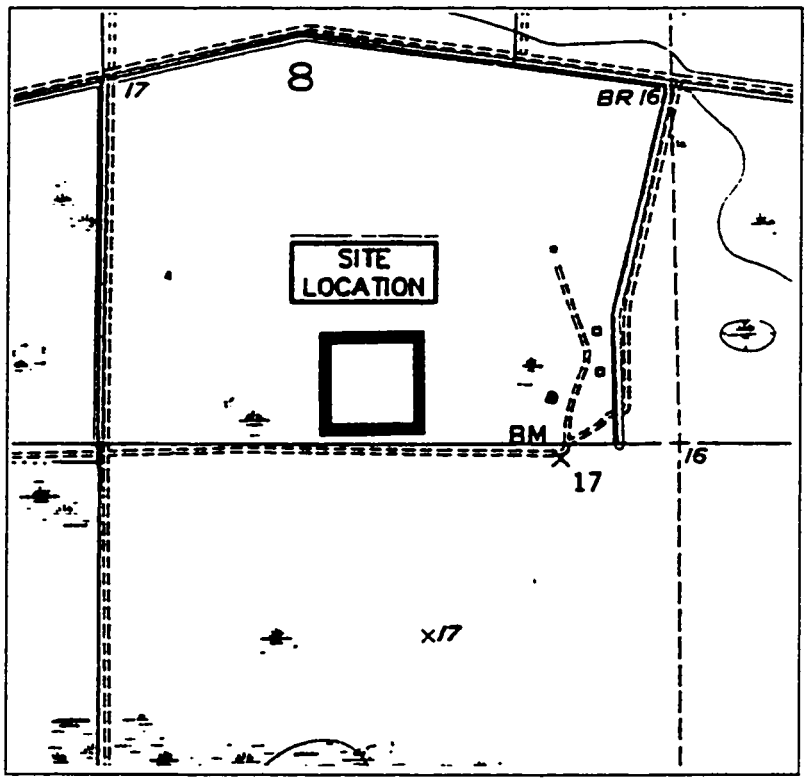


Figure 3-48. Topographical map of the Tosohatchee vat site.

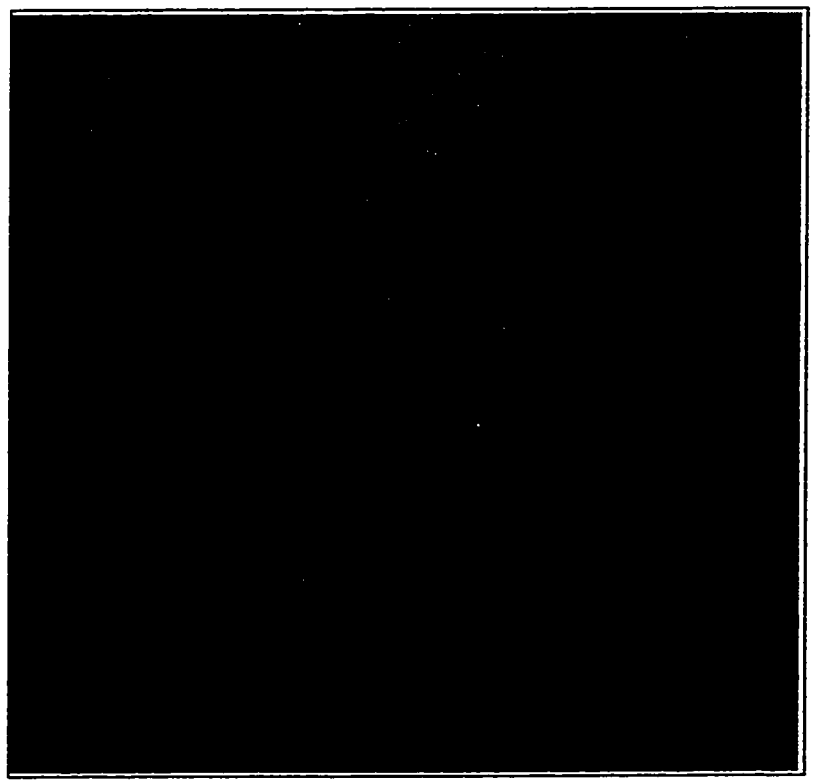


Figure 3-49. Soil survey map of the Tosohatchee vat site. Map unit designations: 7 Candler-Urban land complex, 13 Felda fine sand, and 30 Pineda fine sand.

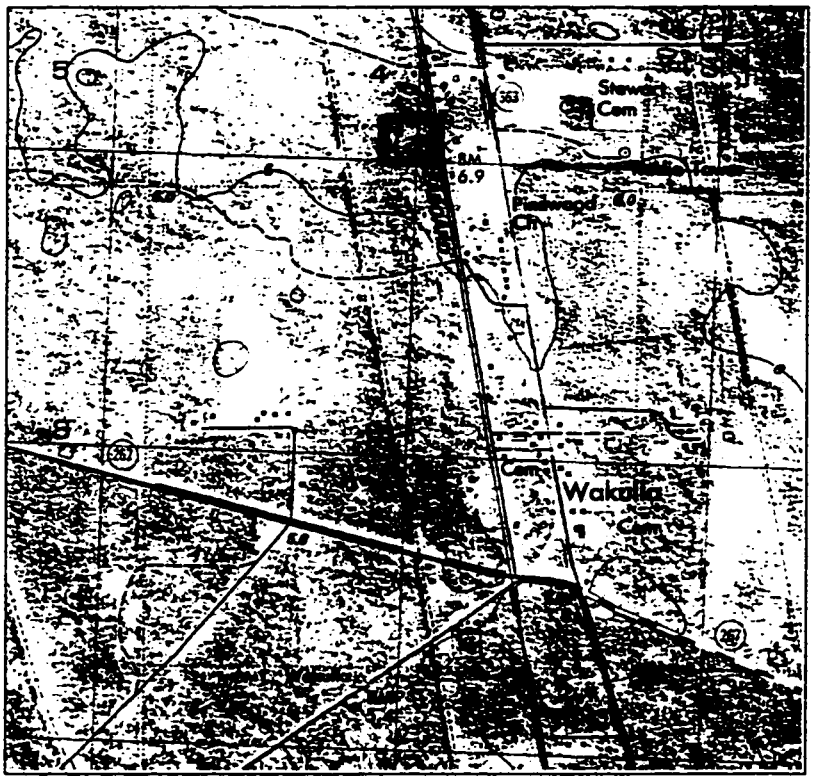


Figure 3-50. Topographical map of the St. Marks Wildlife Refuge vat site.

area to be mapped as Otela fine sand and Shadeville-Seaboard fine sands (Figure 3-51).[61] The Otela series consists of typically moderately well-drained Grossarenic Paleudults. The "Btg" horizon of this soil series usually has fine prominent red mottles. The maximum arsenic concentration would be expected to be located in these mottles. The Shadeville-Seaboard series may or may not have an argillic horizon. The Shadeville portion has sandy clay loam over fractured, porous limestone bedrock. If the arsenic does migrate through the "Bt" horizon, it may eventually reach the water table through porous bedrock. The Seaboard series would not be any better at retaining arsenic since it consists of fine sand over a fractured porous limestone bedrock. Regardless of which soil series the site contains, it appears that the arsenic could have reached the water table. The arsenic sampling survey showed <0.7 to 16 mg/kg outside the vat and 71 mg/kg inside the vat.

Walker Ranch Vat

The Walker Ranch vat, located in Osceola County, FL, was located in an area that was topographically shown as marshy (Figure 3-52). The soil survey report has the site mapped as the Immokalee series (Figure 3-53).[62] The Immokalee soil series is found on nearly level, poorly-drained locations. It has a spodic horizon that usually begins around 94 cm deep.

Figure 3-51. Soil survey map of the St. Marks Wildlife Refuge vat site. Map unit designations: 7 Otela fine sands, 11 Shadeville fine sand, 12 Shadeville-Seaboard fine sand, 27 Moriah-Pilgrims fine sands, and 48 Otela-Ortega sands.

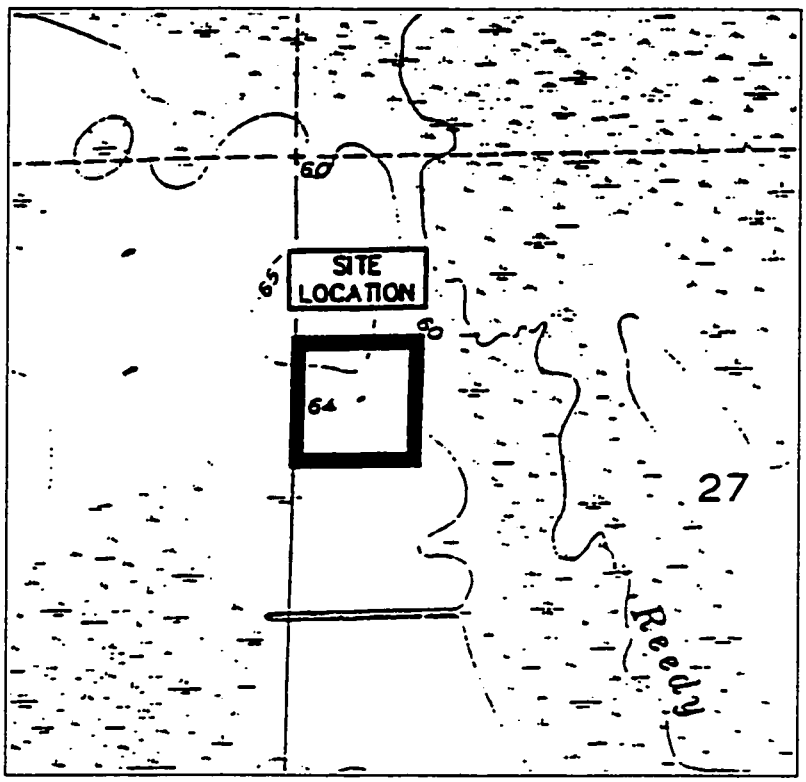


Figure 3-52. Topographical map of the Walker Ranch vat site.

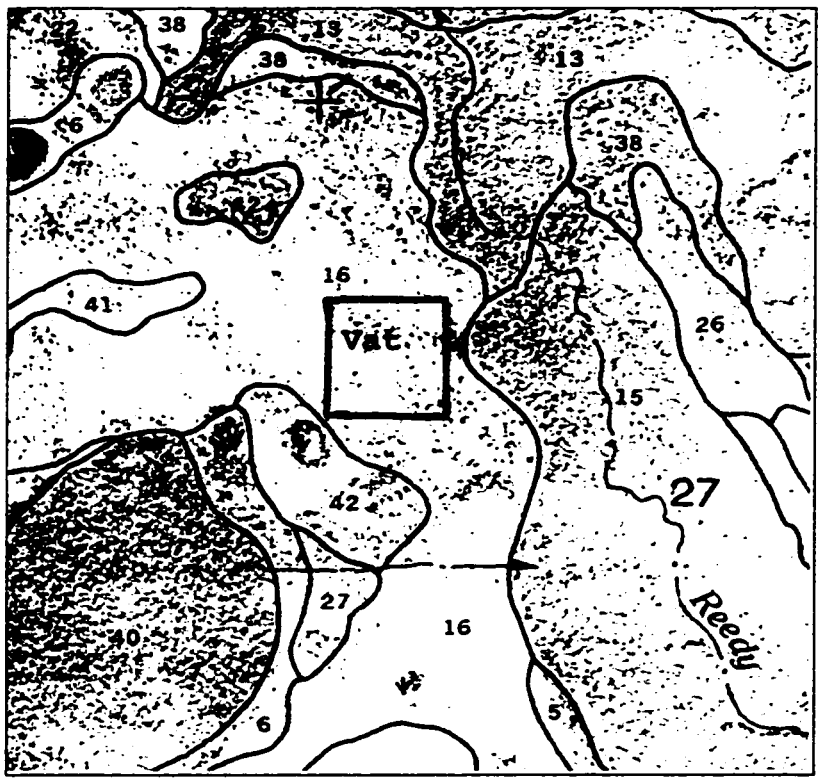


Figure 3-53. Soil survey map of the Walker Ranch vat site. Map unit designations: 6 basinger fine sand, 13 gentry fine sand, 15 Hontoon muck, 16 Immokalee fine sand, 26 Oldsmar fine sand, 27 Ona fine sand, 38 Rivera fine sand, 40 Samsula muck, and 42 Smyrna fine sand.

The arsenic should be slightly retained in this horizon; however, due to the poor drainage, the As plume would be expected to be quite mobile. Indeed, the As survey map, provided by the Woodward-Clyde consultants, revealed very little arsenic in close proximity to the vat. The range was <0.7 to 2.3 mg As/kg soil.

Conclusions

Locating of the vats described in this dissertation was done largely through anecdotal evidence. Without the knowledge of Butch Hunt, Payne's Prairie Security Officer, and Jack Gillem, Payne's Prairie Park Manager, many of these vats would not have been located. Vats were also found by reports submitted by several environmental consulting firms to various state agencies.[19,68]

The various soil series that were found at these vats provided several bits of information. Among these items are: 1) As tends to associate with aluminum and iron oxides/hydroxides found in soil clay layers and 2) if the hydraulic conductivity of the clay is low, the downward transport of As is restricted, although high clay content alone does not necessarily stop vertical movement of the As (i.e., the Dudley Farm site). It was also observed that the topography of an argillic horizon influenced the shape of the As contamination plume (i.e., the Bison Pen and Williston Road

vats). An organic horizon in the soil was also shown to be capable of containing appreciable amounts of As. The eluviated sand horizons held the least amount of As. The Bh horizon contained held less As than found in the upper surface of the argillic horizons; however, if low organic matter and low clay content were found in the soil, then the arsenic contaminant plume was exceedingly difficult to delineate. It has been suggested for these sites that, if the clay contents were concentrated, then the As "trail" could be determined.

These observations, coupled with the development of a quick field test for arsenic in soil, suggest that a more appropriate protocol for evaluating the arsenic contamination at these cattle dipping vat sites may be available. It simply is not efficient to spend days of manual labor digging holes at pre-determined depths and distances with no regard for environmental conditions on-site or to spend days waiting for laboratory analysis of these soil samples for arsenic. It would be time better spent if the soil survey and topography maps were consulted prior to the first visit to the vat site.

Once the mapped soil series is known, the probable depths for sampling can be more accurately planned. For example, in all of the cases studied to date, the horizon with the highest concentration of As was found to be the argillic, if it was present. If iron-bearing (red) nodules with a clay coating are in the soil, then the As will concentrate in this coating, assuming that it contacts the contaminant plume. The same

concentration effect occurs if red redoximorphic features occur in the soil within the plume. If a spodic horizon is present, the plume will migrate a considerable distance from the vat. Arsenic will also leave a trail within these spodic horizons. If the soil is an uncoated Quartzipsamment, the arsenic plume will leave very little trace of its passage. However, if it is a coated Quartzipsamment, the plume's trail should be detectable, although the As concentrations may be low. All of these soil features are mentioned in accompanying descriptions in the soil surveys.[53-62]

The direction of the plume's migration will be the same as the direction of water flow. Equally obvious is the observation that, if you were to empty a vat of its contents, then the direction you'd toss the dip solution is downhill from the vat. The topographical map can give an *a priori* basis for speculating on the direction of groundwater flow. However, only actual on-site sampling and inspection can confirm the soil series and direction of groundwater flow. Prior knowledge of probable soil and water conditions, in conjunction with the arsenic field test kit, make it quite possible to establish the direction and migration distance of a plume in most soils within a single day. Furthermore, a team of three people should be able to fully delineate an arsenic plume in a worst case scenario (i.e., a spodosol with a high water table) in less than a week, if the contaminant can be found at all.

In general, the site sampling protocol should include: 1) prior study of soil survey and topographical maps, 2) on-site inspection to confirm soil and water conditions, and 3) usage of the quick field test for arsenic. In this way, evaluation of the arsenic contamination at cattle dipping vat sites may be conducted in a more cost- and time-efficient manner.

CHAPTER 4
BIOLOGICAL VOLATILIZATION OF ARSENIC

Introduction

The transport of As in soils contaminated by the dumping of waste from cattle dipping vats is highly dependent not only on the structure and composition of the soil, but also on the species of As present. One of the determinants of As form is biological. The biotic influence can be manifested as reduction, oxidation, or transformation of As. It has been hypothesized that these actions have evolved as attempts to negate the toxicity of As. Arsenic may be transformed to a more mobile ionic species, such as the reduction of arsenate to arsenite, to facilitate its removal from the immediate environment. Conversely, oxidation may also be considered a protective mechanism since arsenate is less toxic than arsenite. Transformation of As into a less hazardous compound such as arsenobetaine can occur, as well as the conversion of As into gaseous arsine.[20]

One redistribution mechanism is by volatilization. According to Sandberg and Allen[77], as much as 35% of the As species in soil may be eventually volatilized as arsine, dimethylarsine, and trimethylarsine. Production of volatile

As can be accomplished either aerobically or anaerobically. Under anaerobic conditions, bacteria such as *Methanobacterium*, *Pseudomonas*, and *Alcaligenes* have been cited as the causative agents.[20] The volatilization of As by bacteria under aerobic conditions has been demonstrated for *Staphylococcus aureus* and *E. coli*.[20] Other microorganisms, besides bacteria, have been shown to convert As to the volatile methylated species. Fungi, such as *Candida humicola, Gliocladium roseum* and *Penicillium* sp. have been shown to produce volatile trimethylarsine aerobically.[20] Under aerobic conditions, soil treated with arsenate has been shown to evolve 1.5% of the As as unidentified volatile species.[78]

A study was conducted to establish the amount and location of volatile As species at an arsenic-contaminated cattle dipping vat site. Laboratory studies were undertaken to establish the relationship of oxic conditions in subsurface soils to the volatilization of As. Other experiments were conducted to isolate and identify the causative agent.

Materials and Methods

Two vat sites, at the Williston Road and the Payne's Prairie Bison Pen, were investigated for volatilization of As below the soil surface. The Bison Pen vat site and the Dudley Farm vat site were studied for surface emissions of arsenical gases. All three of these sites were described in Chapter 3 of this dissertation.

The Bison Pen vat site had soil samples taken for chemical and biological experiments using a ten-centimeter bucket auger at a depth of 132 centimeters and at a distance of 12.2 meters south from the vat, where the arsenic contamination reached a maximum of 110 mg As/kg soil. All samples were placed in plastic bags, transported to the laboratory and stored at 4°C until further use. No samples were stored for more than three months to insure biotic viability.

A surface soil gas flux trap was constructed using a 15x30x30 cm box constructed of 0.63-cm thick plexiglass. The box was covered with aluminum foil and rested on a 10-cm aluminum collar driven into the soil.[79] Gas collection at 49.6 L hr^{-1} was facilitated by a 2.5 amp air pump attached to a rotometer. The gas collection box was placed over an undisturbed area in close proximity to the soil that had the maximum As concentration for the two sites that were tested. For the Payne's Prairie Bison Pen vat site, the gas flux trap was located 12 meters south of the center of the vat. For the Dudley Farm location, the plexiglass box was situated 2.1 meters east of the center of the vat. Volatile As gases were collected for six weeks and nine weeks at the Payne's Prairie and Dudley Farm sites, respectively. The gaseous As species were trapped using a Supelco ORBA-32 tube that contained 0.65 g activated charcoal.

Subsurface soil gas samples were collected by passing 30 mL of gas through ORBA-32 tubes six times a month for one year at the Payne's Prairie Bison Pen vat site and for three months at the Williston Road vat site. A subsurface gas sampling apparatus was constructed from 501 stainless steel 0.64 cm diameter tubing with the sampling ports covered by "Gore-Tex" (expanded TFE polymer on loosely woven polyester cloth manufactured by W.L. Gore, Inc.) The sampling apparatus was based on design specifications from Magnussen et al.[80] Subsurface gas sampling probes were installed at the Payne's Prairie Bison Pen vat site to a depth of 132 cm, with as little disturbance to the last 60 cm of soil as possible. Control sampling tubes were installed at this site to an equal depth and at an equal distance from the vat, but on the northern, uphill side where no As had been detected in the soil. The second vat site along Williston Road had a set of subsurface sampling probes placed 67 meters northeast of the center of the vat to a depth of 76 cm, with as little disturbance to the last 30 cm of soil as possible. Subsurface control probes for the Williston Road vat site were installed twenty-five meters southwest of the "hot" subsurface probes. The control probes were entrenched to a depth of 76 cm; however, the soil around the control probes contained no detectable As.

Manifold experiments on the Bison Pen vat soils were conducted by flushing flasks containing 100 g arsenic-

contaminated soil with pre-moistened ambient air or industrial-grade nitrogen. Samples of autoclaved soil and of "live" soil had water content adjusted with deionized sterile water, and of live soil adjusted instead with 1 mL sterile 20% aqueous glucose solution, were examined in duplicate. The evolved volatile As gas was collected on 0.65 g activated coconut charcoal (ORBA-32 tube by Supelco, Inc.).

A fungus was isolated from the Bison Pen vat soil by sequential 1:10 dilutions into a media of thiamine/succinic/glucose solution following Cox and Alexander.[81] The fungus was identified from its microchondial structure as a *Fusarium* species.[82] One hundred milliliters of media with 0.02 g $Na_2HAsO_4.7H_2O$ were inoculated with this fungus. Volatile As was swept from the flask by flushing with pre-moistened ambient air or industrial grade nitrogen. The As fumes were collected on 0.65 g activated coconut charcoal.

All samples (0.65 g charcoal or 0.5 g soil) were digested using HNO_3 acid in Teflon bombs in accordance with U.S.E.P.A. method #3051.[68] All digests were diluted to 100 mL prior to analysis. Analysis for As was accomplished using a Perkin-Elmer Atomic Absorption Spectrophotometer model 2380 equipped with a graphite furnace model HGA-400 and an autosampler model AS-40. Deuterium lamp background correction was employed. Due to unknown interferences, all charcoal samples had to analyzed by the method of standard additions. Results were confirmed

using Perkin-Elmer Hydride System model MHS-10. Operating conditions for the graphite furnace and the hydride generation system were described previously in Chapter 3.

Results and Discussion

Volatile As gas emissions from the soil surface at both the Dudley Farm vat site and the Payne's Prairie Bison Pen vat site were not detected. Collection of gaseous arsenical species was attempted by continuously purging the air in a sample collection box situated over the area of greatest subsurface As contamination (110 mg kg^{-1} soil at the Bison Pen vat site and 767 mg kg^{-1} at the Dudley Farm vat site). At a gas flow rate of 49.6 L hr^{-1}, the 13.5 L collection box was fully purged every 11.2 minutes. These results conflicted with findings reported by Braman.[83] The differences were attributed to variation in arsenic's time of application and its depth of placement. Braman applied sodium arsenite to the soil and grass surface, and immediately placed a bell jar over the applied area for sampling.[83] In contrast, the soil at these cattle dipping vat sites was contaminated more than thirty years ago. Additionally, the majority of As contamination was not located on the soil surface at the sampling points, but rather at a depth greater than 100 cm for both vat sites.

To ascertain that As was being volatilized at these two sites, subsurface probes were installed. Volatile As species

were observed at both the Bison Pen and Williston Road sites (Figures 4-1 and 4-2). Control samples taken at both sites did not show the presence of volatile As species. For the Bison Pen vat site, Spearman rank non-parametric correlation test showed no relationship between arsenic volatilized and rainfall when all twelve datum pairs of arsenic concentration (ng mL^{-1}) and rainfall (cm) were used (Figure 4-1). On the other hand, when the two months of excessive rainfall (>25 cm) were excluded, then a slight correlation was found. The rank correlation coefficient was 0.612 at a significance level of 0.06.[84] Since the Williston Road vat site had only three datum pairs of As concentration (ng mL-1) and rainfall (cm), no statistical analysis was performed (Figure 4-2). The Williston Road vat study does confirm that subsurface As volatilization was not an isolated event, however. Possible explanations for the low Spearman rank correlation found between As volatilization and rainfall with the Bison Pen vat site data include: 1) that, with non-excessive rainfall, there was an influx of nutrients that stimulated As production, while excessive rainfall may have limited volatile As species by converting the gaseous arsenicals to another form; or 2) that the excessive rainfall caused oxygen depletion in the system, which adversely affected the rate of volatile arsenic formation.

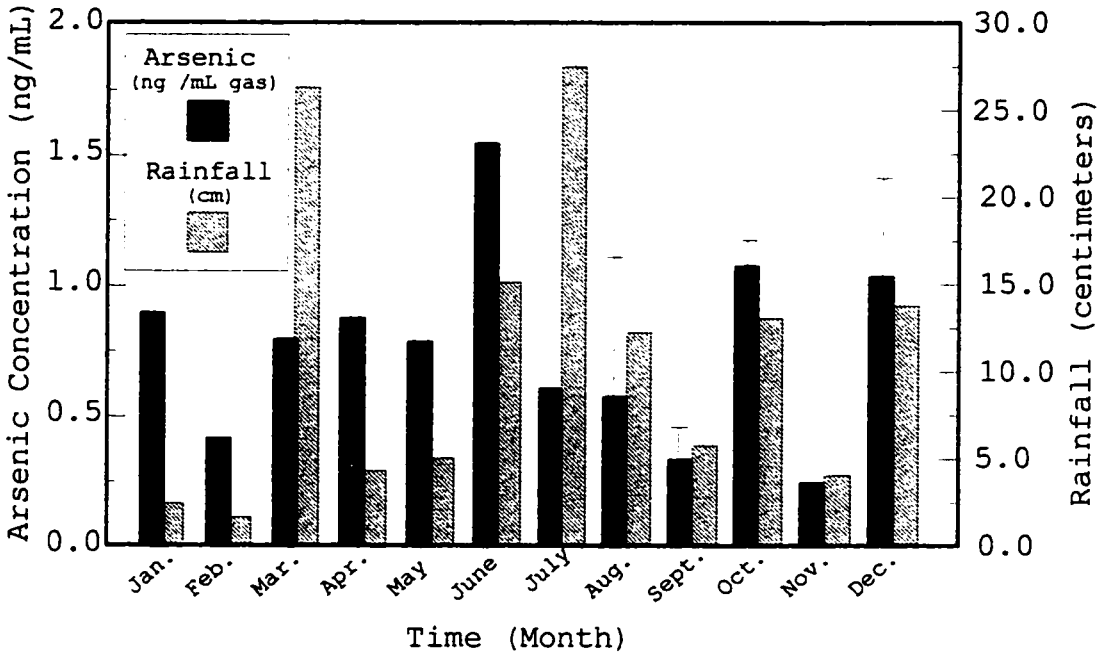


Figure 4-1. Subsurface volatile As gas flux and rainfall for 1996 at the Payne's Prairie Bison Pen vat site.

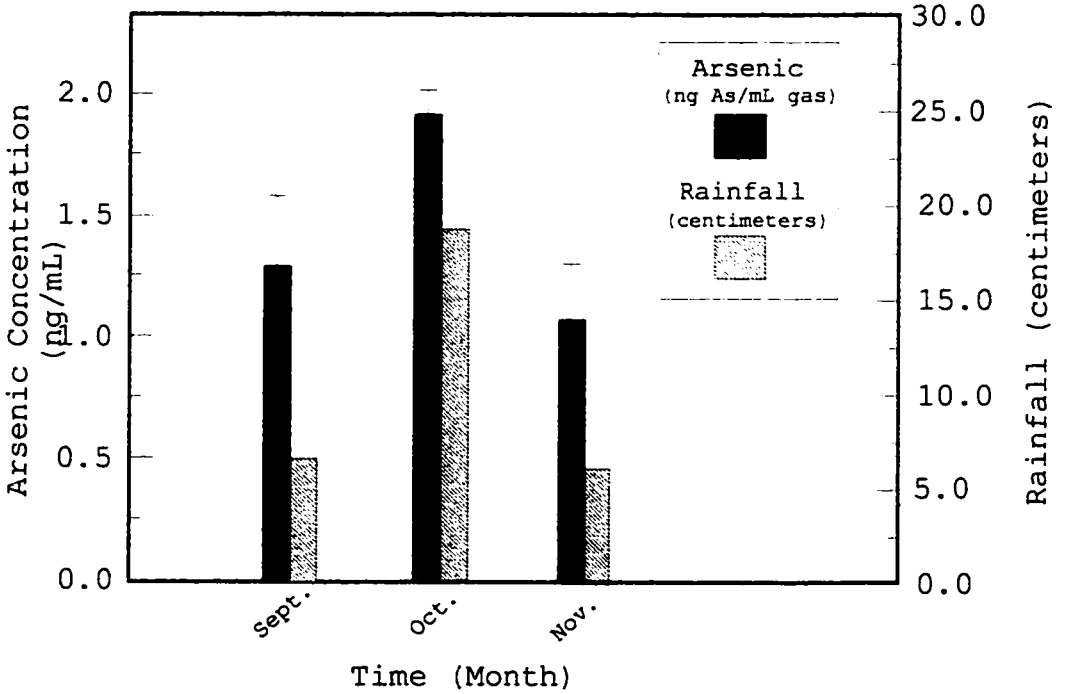


Figure 4-2. Subsurface volatile As gas flux and rainfall for three months in 1997 at the Williston Road vat site.

The data in Figure 4-1 suggest that the arsenic was being volatilized *in situ* at the Payne's Prairie Bison Pen site. In laboratory studies, a lesser amount of arsenic was volatilized under low oxic (O = 250 ppm) than under high oxic (ambient air) conditions with and without glucose (Figure 4-3). The addition of glucose apparently had no effect under low oxic conditions. In contrast, arsenic volatilization was stimulated by glucose addition under high oxic conditions. Hyphae were found to develop throughout the soil samples in the high oxic/glucose flasks.

A *Fusarium* species that was isolated from the soil was placed in arsenic media under both high and low oxic conditions (Figure 4-4). To test the hypothesis that re-adsorption by overlaying soil was inhibiting the release of volatile arsenic to the atmosphere, ten grams of 0-5 cm surface soil were packed into small plastic columns and placed in line after the inoculated fungal media flask, but before the charcoal collection tube, for two of the high oxic samples. Initially, the soil appeared to reduce the amount of arsenic reaching the carbon trap; however, the student's t-test revealed that there was no statistical difference in the means with or without the soil columns. In comparing the effects of the oxygen levels, it was found that low levels stimulated the release of volatile arsenic species by the *Fusarium* species. This was attributed to the formation of a fungal mat on the surface of

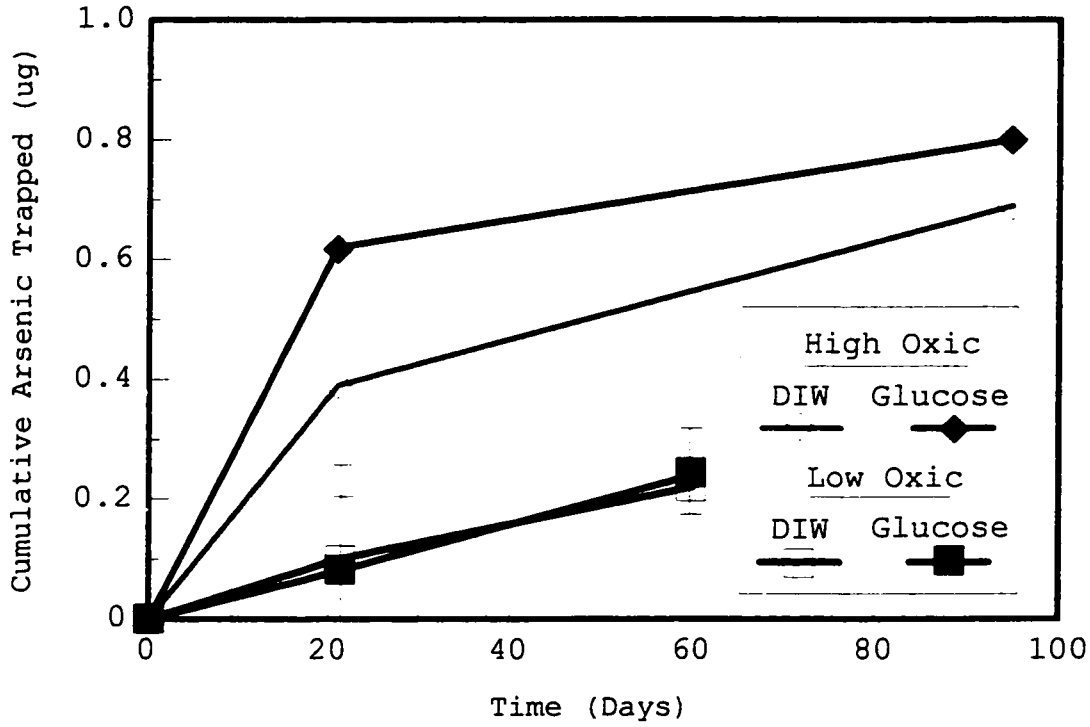


Figure 4-3. Cumulative volatile As evolved from contaminated subsurface soil from the Bison Pen site under various oxic conditions.

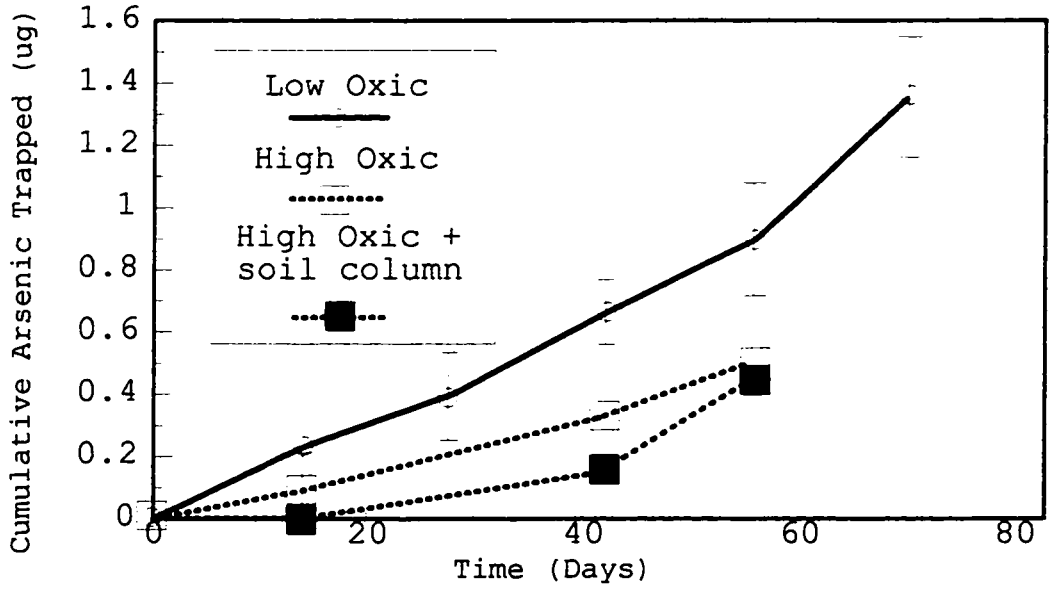


Figure 4-4. Volatilization of As by *Fusarium* sp. under various oxic conditions with and without a soil column scrubber.

the media for the low oxic levels. In contrast, with higher oxygen content, the fungus was distributed throughout the media. For the high oxic cases, arsenic species produced may not have had the opportunity to evolve from the aqueous solution before being converted to nonvolatile species.[18] Stability diagrams for As in aqueous systems at pH 4.0 to 10.0 show that, regardless of the value for pE, arsenic acid is the only stable ionic species.[20] This suggests that conversion kinetics determine the amount of gaseous As evolved.

Conclusions

No volatile As was emitted from surface soil of the Dudley Farm or Payne's Prairie Bison Pen vat sites. However, gaseous arsenic was collected from the subsurface at the Payne's Prairie Bison Pen vat site and at the Williston Road vat site. A slight correlation was found to exist between the amount of rainfall and the amount of gaseous As produced.

In laboratory studies, contaminated Bison Pen vat soil was found to emit more gaseous As in high oxic conditions than in low oxic conditions. A *Fusarium* species was isolated from this soil that could volatilize As, though it exhibited a different pattern of As emission than the soil samples. The fungus volatilized more As in low oxic conditions than in high oxic levels. This was attributed to the formation of a fungal mat at the surface of the liquid media in low oxic conditions. Presumably, this mat allowed the residence time of the

volatile As to be shortened to such an extent that the amount of conversion of the gas to a non-volatile species was reduced. Alternatively, it may be that other microorganisms in the soil, as well as the *Fusarium* species, are causing the gaseous arsenic to form.

Further research needs to investigate whether all vat sites have subsurface arsenical gas being formed and whether any sites have this gas being emitted at present from the surface. Another research area, which has potential, is the isolation and identification of other soil microorganisms that can volatilize As.

CHAPTER 5
COLUMN STUDIES ON THE MOBILITY OF ARSENIC

Introduction

Mobility of As is dependent on several factors, including its speciation and its oxidation state. Soil characteristics also play an important role in such movement. The oxides and hydroxides of aluminum, iron, and manganese are the primary controlling determinants of As sorption by soil. Arsenite undergoes similar sorption, but to a lesser extent. Sorption may occur by ligand exchange or by electrostatic attraction.[85] Ligand exchange may occur with surface hydroxide or aqueous groups from hydrous metal oxides, from phyllosilicate edges, and from calcite.[86] Immobilization of As by metal oxides has been considered to be a more dominant mechanism than immobilization by organic matter.[21]

The release of As once it has been adsorbed onto the soil is also a well researched topic. Extractants such as KNO_3, KH_2PO_4, NH_4NO_3, NH_4Cl, NH_4F, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NaOH, Na_2HPO_4/NaH_2PO_4, CH_3COONH_4, HCl, HNO_3 and H_2SO_4 have all been used to remove As from soil by column leaching or batch extraction.[47] Almost without exception, these studies were performed on soils that had been treated in one manner or

another so that the biotic viability of the soil was lessened or destroyed.

As stated previously, the mobility of As is dependent on its species and oxidation state. Both of these factors can be changed by either abiotic or biotic process. Bacterial oxidation and/or reduction of arsenic has been demonstrated by other researchers.[85] Oxidation state of the hydrous metal oxides may also influence the mobility of As. It has been stated that the desorption of As can be highly dependent on the reduction of Fe^{3+} to Fe^{2+}.[21]

This investigation focused on the desorption of As from soil under various oxic conditions and solution flow rates. Extremely slow flow rates were accomplished by placing the aqueous solutions in the vertical columns under a low suction gradient. These systems have been referred to as differential pressure columns utilizing an average flow velocity.[87] Various potassium solutions with differing anions (chloride, nitrate, and phosphate) were sequentially eluted through these columns in the hopes of elucidating their effects on biotic and abiotic desorption mechanisms. A column study at higher flow rates was undertaken to demonstrate the applicability of using a one-dimensional transport model in determining the retardation factor for arsenate in a typical Florida cattle dipping vat soil. This column investigation involved having the aqueous solutions mechanically pumped at a steady rate under high pressure.

Materials and Methods

A total of five column studies were conducted. Four columns were set up in a manner similar to that described by Nielson and Biggar.[87] These column experiments are referred to as "differential pressure columns" since solution was generally inputted and removed from the column under suction. Water flow occurred as a result of both suction and gravity gradients. A fifth column study was conducted by pumping solution through a water-saturated column at a constant flow rate. All soils used for the differential pressure columns were collected from As contaminated cattle dipping vat sites. The soils were stored in plastic bags in a 4°C refrigerator until used. No soil was stored longer than three months, to ensure microbial viability.

All of the contaminated soils had their As concentrations determined by nitric acid digestion and graphite furnace atomic absorption spectrometry as described in the third chapter of this dissertation.

The first column consisted of a sample of the E horizon taken from the Bison Pen vat site. It was located 12.5 m south of the vat and at a depth of 45-60 cm below the surface. Total recoverable As in this sample was 21.5 mg/kg soil. This column was aerobic and utilized unsaturated water flow. The column was constructed from high density polyethylene (HDPE) and measured approximately 10 cm in length by 1.5 cm in

diameter. The column contained fused glass frits at both ends. The glass frits were either "coarse" 40-60 micron mesh or "medium" 10-15 micron mesh (Aldrich, Inc., Milwaukee, WI). A glass frit sandwiched between two silicone rubber o-rings was inserted into a cap to which a short length of 0.64 cm "Tygon" tubing had been attached. A piece of column of approximately 5 cm in length was wrapped with Teflon tape and pushed into the end of the column until it was tight against the inner silicone o-ring. The column was packed full of soil, making sure that good contact occurred between soil and frit. The water content was adjusted using boiled, deionized water. A second cap end was prepared in identical manner. The two 5 cm column segments were joined together and fastened using transparent tape. In order to insure good aeration, 0.16 cm diameter holes were drilled into the body of the tube (about 1.27 cm apart) in a diamond pattern (Figure 5-1).

The second column also consisted of material from the E horizon taken from the Bison Pen vat site, but this column experiment was conducted under anaerobic, unsaturated conditions. The column for this experiment was also made from HDPE, but was a single piece with no holes drilled into the body of the column. Soil with the desired moisture content was sealed into the column by pressing the end caps, containing o-rings and glass frits, tightly onto the ends of the column after wrapping with Teflon tape. Nitrogen gas was

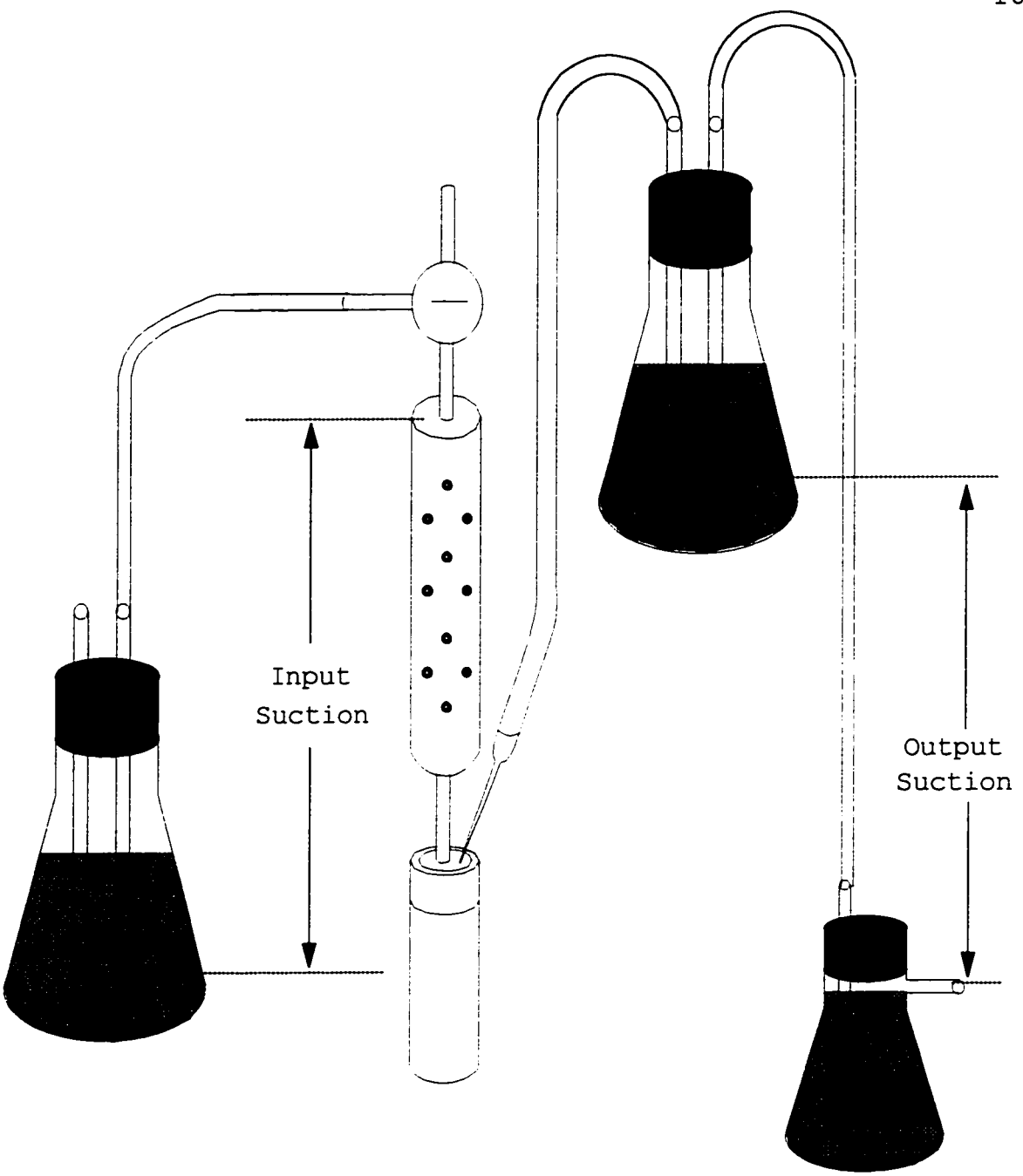


Figure 5-1. Schematic cross-section of apparatus used for the aerobic, unsaturated, differential pressure column.

used to purge both the solution entering the column and the vial used to collect column effluent (Figure 5-2). Suctions were adjusted at column inlet and outlet to obtain the desired flow rates.

The third column consisted of the Bt material taken from the Bison Pen vat site at a depth of 152-165 cm and 12.5 m south of the vat. Total recoverable As was 55.1 mg/kg. This column was flushed under aerobic, unsaturated conditions. It was similar in most respects to the first column except that the column itself was constructed from polyvinyl chloride (PVC) with holes drilled in the side. Glass frits were used at each end of the column so that input and effluent solutions could be maintained under the desired suctions. Soil was packed into the column and the water content was adjusted prior to placing the end caps on the column.

The fourth column consisted of the A horizon material taken from the Aqualf at the Williston Road vat site. The soil was taken from the 15 to 30 cm depth at a distance of about 67 m south-southwest of the vat. It had a total recoverable As concentration of 51.2 mg/kg. Because of the high organic matter content, water flow was extremely slow through this material. In order to maintain a reasonable flow rate, solution was ponded on this soil to provide a positive pressure head for water flow. All solutions were exposed to ambient air and no attempt was made to maintain anaerobic

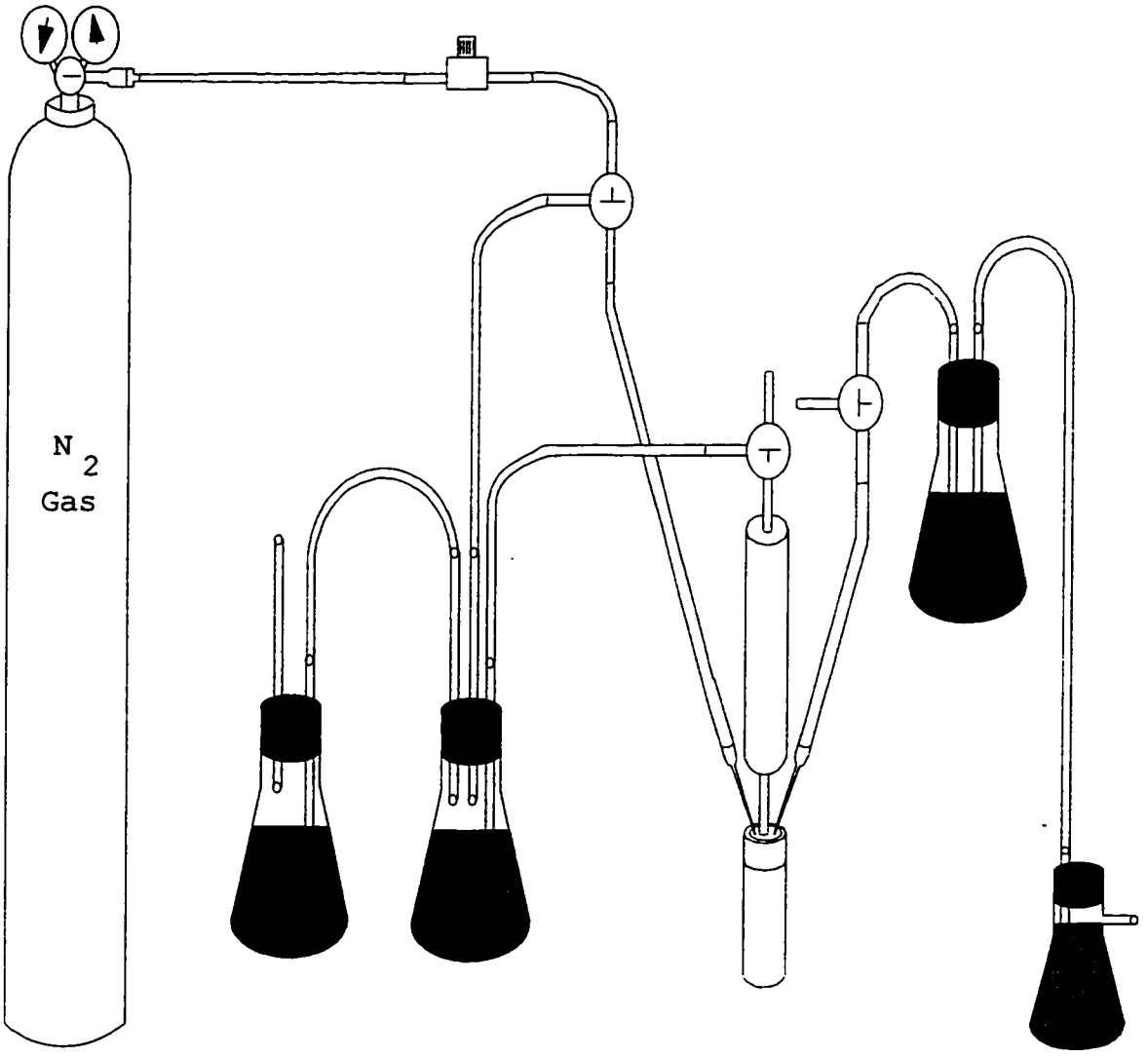


Figure 5-2. Schematic cross-section of apparatus used for the low oxic, unsaturated, differential pressure column.

conditions within the system. A schematic of the column and suction apparatus is shown in Figure 5-3.

The differential pressure columns had solution delivered by using differential pressure between the inlet and outlet of the column.[87] Flow rate for this type of column is susceptible to temperature and barometric pressure changes. Whenever available, an incubator was used to maintain a constant temperature of 25°C. If an incubator was not available, the ambient temperature was recorded and will be noted with the results for that particular column study. No attempts were made to control fluctuations in flow due to changes in barometric pressure.

All columns were flushed with 50 mM potassium chloride (pH = 5.71) followed by 50 mM potassium nitrate (pH = 5.91) and, finally, the columns were flushed with 50 mM potassium phosphate buffer (3.402 g KH_2PO_4 and 4.331 g K_2HPO_4 in 1.0 L distilled deionized water, pH = 6.86). The unsaturated columns had 0.8 g glucose per 1.0 L of eluant; whereas no glucose was added to the eluant for the saturated, ponded column. The soil in this column was judged to have an adequate amount of organic matter already present to insure good microbial activity.

After collection, all effluent fractions were weighed, filtered through a 0.45 μm membrane filter, preserved with 0.1 mL HNO3 and refrigerated at 4°C until analyzed.

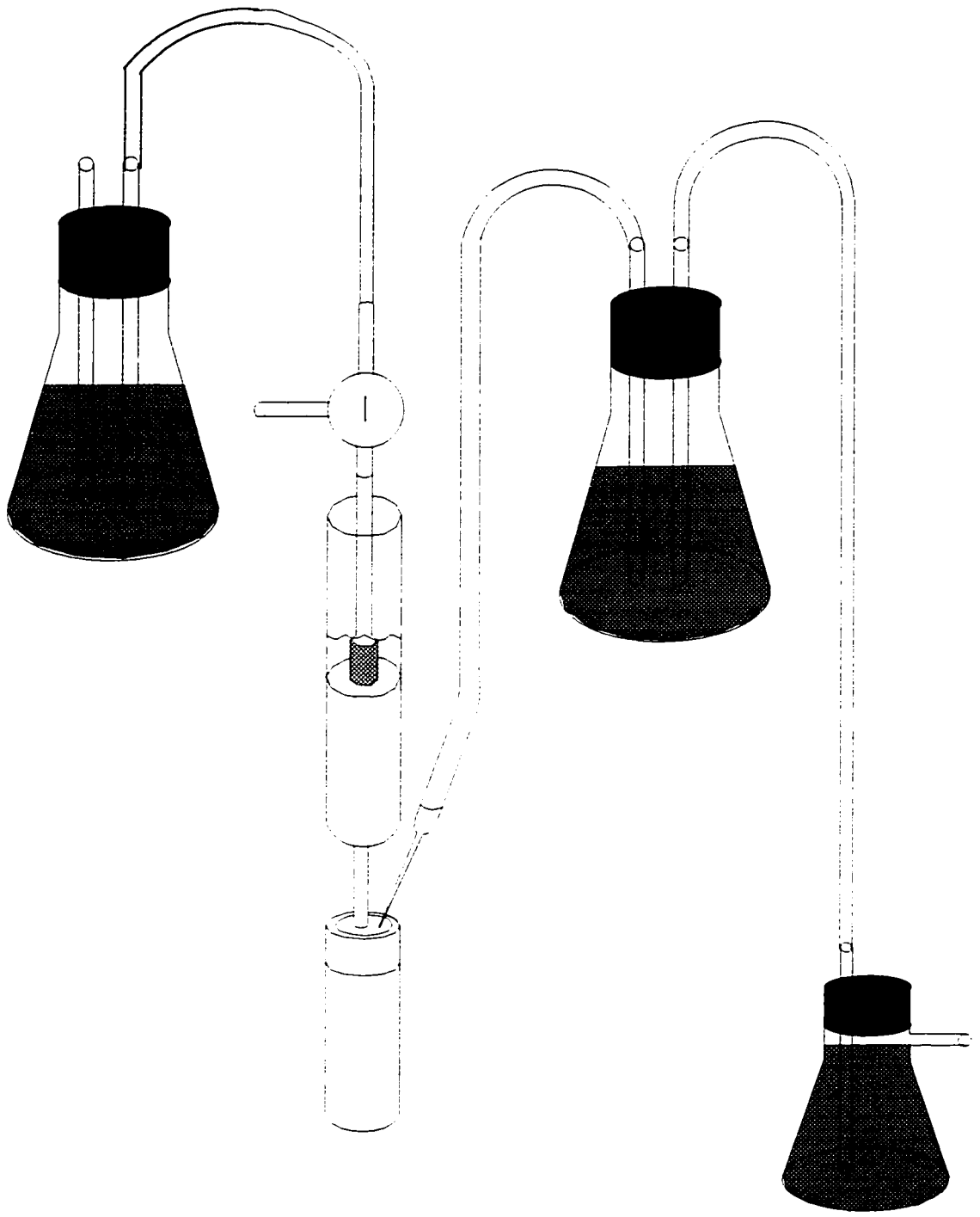


Figure 5-3. Schematic cross-section of apparatus used for the ponded, saturated, differential pressure column.

The fifth column study that was conducted involved an uncontaminated soil. This soil was from the Payne's Prairie State Preserve Bison Pen vat site. Soil was sampled from the 0-5 cm depth 54.9 meters south of the vat. The soil was analyzed for As; however, none was detected. The soil column was taken as intact as possible by pushing a glass column into the soil after surface litter had been removed. The glass column (Sigma-Aldrich, Inc., Supelco Division, Bellefonte, PA) measured 2.5 cm (internal diameter = i.d.), and the soil column length was 5 cm. More intact soil cores were taken using two brass rings (i.d. = 5.4 cm, height = 3 cm) that could be stacked; hence, soil was sampled to a cumulative depth of 6 cm. These latter two soil cores were used to determine porosity and bulk density. All soil cores were wrapped in plastic and stored at 4°C until used. No soil core was stored more than 3 months before usage.

The uncontaminated surface soil in the glass column was connected to a Shimadzu LC-10AS liquid chromatograph pump using 0.16 mm outer diameter plastic tubing and zero dead volume connectors. The soil column was initially saturated with 30 mM potassium chloride by pumping the solution in from the bottom of the column at a rate of 0.01 mL/minute. The column then was inverted after approximately two pore volumes of eluant were flushed out. The column was flushed with 42.3 mL 30 mM KCl at 3.27 mL/minute, with the flow going top to bottom. At this time, the potassium chloride solution was

switched to an arsenate solution (4.873 g $Na_2HAsO_4 \cdot 7H2O$) per 1.0 L distilled, deionized water). Effluent fractions were collected at five-minute intervals using an Isco Retriever 500 Fraction Collector (Isco Inc., Lincoln, NE). All fractions had weights recorded and 0.5 mL aliquot removed for chloride analysis. A one milliliter aliquot also was removed for As analysis by graphite furnace atomic absorption spectrometry after microwave digestion with nitric acid.

Chloride analysis of the effluent aliquots was performed for all column studies.[88] The procedure involved transferring 0.5 mL aliquot from the column effluent to a 35 mL culture tube. This aliquot was dried at 60°C in an oven. Upon cooling, twenty milliliters of 0.1 N HNO_3 were added to dissolve the residue in the tube. Chloride standards were made by drying 0.1 g NaCl in an oven at 150°C for one hour, and then allowing it to cool in a desiccator for 0.5 hours. A stock solution of 1000 mg/mL $NaCl_{(aq)}$ was made by dissolving the dried sodium chloride in 100 mL distilled, deionized water. Serial dilutions gave chloride standards of 50, 100 and 150 μg/mL. Twenty milliliters of standard or sample were used for chloride analysis after the ionic strength was adjusted by addition of 0.4 mL KNO_3 ionic strength adjuster solution (Fisher Scientific, Orlando, FL). A magnetic stir bar aided in mixing. Chloride concentration was measured using a chloride ion-specific electrode in conjunction with a double junction reference electrode. Since all of these

column studies involved replacement of the chloride ion with a different anion, the pore volume of the column was calculated by finding the volume which passed through the column from the time when the chloride influx solution was replaced to the time when the chloride concentration was only half of its original concentration on the effluent curve.

Intact soil cores were taken adjacent to the area from which the soil column was filled. These cores were sampled by pounding two stacked brass rings into the soil and removing by careful excavation. Each ring measured 3.0 cm height by 5.4 cm internal diameter. The rings were separated and loose soil was removed from the core by "shaving" with a flat-blade spatula. The o-ring in the plexiglass pressure cell (Soil Moisture Equipment Co., Santa Barbara, CA) was lubricated with "Cellu-Solve" grease (Fisher Scientific, Orlando, FL) and the core was inserted so that good contact between the porous porcelain plate and the soil was maintained. The bottom of the cell was injected with deionized water by syringe. The cell was placed in a water bath and allowed to saturate by capillary action. Saturation was confirmed by adding one drop of water to the top of the cell and, subsequently, having one drop of water exit the bottom. Total weight of the cell was recorded for saturated conditions. The soil was dried at 104°C overnight and the dry soil weight recorded.

The retention of As and P was investigated as well, using adsorption isotherms. Isotherm determinations were

based on a procedure described by M. Zhou, which entailed a modification of the Murphy-Riley colorimetric test.[90,91] In general, ten grams of soil were allowed to equilibrate overnight with 2.0 mL of 50 mM $KCL_{(aq)}$ that contained from 0 to 2000 mg/L of arsenate or phosphate. The soil plus solution was stored in acid-washed glass scintillation vials in an incubator maintained at 25°C. The following day, the samples were transferred to plastic centrifuge tubes that had Whatman #1 filter paper covering six holes drilled in the bottom. A plastic collection vessel was attached by cellophane tape to the bottom of the centrifuge tube. After centrifuging at 1500 RPM for five minutes, the soil solution was filtered through a 0.45 μm membrane filter, by syringe. A 100 mL aliquot was transferred to a clean, acid-washed glass centrifuge tube and dried at 70°C. After drying, 20 mL of 0.1 M HNO_3 were added to dissolve the residue. A half milliliter aliquot of this solution then was transferred to another acid-washed 35 mL glass centrifuge tube. Ten mL of Murphy-Riley ascorbic acid/molybdate reagent was added. The tubes were allowed to sit at ambient temperature and the color was considered to be fully developed after two hours. Absorbance of the blur solution was measured at a wavelength of 880 nmm using a Spectronic 20 ultraviolet-visible light spectrometer (Bausch and Lomb, Rochester, NY). The total amount of P or As absorbed was calculated by: $S=\frac{(Cos-Cps)x2}{10}$ where S is the amount of analyte adsorbed (μg/g soil), Cos is the original

concentration (μg/mL) of analyte, and Cps is analyte concentration (μg/mL) in the pore solution after twenty-four hours of equilibration with the soil.

Results and Discussion

Differential Pressure Column Studies

The differential pressure column studies were all performed using soil that had been contaminated with As and then weathered for more than thirty years since the last application of cattle dipping vat solution. Leaching of the columns was accomplished by sequential applications with potassium salt solutions of chloride, nitrate, and phosphate. All three anions are commonly found in commercial fertilizers in varying amounts. The effect of these anions, as well as the effect of Eh and pH, on As adsorption and/or desorption for soils have been the subject of several studies.[45,47,85,86,92] The previous investigations were batch adsorption and/or desorption experiments however, and did not involve column leaching. Another common feature was the lack of care to insure biotic viability. Often the soil had been previously air-dried and stored at room temperature. In the column studies presented in this section, the soil was handled so that microbial activity would remain relatively uninhibited.

The first differential pressure column study involved the "E" horizon (45-60 cm depth) from the Bison Pen vat site

under aerobic and unsaturated conditions (Table 5-1). The effects of leaching with aqueous solutions of KCl or KNO_3 resulted in little displacement of As from the soil (Figure 5-4) under high oxic conditions. It is interesting to note that the chloride anion appeared to be capable of displacing more arsenate than the nitrate anion. One possible hypothesis that explains this behavior invokes the supposition of low oxic micro-sites within the soil column that promote the reduction of arsenate to the more mobile arsenite ion by microorganisms under chloride elution; whereas, the presence of nitrate could inhibit this phenomenon. In fact, a testament to biological viability of this soil came from the observation of fungal mycelia that grew out of the holes drilled in the side of the column. Further evidence for this hypothesis was obtained when the column was placed under $N_{2(g)}$ in the second study. Upon leaching with phosphate buffer, the amount of As eluted increased substantially (Figure 5-5). There was certainly an anionic displacement mechanism, particularly in light of the homologous chemistry exhibited between phosphate and arsenate. Batch extractions on soils that have been air-dried, sieved, and/or stored at room temperature, all exhibit significant displacement of arsenate by phosphate.[47,86] One investigation using batch extractions concluded that 1 N NH_4Cl and 0.5 M NH_4NO_3 removed less than 0.1 μg As/g soil, while 0.5 M KH_2PO_4 could extract arsenic in the percent recovery range 10.2 to 37.2, depending on the soil type.[47] A second investigation

Table 5-1. Selected soil column characteristics.

Soil	Horizon	Depth (cm)	Soil Dry Weight (g)	Oxic Level	Moisture (g H_2O/g dry soil)	Inlet Height (cm)	Outlet Height (cm)	Bulk Density (g/cm^3)	Porosity[1] (cm^3/cm^3_T)
Bison Pen Millhopper sand	E	45-60	31.35	High	0.133	37.0	30.5	1.69	0.362
	E	45-60	32.63	Low	0.134	26.3	18.2	1.76	0.336
	Bt	152-165	31.25	High	0.150	27.0	15.0	1.62	0.389
Williston Road Aqualf soil	A	15-30		Low		6.0	25.5		
Bison Pen Millhopper sand	A	0-5	37.31	Low	0.092	---	---	1.52	0.141

1) Assumed particle density for these soils = 2.65 g/cm^3

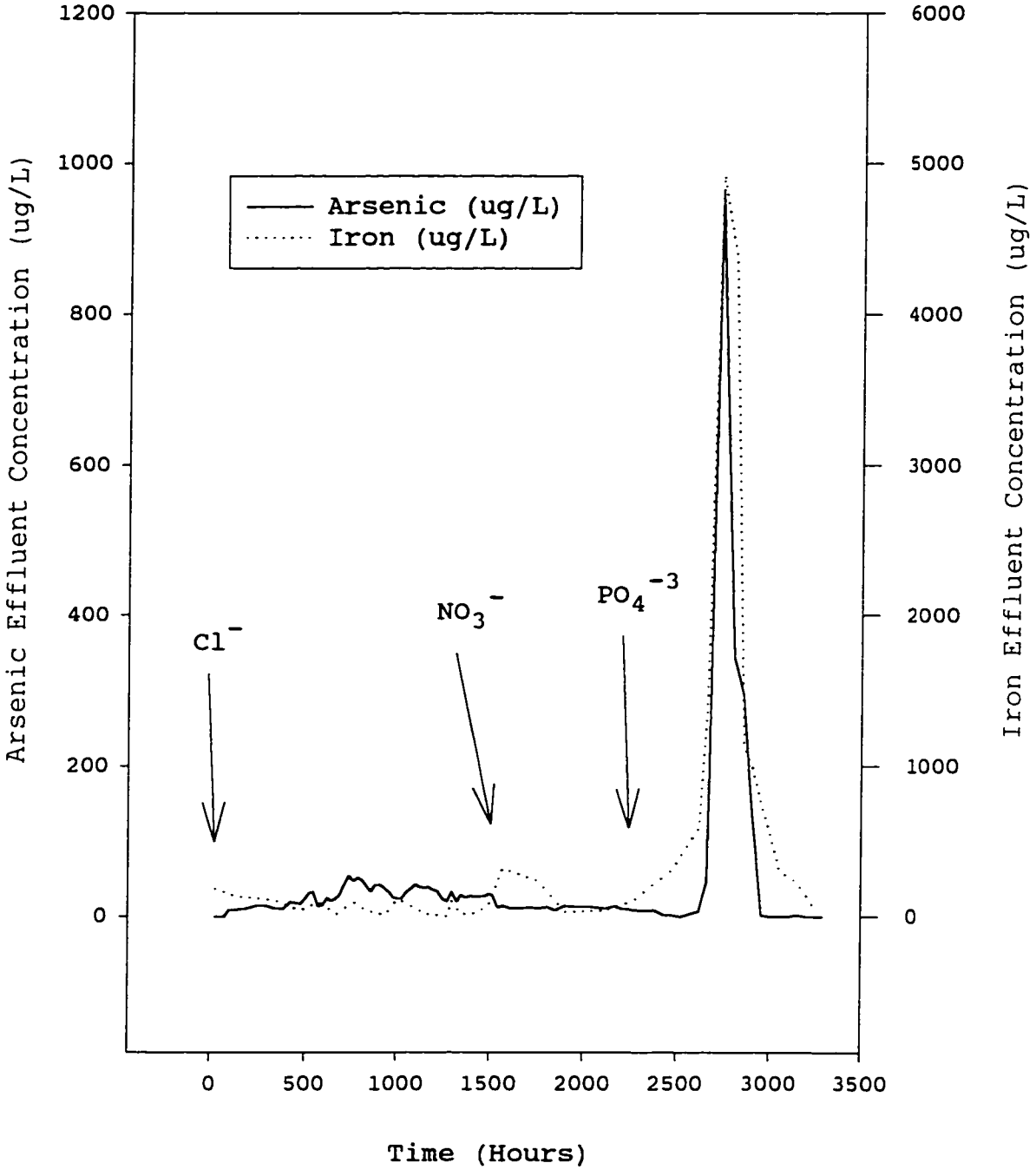


Figure 5-4. Effluent from an aerobic, unsaturated column of Payne's Prairie Bison Pen vat "E" soil (45-60 cm depth) sequentially eluted with 50 mM potassium chloride, nitrate, and phosphate solutions.

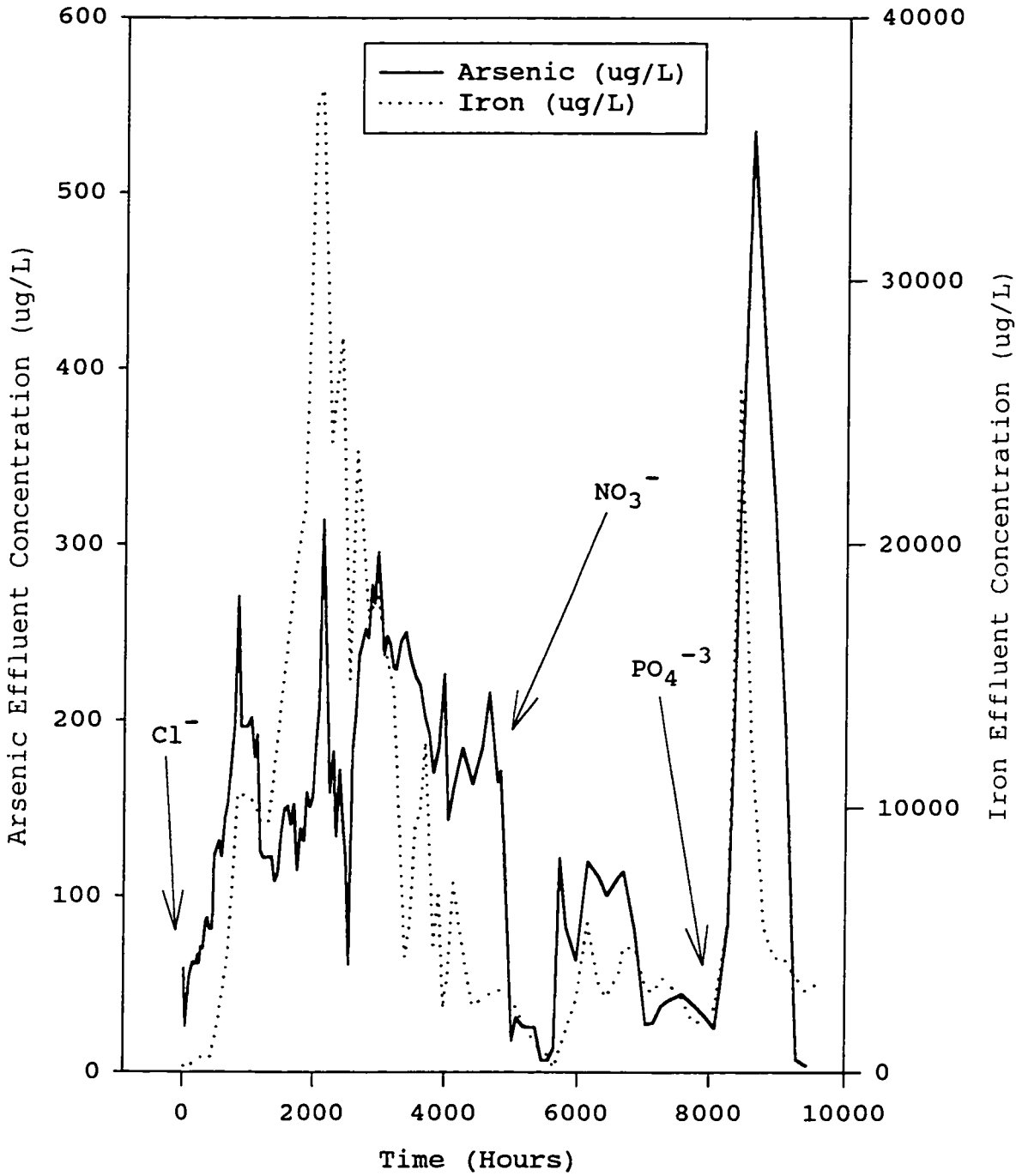


Figure 5-5. Effluent from a micro-aerobic, unsaturated column of Payne's Prairie Bison Pen vat "E" soil (45-60 cm depth) sequentially eluted with 50 mM potassium chloride, nitrate, and phosphate solutions.

demonstrated that the cations, NH_4^+ and Ca^{+2}, had no effect on phosphate displacement of arsenate.[86] These researchers suggested that the dissolved phosphate controlled As solubility through specific anion exchange, and that the solubility of the phosphate was determined by meta-stable phosphate minerals.[86] As previously noted, the rather harsh treatment of soils in these studies would inhibit, if not preclude altogether, their biotic viability.

The above arguments for an anionic displacement mechanism are very convincing and should not be ignored. However, in these column studies on the Bison Pen vat site "E" horizon soil, biological activity was a contributing factor to the release of As from the soil upon the addition of phosphate anions, since iron was released to the effluent concurrently. It should be noted, at this point, that the column system had been supplied with potassium, nitrogen, and carbon (as glucose) before the nutrient, phosphate, was added. These column studies demonstrated that iron was released from the soil concurrent with the release of As (Figure 5-4 and 5-5). Bacterial reduction of iron oxides has long been known to be important in increasing the nutrient availability of iron and in determining the movement of iron in soil.[85] It has been suggested that the As will adsorb preferentially to oxalate-extractable amorphous Al and Fe compounds.[86] Other researchers have demonstrated a high correlation existed between aluminum and iron minerals with the adsorption of As.[84] The results of

these column studies suggested that as iron was released from the soil under these conditions, then As is also mobilized. The effluents in these studies were analyzed for aluminum; however, none was detected in the leachate, even though aluminum was present in this soil horizon at a total content of 960 mg Al/kg soil.

Several attempts at clarifying the roles of the biotic and the abiotic release mechanisms were made by trying to maintain a sterile soil column. The soil and column material were autoclaved three times for 1-hour periods. The solutions were autoclaved and received either 10% chloroform or a mixture of ampicillin/tetracycline. Effluents were tested for microbial activity by streaking on an L-plate (200 mL deionized water + 1 g Yeast extract + 2 g Tryptone + 1 g NaCl + 4 g agar). In all cases, biological growth occurred on the agar plates, so no column remained sterile for any appreciable time.

More success was achieved by placing the column in a purging nitrogen gas, instead of in the ambient atmosphere. These conditions are described as micro-aerobic or low oxic since: 1) the gas manufacturer (Liquid Air, Jacksonville, FL) claimed the $N_{2(g)}$ had less than 250 ppm O_2; 2) no oxygen scrubber was employed; and 3) the tubing and column were not impermeable to $O_{2(g)}$. Given these conditions, elution of the micro-aerobic unsaturated column with 50 mM potassium chloride yielded a leachate that typically contained an As

concentration of 100-300 μg/L (Figure 5-5). This is two to six times more than the U.S.E.P.A. limit for drinking water, and two to six times the effluent concentration under aerobic conditions.[27] Upon switching the eluant anion from chloride to nitrate, there was a decrease in the amount of leachate As. After 5800 hours of operation; however, the air conditioning in the laboratory became non-functional. The column thus was subjected to a 10°C temperature increase from 22° to 32°C. It is believed that this increase in temperature was responsible for an increase in biological activity which, in turn, was directly related to an increase in iron and arsenic for the column's effluent. When the ambient temperature returned to 22°C at 6975 hours, there was a decrease in the As concentration of the leachate once more.

When the eluting anion was changed from nitrate to phosphate, it resulted in a large increase in the iron and arsenic concentrations in the column effluent. This is similar to the behavior observed for the high oxic, unsaturated column; however, the maximum As concentration was roughly 2-fold greater under aerobic conditions than for the low oxic conditions. In contrast, the iron concentration was nearly seven times greater for the low oxic column's leachate than for leachate from the high oxic column. It is hypothesized that the variation in iron release was due to greater biological reduction of iron from ferric to ferrous (a more mobile species) under the less oxic conditions. The

lower As release by phosphate from this same column was probably due to there being a finite amount of arsenic present, with the greater initial release of As lowering the amount that could be subsequently released by phosphate later. Overall, the low oxic column released a total of 41.8 μg arsenic (5.9% of the total As available) in comparison to the high oxic column's release of 14.7 μg arsenic (2.2% of the total As available).

The third column to be set up was under aerobic and unsaturated conditions using "Bt" horizon (152-165 cm depth) material from the same site as the previous columns. The total amount of As in this soil horizon was approximately fifty times greater than for the "E" horizon, although the iron content was lower while aluminum was higher than in the general soil. However, it should be noted that the "E" horizon came from directly above the argillic horizon and contained many red concretions which would have elevated the iron concentration. There was little As leached from the column when 50 mM potassium chloride or potassium nitrate solutions were used (Figure 5-6). Once again, the introduction of the phosphate anion caused a massive release of arsenic and iron from the soil. Total As eluted from this column was 1320 μg, which was 76.8% of the As in the soil. It was interesting that release of iron occurred with potassium chloride elution even though little As was eluted with it. Another facet of interest was that the elution of iron after phosphate

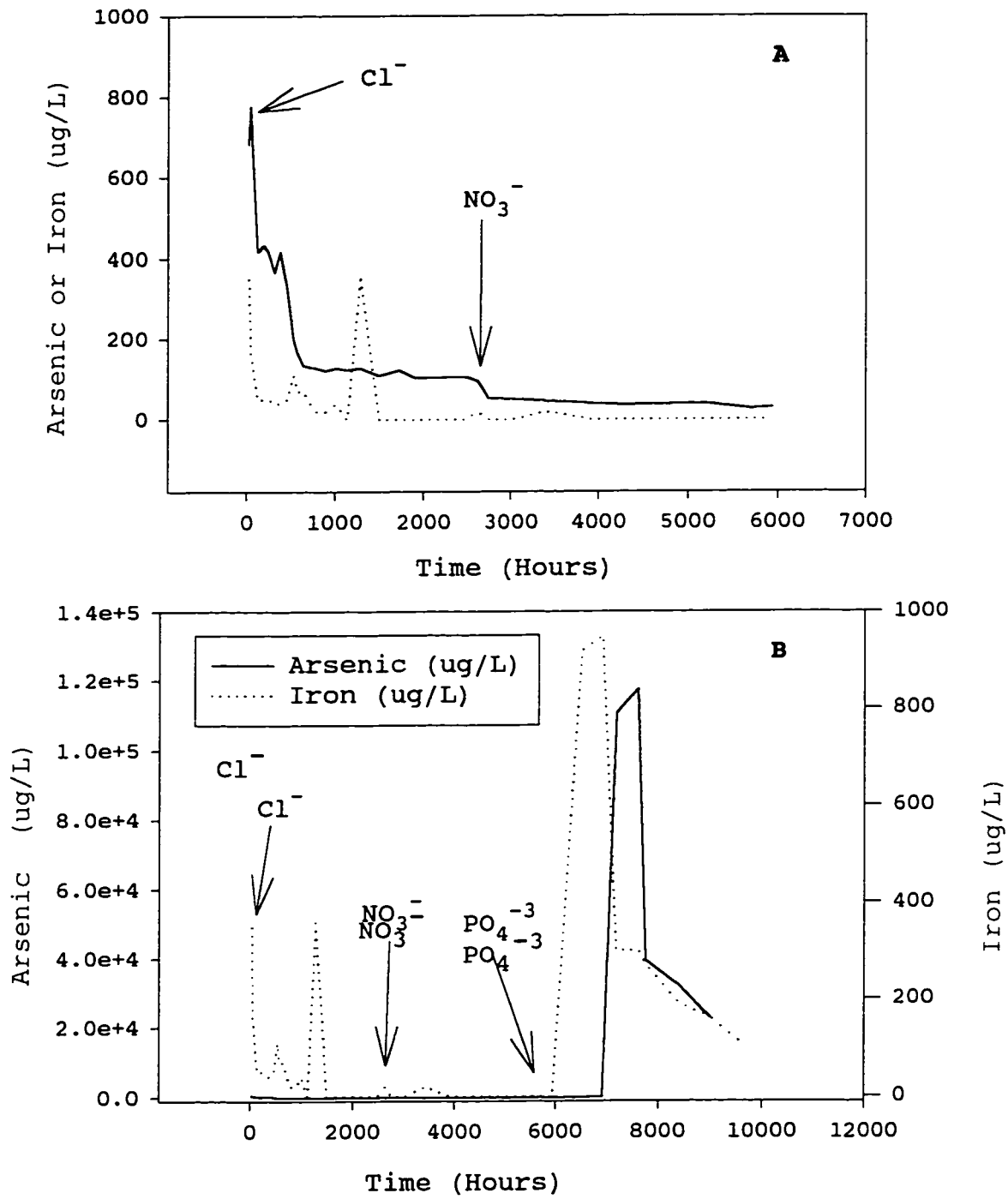


Figure 5-6. Iron and arsenic in effluent from an aerobic, unsaturated column of Payne's Prairie Bison Pen vat "Bt" soil (152-165 cm depth) sequentially eluted with 50 mM potassium chloride, nitrate, and phosphate solutions. Graph A is different scaling than Graph B.

addition occurred before the elution of As from the soil. The lag in As elution upon release of iron from the soil may be explained by re-adsorption of the arsenical anions by the aluminum oxides and hydroxides that are present in the Bt horizon. Elution of aluminum by this column occurred with chloride and nitrate, but was negligible in the case of phosphate (Figure 5-7). Given these column conditions and for this soil sample, there appeared to be no correlation between the arsenic and aluminum concentrations in the leachate solutions. In contrast, the release of iron preceded the release of As from this soil.

A similar elution pattern of iron release before As release was observed in the fourth column investigation, although the effect was not as dramatic (Figure 5-8). The fourth column study was done using ponded and saturated column conditions using an "A" horizon that contained 3.3% organic matter. Since the organic matter content was three times greater than for any soil previously tested, the decision was made to forego the addition of a second carbon source, such as glucose. One of the drawbacks of this column design was its susceptibility to atmospheric pressure fluctuations. The amount of ponding on the column would vary from 0.64 cm to 2 cm and the flow rate through influence of the differential pressure column would vary with temperature and barometric pressure. Generally, the longer a column was maintained, the slower its flow rate (Table 5-2). An exception to this

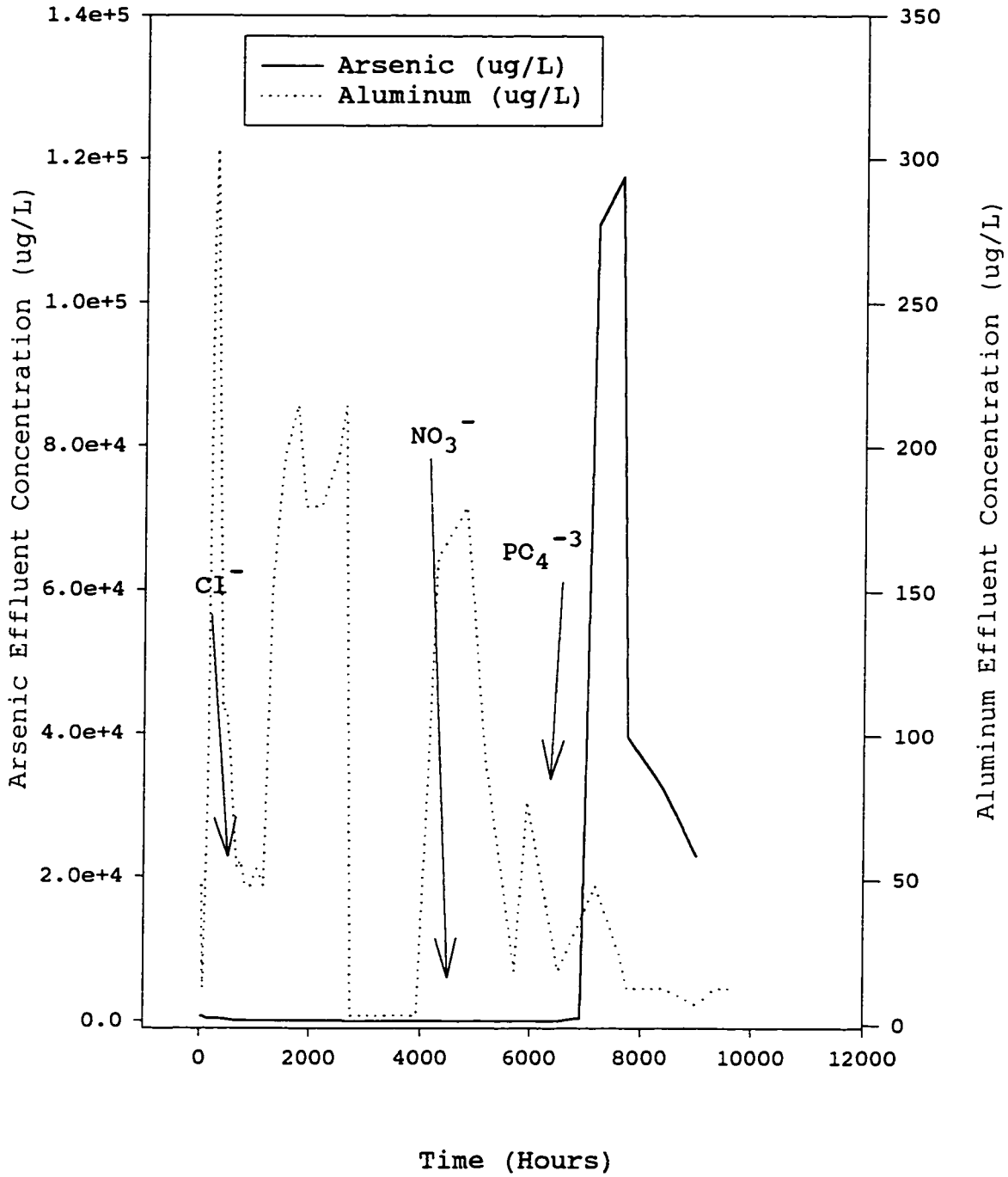


Figure 5-7. Aluminum and arsenic in effluent from an aerobic, unsaturated column of Payne's Prairie Bison Pen vat "Bt" soil (152-165 cm depth) sequentially eluted with 50 mM potassium chloride, nitrate, and phosphate solutions.

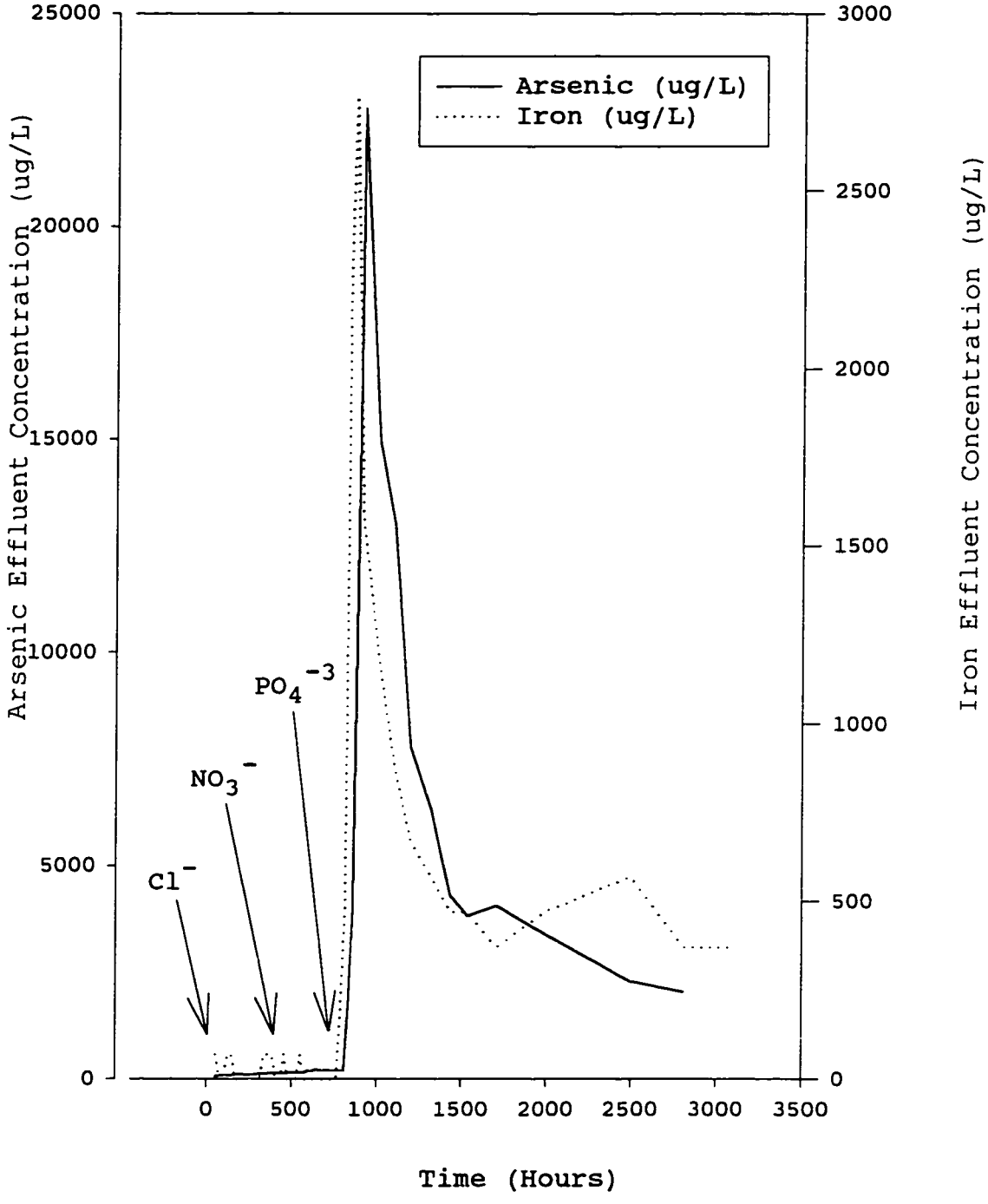


Figure 5-8. Iron and arsenic in effluent from a ponded, saturated column of S.W. Williston Road vat "A" soil (15-30 cm depth) sequentially eluted with 50 mM potassium chloride, nitrate, and phosphate solutions.

Table 5-2. Flow rate variations after sequential elution of differential pressure columns.

Eluant	High Oxic "E" Column Flow Rate[a] (mL/hr)	Low Oxic "E" Column Flow Rate[a] (mL/hr)	High Oxic "Bt" Column Flow Rate[a] (mL/hr)	Ponded, Saturated "A" Column Flow Rate[a] (mL/hr)
KCl	0.197 ± 0.095	0.071 ± 0.031	0.052 ± 0.031	0.671 ± 0.084
KNO_3	0.111 ± 0.075	0.006 ± 0.003	0.006 ± 0.003	0.575 ± 0.047
KH_2PO_4/K_2HPO_4	0.083 ± 0.058	0.009 ± 0.006	0.009 ± 0.006	0.158 ± 0.179

a) plus or minus the standard deviation

trend was the high oxic "Bt" column study, wherein the slowest rate occurred during the period when it was being leached with potassium nitrate. It was noted that the "Bt" column also had the highest amount of aluminum in its effluent under leaching by chloride or nitrate solutions (Figure 5-7). In all cases, it was noted that the time frame where the leachate was highest in iron and/or aluminum coincided with a drop in the flow rate. Both facets could indicate a change in soil structure within the differential pressure columns. The ponded, saturated column study was no exception to this pattern. During the leaching of "A" horizon soil with potassium chloride or potassium nitrate, the flow rate averaged 0.623 mL/hour. Under phosphate buffer elution, the leachate's iron concentration reached a maximum of 2,770 μg/L while aluminum reached 36,530 μg/L and, forty-eight hours later, the As reached its maximum concentration of 293.3 μg/L (Figure 5-8 and 5-9). Overall, a total of 882 μg As (61.5%) was released. Concurrent with the increase in ionic leaching under phosphate elution of the soil, the flow rate dropped to 0.158 mL/hour with a standard deviation of 0.179 mL/hour. It remained inconclusive whether the decrease in flow rate was due to: 1) collapse of the soil pore structure or 2) clogging of the glass frit at the bottom of the columns either by colloidal movement and coagulation or by precipitation reactions occurring within the frit itself.

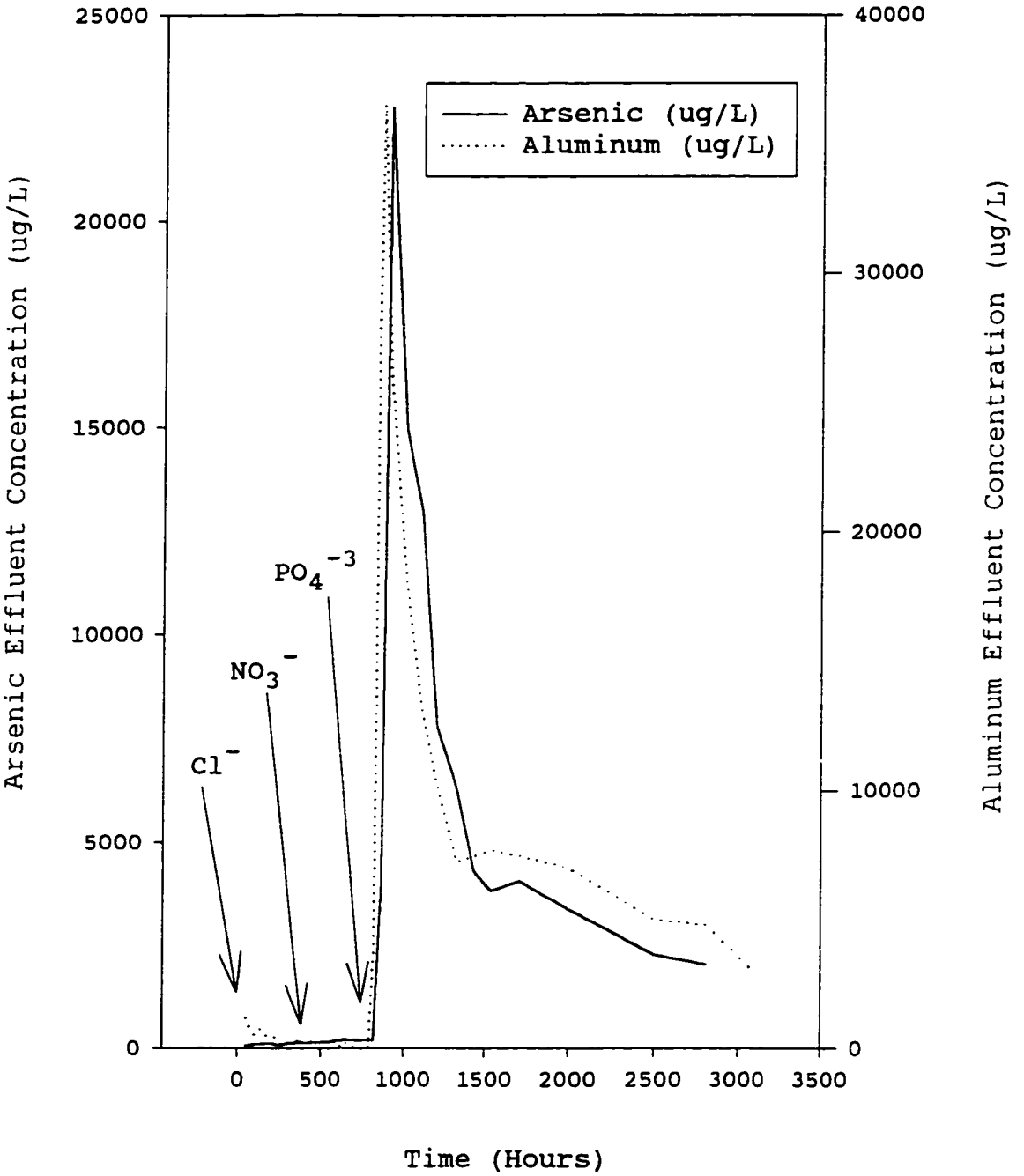


Figure 5-9. Aluminum and arsenic in effluent from a ponded, saturated column of S.W. Williston Road vat "A" soil (15-30 cm depth) sequentially eluted with 50 mM potassium chloride, nitrate, and phosphate solutions.

Mechanically Pumped Column Study

An attempt to take an intact soil core for a column study was made by pushing a glass tube into the soil. Due to the blunt ends of the tube; however, some compaction was inevitable. The soil column was connected to a pump and saturated with 50 mM potassium chloride from bottom of the column. The flow then was reversed and the column leached with a solution of sodium arsenate (4.86 g/L). Concentration of the arsenic was based on historical recipes for manufacture of the cattle dipping vat solution, which called for 1.92 mg AsO_3 per mL of solution. The fractions were collected and analyzed for arsenic and chloride (Figure 5-10). Pore volume of the column was determined from the chloride data to be 15.99 mL. The saturated water content was determined for intact soil cores taken at the same time and place as the soil column. These data were used to calculate the gravimetric water content (0.0092 mL water/g soil) by the difference in weight of the saturated soil and dried soil divided by the weight of the dry soil. Since the height (3 cm) and internal diameter (5.4 cm) of the soil core were known, then the bulk density of the soil could be determined by dividing the weight of the dry soil by its volume (Table 5-1). Porosity was found by multiplying soil bulk density by the gravimetric water content and dividing by the density of water (Table 5-1).

Flow rate of the pump was set by using a typical flux for

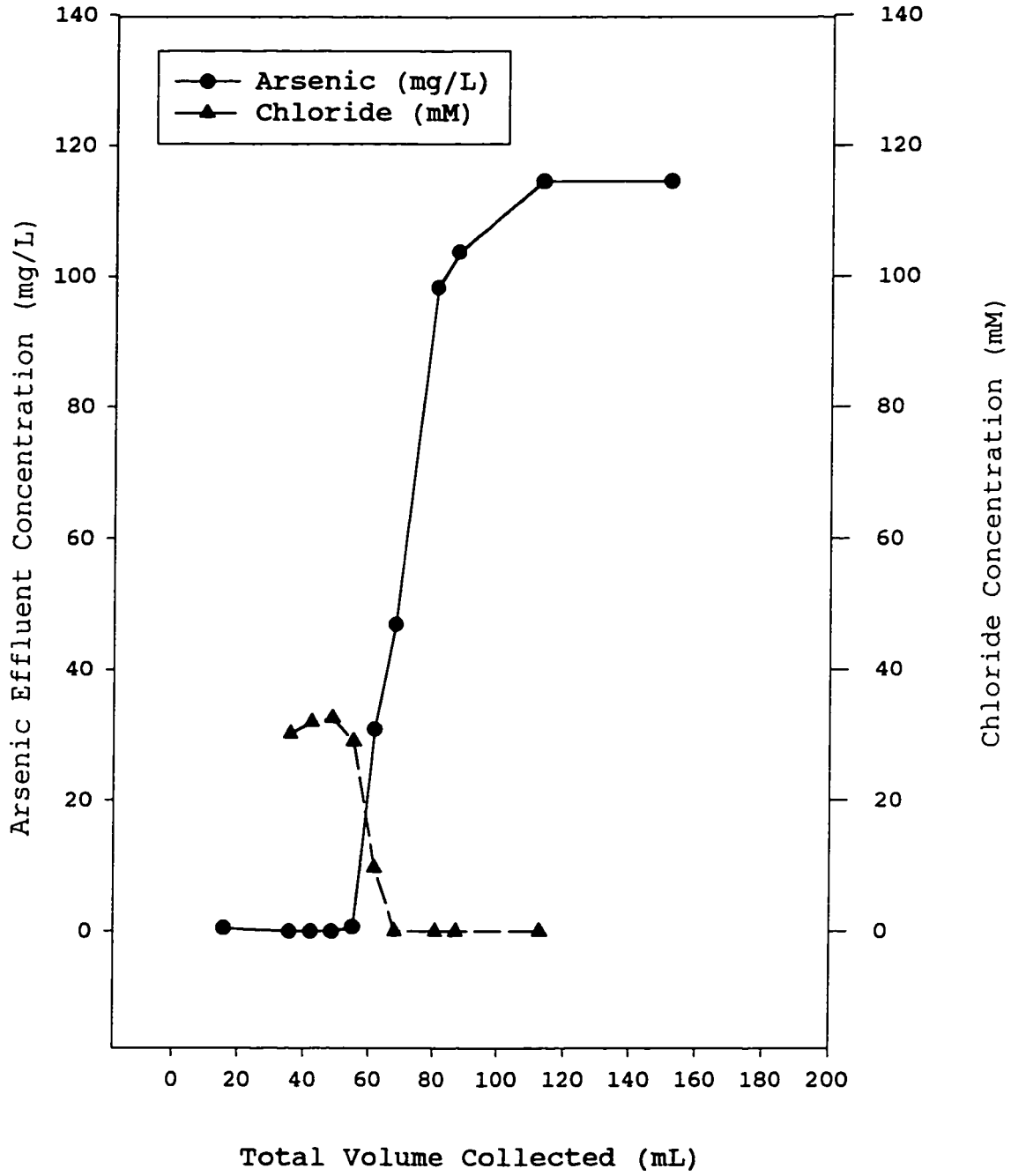


Figure 5-10. Chloride and arsenic in effluent from a pumped, saturated column of Payne's Prairie Bison Pen vat "A" soil (0-5 cm depth) initially saturated with 30 mM potassium chloride, then eluted with solution of sodium arsenate (4.86 g/L).

water in a Florida soil as 20 $cm^3/cm^2 \cdot hour$. Since the internal diameter of the column was 2.5 cm, the flow rate was found to be 3.27 cm^3/minute. This meant that the pore velocity could be calculated as flow rate divided by porosity, or 23.4 cm/min.

Basically, column flow rates and the concentrations of As solution were set up to mimic the dumping of an oxidized cattle dipping vat solution onto a typical Florida soil adjacent to the dipping vat.

Adsorption isotherms were constructed from experimental data using the Payne's Prairie Bison Pen "A horizon" soil (0-15 cm depth) and either sodium phosphate or sodium arsenate solutions (Figure 5-11). The plot of $\log_{10}S$ versus $\log_{10}C_{ps}$ yielded linear relationships for both arsenate (linear regression coefficient R^2 = 0.995) and phosphate (R^2 = 0.9997). This linear relationship between $\log_{10}S$ and $\log_{10}C_{ps}$ is typical of a Freundlich isotherm, and can be expressed by the equation $S=K_dC_{ps}^n$, where S is analyte sorbed onto the soil (ug/g), K_d is the distribution coefficient, C_{ps} is equilibrium concentration of the analyte in the soil pore solution (ug/mL), and n affects curve shape and is referred to as a Freundlich constant.[95]

By taking the log of the Freundlich expression, the equation is converted into the linear form y = mx + b, where the slope of the line represents the Freundlich constant (n)

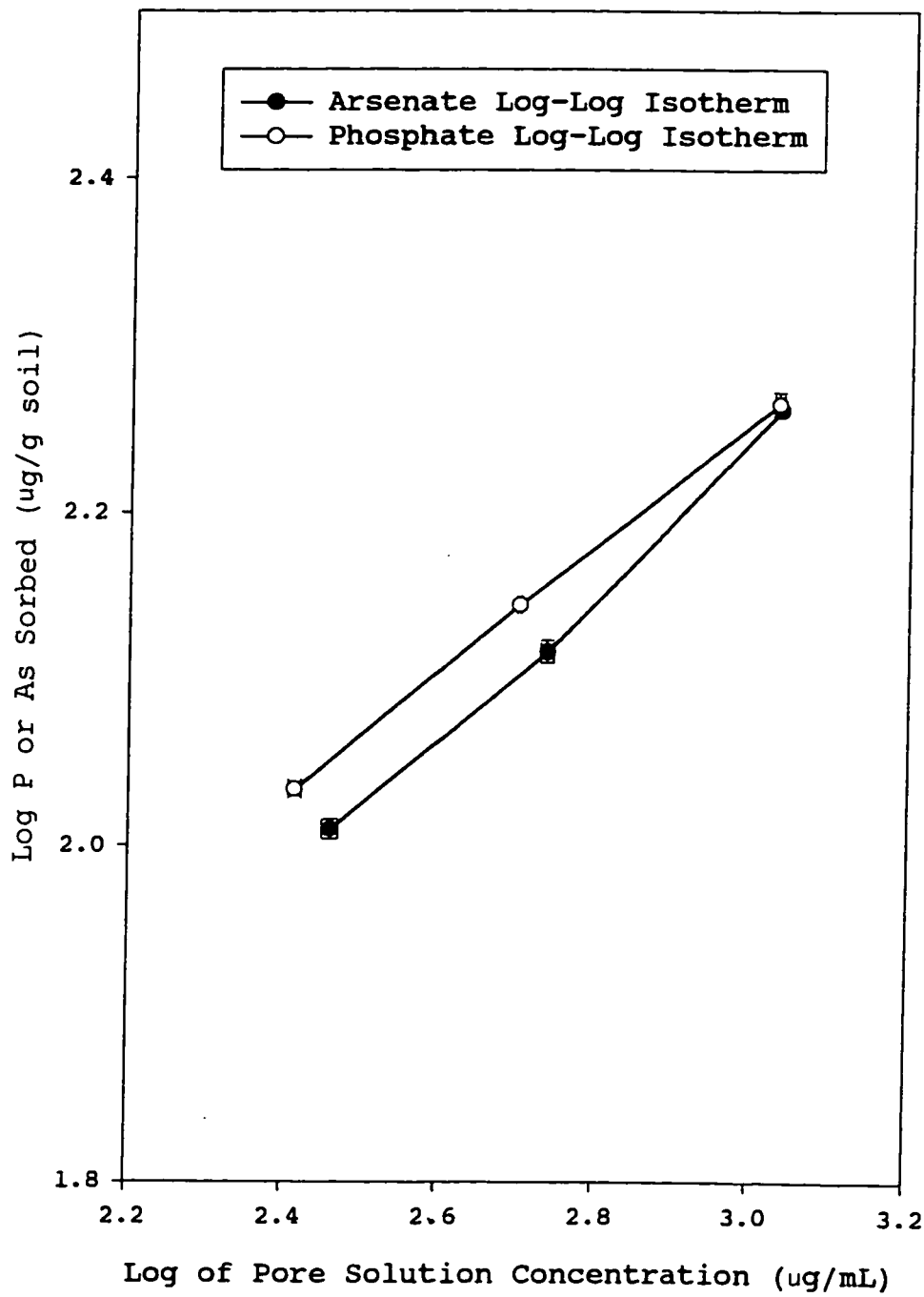


Figure 5-11. Phosphate and arsenate log-log isotherms for Payne's Prairie Bison Pen vat "A" soil (0-5 cm depth).

and the intercept corresponds to $\log_{10}$ of the distribution coefficient (K_d). For phosphate K_d = 14.5 and n = 0.36 for this soil, while the arsenate values were 8.49 and 0.44, respectively. The K_d value found for arsenate was within the range reported in the literature of 1.9 to 18.0, based on 37 different studies. The median was reported as 6.7 with a standard deviation of 0.52.[96]

If the Freundlich constant, n, was assumed to be equal to unity, then the distribution coefficient could be considered as a gauge of anion adsorption. Another useful aspect of assuming n=1 is that the Freundlich equation is reduced to a linear equation without the necessity of taking the log of the expression. For this simplified expression, a retardation equation can then be derived.[97] This equation relates retardation to the distribution coefficient as: $R = 1 + (\rho_b K_d)/\theta_{sat}$, where R is the retardation factor, ρ_b is the bulk density (g/cm^3), K_d is the distribution coefficient, and θ_{sat} is the porosity (cm^3/cm^3). For the soil used in this column study, R equals 93.4. Since the pore velocity was 23.4 cm/min and the length of the soil column was 5.0 cm, this meant that the break-through time for a non-absorbed analyte was 0.213 minutes. For arsenate, with its retardation factor of 93.4, the break-through time was calculated as 19.9 minutes. In terms of pore volumes, this was calculated as 4.07. The column effluents were collected as fractions consisting of 0.4 pore volumes. The analyzed fractions showed that break-

through occurred between 3.85 and 4.25 pore volumes. It is obvious (Figure 5-12) that, as a first approximation, this method of calculating the retardation factor is acceptable.

Conclusions

In general, differential pressure column studies indicate that the removal of As from soil is best accomplished with low oxic conditions. For the "E" horizon from the Bison Pen vat site, the total amount of As removed with low oxic levels was almost triple the concentration of As eluted under aerobic conditions.

Of the three anions investigated, phosphate was much more effective then chloride or nitrate in releasing As from the soil. Phosphate has homologous chemistry with As and could readily displace the As from the soil chemically. Phosphate is also a necessary macro-nutrient and may stimulate microbial growth, especially after potassium, nitrogen, and carbon sources have been supplied. This increased biotic activity can, under low oxic conditions or at anaerobic micro-sites, cause reduction of iron and solubilization of humic/fulvic complexes. Both would cause an increase in the amount of As in the effluent from a soil column. Several unsuccessful attempts were made to maintain a sterile column, to elucidate the biotic versus chemical displacement of As in soil.

Both the chloride and nitrate anions were ineffective in displacing As from soil. In fact, it appeared that nitrate

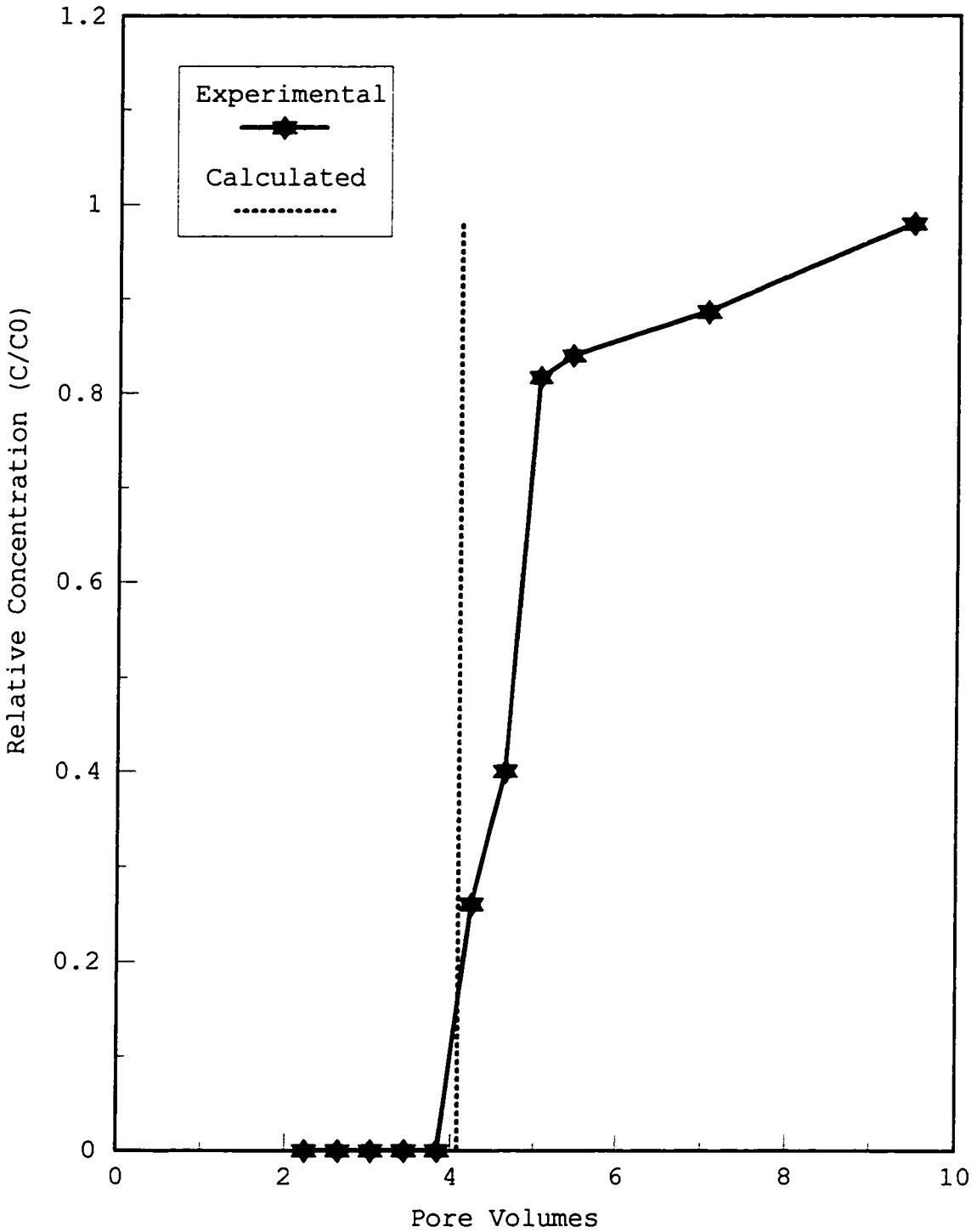


Figure 5-12. Comparison of calculated and experimental break-through of arsenic in the Payne's Prairie Bison Pen "A horizon" soil column.

had a slight repressive effect on the elution of As from soil columns.

Elution of As from the soil columns was either preceded by or accompanied by the elution of iron, though no relationship was found between the release of aluminum and the As concentration in the effluent. In fact, only the "Bt" horizon from the Bison Pen vat site and the "A" horizon from the Williston Road site released enough aluminum to be detected.

Using the "A" horizon from the Bison Pen vat site, it was shown that a one-dimensional transport model based on the Freundlich relationship could be used to predict the break-through of As from a soil column. The assumptions made in calculating a retardation factor were justified by the accuracy of the prediction.

Further research should include evaluation of the transport model in order to predict the break-through of As from soil columns eluted with solutions containing As and organic compounds similar to those found in some of the formulations for cattle dipping mixtures. It would also be of interest to speciate the arsenic, iron, and aluminum being eluted from these columns. Other questions include: 1) to what extent biotic influences versus chemical mechanisms play a part in the extent of As elution from soil columns upon phosphate addition, and 2) how much As would be eluted by a mixture of anions such as nitrate and phosphate.

CHAPTER 6
SURFACTANT EXTRACTION OF ARSENIC FROM SOIL

Introduction

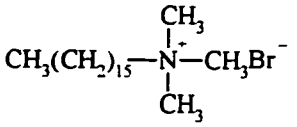
Extraction by solvents was reviewed in the previous chapter. Another type of remediation technique for treating As contaminated soil involves the use of surfactants with or without a chelating agent. In general, if the process is completed *in situ*, it is referred to as soil surfactant flushing. The *ex situ* method, whereby the soil is excavated prior to treatment, is termed soil surfactant washing.[98] If the process is to be done *in situ*, then the site must be carefully selected, since soil flushing engenders mobilization of the contaminant. Generally, the surfactant mixture is applied via an injection well and the surfactant-contaminated solution is removed by a recovery well. An unsuitable site subjected to this treatment may make remediation more difficult. On the other hand, *ex situ* treatment confines the contaminant within its system; however, it does require excavation of a considerable amount of soil. This may not be a practical alternative in many cases.

Other practicalities to be considered involve recovery of the surfactant for recycling, extraction efficiency of the

surfactant system, cost of the surfactants, and chelating agents (if used) and the biodegradability of the reagents, particularly for *in situ* remediation efforts. A further consideration for *in situ* remediation is delivery of the surfactant mixture to the contaminant. If the soil has a high clay content or has low permeability due to other factors, then the *ex situ* soil washing procedure may be more efficient than an *in situ* soil flushing method. Soil flushing may also be made impractical by virtue of the surfactant's biodegradability. If the solutions are not at all inhibitory, then the soil flushing reagents may serve as a nutrient source for microorganisms that produce polysaccharides, which could plug soil pores so that the contaminant cannot be reached and/or recovered.[99]

The scope of this dissertation does not cover all aspects of soil flushing or washing to remediate soil contaminated with As. In fact, the emphasis in this section has been placed solely on the extraction of As from contaminated soil by surfactants. For contrast, a cationic surfactant called hexadecyltrimethylammonium bromide (HdtABr) and a zwitterionic surfactant named 3-[3-cholamidopropyl)-dimethylammonia]-1-propane sulfonate (CHAPS) were used to extract As from soil (Figures 6-1a and b). Since As in soil is predominantly a negatively charged species, the cationic surfactant should bind to it easily through ionic interactions. If the concentration of the surfactant is above the critical micelle

A



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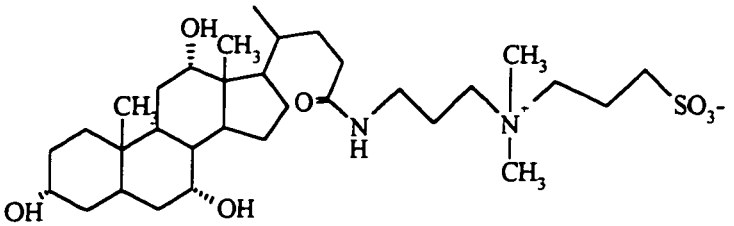

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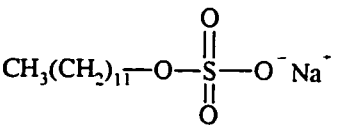

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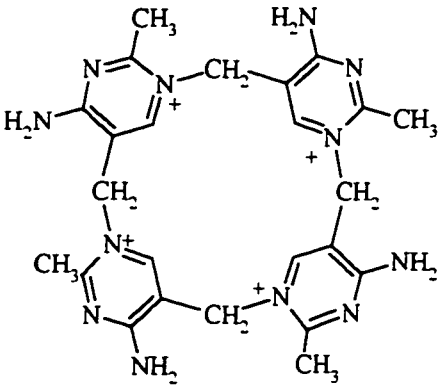

Figure 6-1. Chemical structures of a)hexadecyltrimethyl ammonium bromide (HdtABr); b) 3-[3-cholamidopropyl)-dimethylammonia]-1-propane sulfonate (CHAPS); c) sodium dodecylsulfate (SDS); and d) [16-pyrimidinium crown-4]$^{4+}$.

concentration (CMC), the hypothesis is that the arsenical anion would be in the palisade area of the micelle. It was theorized that this would prevent re-formation of arsenic-soil bonds. The zwitterionic surfactant was expected to behave in similar fashion, since a zwitterion is an ion that carries both positive and negative charges. The negative charge for the CHAPS surfactant is on the outside of the micelle, the positive charge recessed inward and the center of the micelle contains the non-polar tail of the surfactant. The non-polar tail of CHAPS contains hydroxyl groups, allowing for hydrogen bonding to the oxyanionic arsenic. This attraction as well as coulombic attraction between the positively-charged portion of the zwitterionic surfactant and the negatively-charged arsenical ion was hypothesized to be an effective scavenger. The outer negative charge on the micelle was expected to repulse the negative charge found on the soil particle; hence preventing re-adsorption of As. Obviously, if the negative outer charge repulses arsenical anions, then extraction efficiency would be low.

The final surfactant system involved an anionic surfactant, sodium dodecylsulfate (SDS) (Figure 6-1c). Since this surfactant and the contaminant both exhibit negative charges, the extraction efficiency would be expected to be negligible, unless the charge is reversed on one of the components. Complexation of the arsenical anions by a highly-charged chelator would accomplish this goal. In fact, this

method of chelate/surfactant washing has been used to extract As, Cd, Cr, Cu, Pb, Ni, and Zn anions from composite soil prepared in the laboratory. A recovery of 93% was found using a chelating agent, ethylene diaminetetraacetic acid (EDTA), with an anionic phosphatic surfactant at a pH of 8 to 12.[100] While this pH range was necessary to fully deprotonate EDTA, it makes this system impractical for *in situ* flushing of Florida soils where the pH is typically 5.5 to 6.5.

The perfect chelator for *in situ* remediation would have to: 1) complex the As oxyanions, 2) maintain pH in the normal range for the soil, 3) be capable of 100% extraction from a variety of soil types and 4) be non-toxic initially as well as in its degradation products. A potential chelator, [16-pyrimidinium crown-4]$^{4+}$ was chosen (Figure 6-1d). This macrocycle has a "hole" of 1.3 Å, which is far too small to encircle nitrate, or the even larger arsenical anion. This chelating agent has been shown to enfold the nitrate anion in a manner analogous to a hand covering a ball.[101] The pH of this chelating agent in deionized water is 6.8. It also has the potential for biodegradability, since it is synthesized from thiamine hydrochloride (Vitamin B_1). With the macrocycle having a positive charge of four and with the maximum negative charge of arsenate being negative three, a positively charged complex should be formed. Hence, it was hypothesized that the complex would be extractable from soil using an anionic surfactant.

Materials and Methods

Chemicals used were of analytical quality and used as received from the supplier. Sodium dodecylsulfate (SDS), thiamine hydrochloride (Vitamin B1), methanol, and zinc acetate were obtained from Fisher Scientific Co. Hexadecyltrimethylammonium bromide (HdtaBr) was supplied by Sigma Chemical Co. The zwitterionic surfactant, 3-[(3-cholamidopropyl)-dimethyl ammonia]-1-propane sulfonate (CHAPS), was obtained from Pierce, Inc.

The highly positively-charged macrocycle, [16-pyrimidinium crown - 4]$^{4+}$, was synthesized based on a procedure described by Cramer et al.[101] Zinc acetate (4.39 g) was dissolved in 25 mL deionized, distilled water in a 125 mL Erlenmeyer flask. Thiamine hydrochloride (13.49 g) was added and the flask hand-shaken until dissolution was complete. The flask then was loosely capped and placed in a shaking water bath set initially at 23°C. The temperature was raised to 60°C and held for ≈12 hours. The light yellow supernatant was vacuum-filtered through Whatman #42 filter paper, and the white crystals were rinsed three times with 10 mL of methanol. All supernatant collections were pooled and subsequent slow evaporation of the supernatant resulted in the formation of more white crystals. Final yield was 72%.

In all experiments, a known weight of soil that was contaminated with As from cattle-dipping vat waste was placed

into a 35 mL screw-top glass culture tube. The soil samples came from the "Bison Pen" vat in Payne's Prairie State Preserve. One set of soil samples was from the E horizon located at a depth of 45-60 cm, and other soil samples were from the Bt horizon at 145-160 cm depth. All of these samples were taken 3 meters downhill from, and south of, the vat. The amount of As in the soil had been determined as 1.1 ug/g for the E horizon and 55.1 ug/g for the Bt horizon. The first set of experiments involved the anionic surfactant, sodium dodecylsulfate (NaSDS), and the highly positive charged macrocycle, [16-pyrimidium crown -4]$^{4+}$. To a known weight of soil was added either a) a constant volume (25 mL) of [16 pyrimidium crown -4]$^{4+}$ in deionized distilled water (5.0 g/100 mL) with 0, 5, 10 or 30 mM NaSDS; b) various volumes (2, 7, 15 and 25 mL) of the 6.0 g/100 mL crown solution and enough deionized, distilled water (DDIW) to bring the volume to 25 mL with 30 mM NaSDS; or c) constant amounts of crown and surfactant at the highest concentration with the weight of soil being varied. These tubes were capped using teflon tape and teflon-lined septa caps and the tubes were placed on a rotary mixer. After 24 hours, the tubes were removed and opened. To those tubes that had a constant amount of crown solution, various amounts of aqueous sodium dodecylsulfate solution (1.44 g/25 mL)were added. Other experiments had the chelating agent and the anionic surfactant mixed together prior to adding soil, with the shaking time varied. No

difference in extraction efficiency was noted between these two methods for equivalent shaking times. The amount of SDS solution was calculated to give 0 and 5 mM (below the critical micelle concentration, CMC), and to give 10 and 30 mM (above CMC) in the final solution. The CMC of sodium dodecylsulfate is generally accepted as ≈8.2 mM.[102] DDIW was added, when necessary, to achieve a final volume of 29.4 mL in all tubes. To the tubes that had various amounts of crown solution, there was added enough aqueous sodium dodecylsulfate to yield 30 mM as a final concentration. After mixing on the rotary shaker for a pre-set time, the tubes were centrifuged at 1500 RPM for 10 minutes. Five mL of the supernatant then were removed by Class A pipette and placed in a teflon digestion bomb. All samples were digested by microwave after the addition of 5 mL of HNO_3 according to U.S.E.P.A. method #3051, and analyzed by graphite furnace.[68] Instrument model numbers and operation conditions were described in Chapter 3.

The CMC effect on As extraction efficiency was tested in a similar fashion for two surfactants, CHAPS and HdtABr. A stock aqueous solution of CHAPS (18 mg/mL) was diluted to yield 0.0, 5.0 mM (below the CMC), 10.0, 30.0 mM (above the CMC) in 29.4 mL and added to 0.5 g soil.[103] For HdtaBr, the aqueous solution (0.3 mg/mL) was diluted to 0.0, 0.75 mM (below the CMC), 1.0, 3.0 mM (above the CMC) in 29.4 mL and added to 0.5 g soil.[104] Samples were mixed, centrifuged, digested, and analyzed using the methods described previously.

Results and Discussion

The surfactant extraction experiments were broken into two stages consisting of a) comparison of concentration versus extraction efficiency for the three surfactant systems and b) optimizing the concentration and shaking time of the best system to maximize extraction efficiency. Initially, effect of the surfactant concentration on As extraction efficiency was investigated. Remediation of soil, whether by flushing or washing procedures, requires knowledge of not only the overall effectiveness of the extracting solution, but effect of the critical micelle concentration (CMC) as well. For two out of three surfactant systems, sand found in the E horizon allowed for a sharp demarcation at the CMC characteristic for that particular surfactant (Figures 6-2, 6-3 and 6-4). The student's t-test yielded a significance of 0.047 for CHAPS extraction and 0.096 for Crown/SDS extraction between the two concentrations bordering the CMC. This indicates that there was a significant difference in the extraction efficiency which was attributed to the formation of micelles. However, for the HdtABr extraction, the student's t-test had a markedly lower significance factor of 0.267. The CMC for HdtABr in distilled water is reported to be 0.89 mM.[96] However, in the same report, the authors stated that "values of the CMCs, which were only precise for detergents diluted

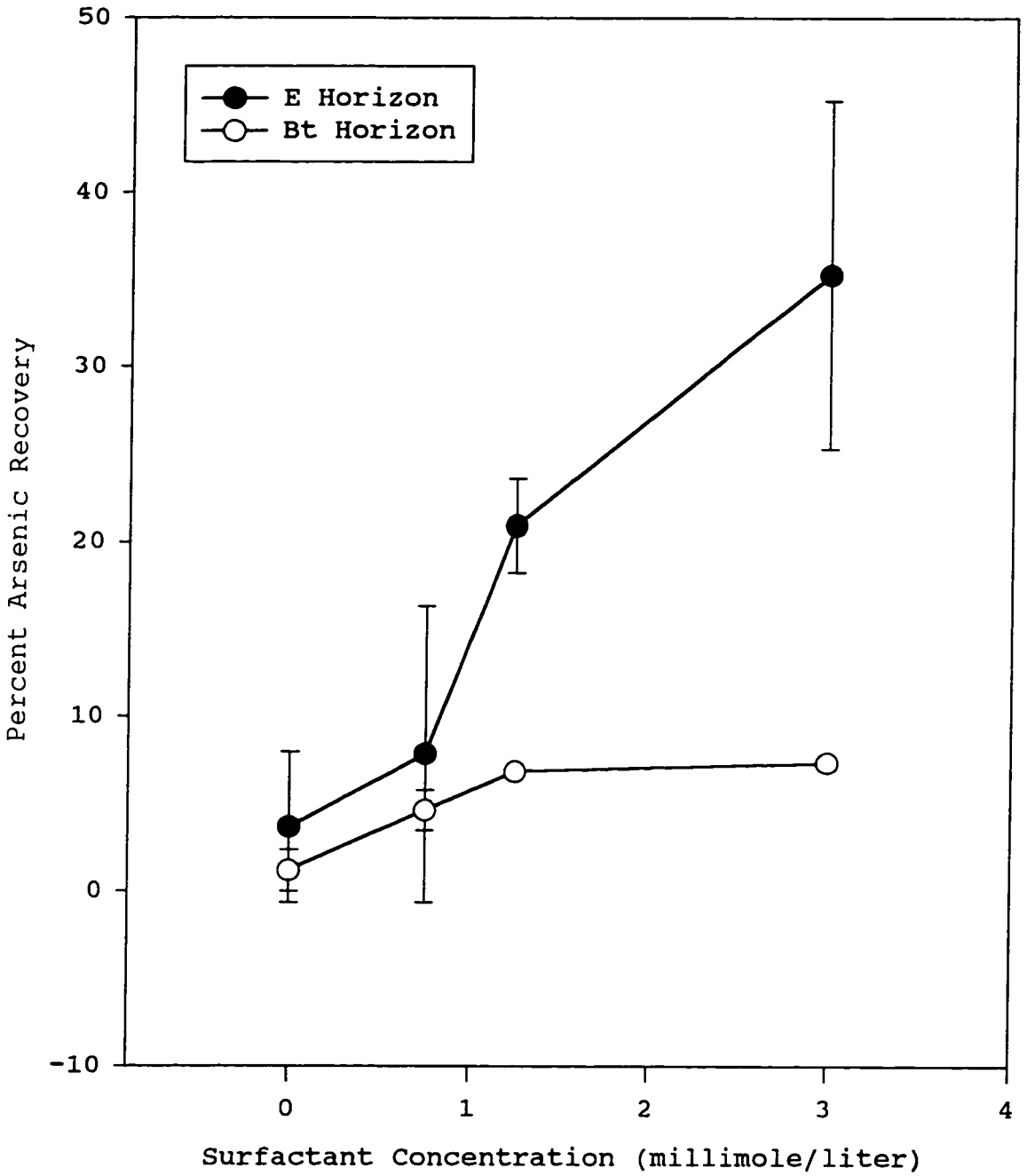

Figure 6-2. Extraction of arsenic from Payne's Prairie Bison Pen vat soil using HdtABr, hexadecyltrimethylammonium bromide (a cationic surfactant).

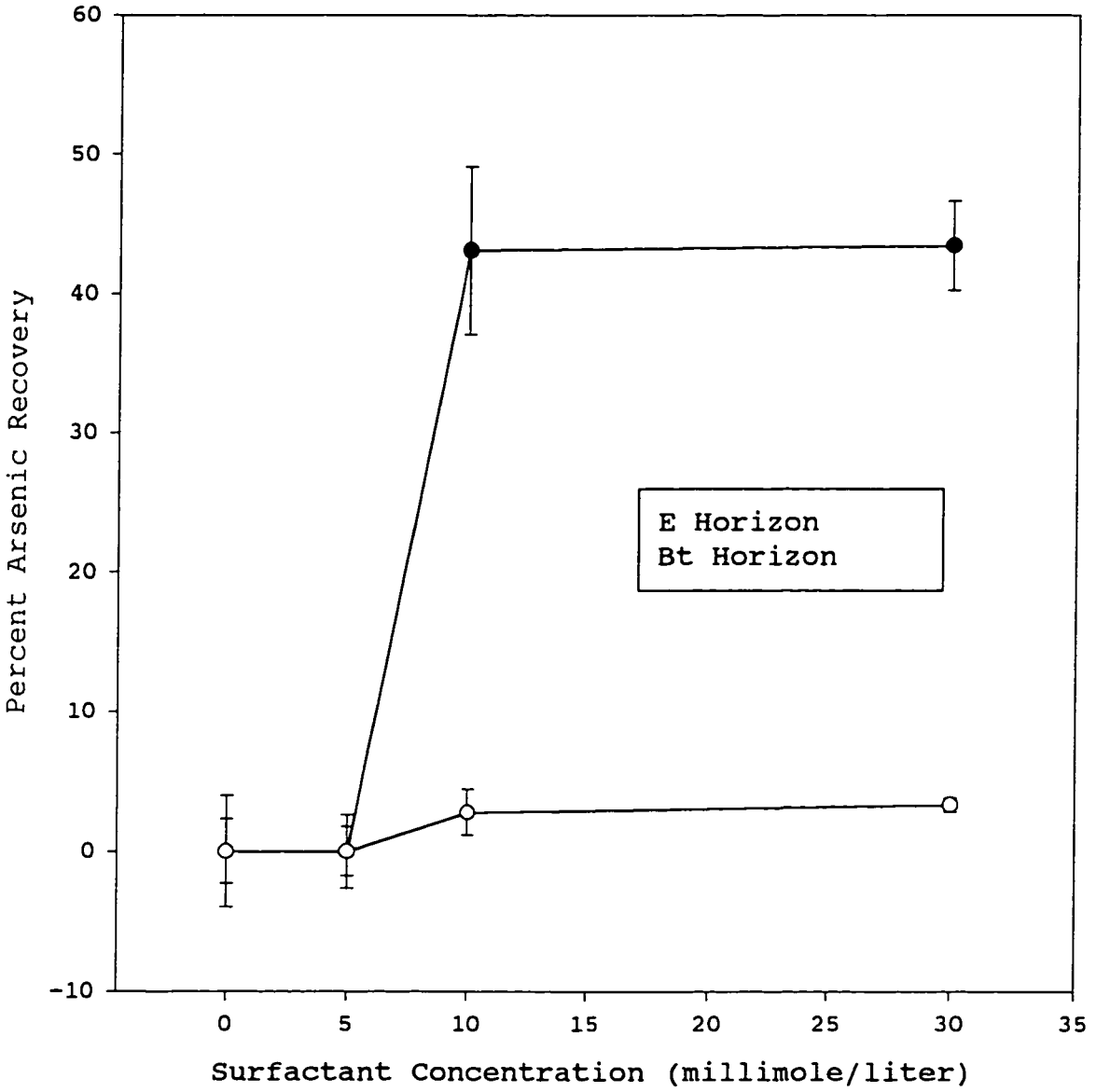

Figure 6-3. Extraction of arsenic from Payne's Prairie Bison Pen vat soil using CHAPS, 3-[(3-cholamidopropyl)-dimethylammonium]-1-propanesulfonate (a zwitterionic surfactant).

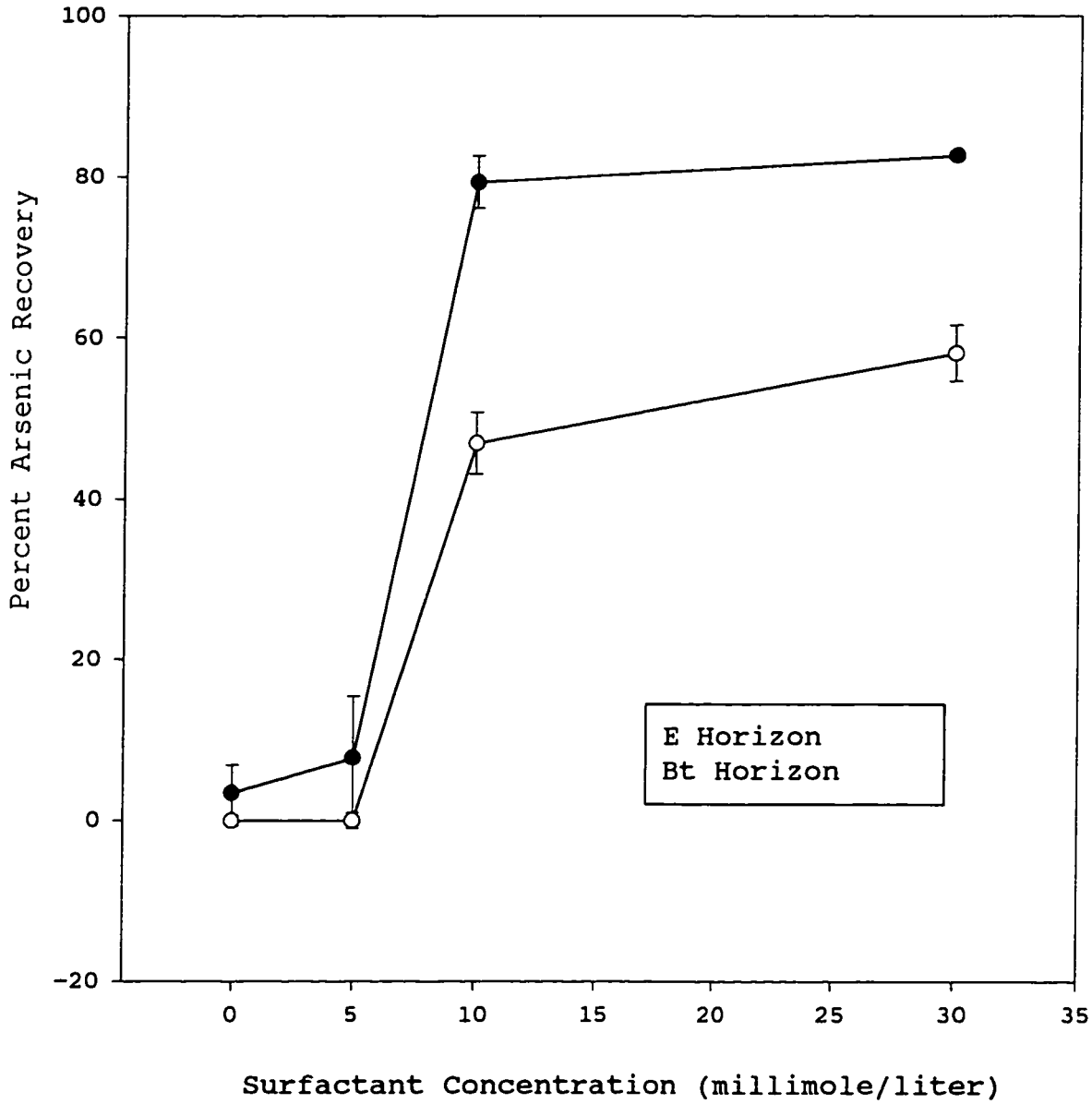

Figure 6-4. Extraction of arsenic from Payne's Prairie Bison Pen vat soil using sodium dodecylsulfate (an anionic surfactnt) with [16-pyrimidinium crown-4]$^{+4}$.

with distilled water but not when an excess of counterion was added" as in this study. In the case of HdtABr extraction for these contaminated soils (Figure 6-2), one of the counterions to the cationic surfactant would be the oxyanions of As. In fact, demarcation of the CMC becomes not so much a single concentration, but rather a range as the concentration of counterions increases.[104] This implies that, as the soluble ion concentration increases, any effects that are reliant upon micelle formation will not be apparent for some surfactants. The formation of a critical micelle concentration range will depend not only on the counterions involved, but on the nature of the surfactant as well. The greater slope shown for HdtABr, in comparison to the other two surfactant systems, may be due to such interactions.

This behavior pattern of surfactants is further exemplified by the series of extractions done on the Bt horizon soil samples from the Payne's Prairie Bison Vat Site. The three surfactant systems showed a shift in the slope of the extraction curve around the critical micelle concentration when Bt horizon soils were extracted (Figures 6-2, 6-3 and 6-4). For the E horizon soil samples, the extraction efficiencies ranged from 35.3% (cationic surfactant) to 43.4% (zwitterionic surfactant), and finally to 82.7% (chelator and anionic surfactant) at the initial test ratio of 1 part soil to ≈60 parts solution after the CMC was exceeded. For the Bt horizon soil samples, which contained a higher clay content,

the As proved to be more difficult to remove from the soil matrix. For these soil samples, the extraction efficiencies at maximum surfactant concentration ranged from 3.3% (zwitterionic surfactant) to 7.3% (cationic surfactant) to 58.1% (anionic surfactant with chelating agent) for the given soil:solution ratio with the surfactant above the CMC level.

The overall drop in extraction efficiencies for each surfactant system when comparing E to Bt horizon soil samples was probably due to the increase in the negative charge of the soil particles. The particle fractions found in the E horizon soil samples were 95.8% sand, 3.4% silt and 0.8% clay; whereas the Bt horizon soil samples had particle fractions consisting of 91.4% sand, 5.3% silt and 3.3% clay. This increase of 2.5% clay should yield a concurrent increase in overall negative charge of the soil. This negative charge would attract not only the iron and aluminum cations (with which arsenic oxyanions will preferentially complex), but would also attract and hold the positively charged components of these extraction systems.[105] This adsorption phenomenon could account for shifts in the slope of the curves as well as some of the decrease in extraction efficiencies. Another probable reason for the drop in extraction efficiencies involves the increase in iron and aluminum concentrations that occurs with increase in clay content. An increase in competition by cations available to complex the arsenical anions implies that there should be a decrease in efficiency for any surfactant

extraction system. The decrease in extraction efficiency was exceptionally sharp for the zwitterionic surfactant system (Figure 6-3). It is hypothesized that not only would the positively charged portion of the zwitterionic surfactant be electrostatically attracted to the negatively charged face of clay, but the negatively charged sulfate tail of the zwitterion would be adsorbed at the positively charged edges of the clay particles.[9] With such an aptitude for adsorption, an increase in clay content would have a greater adverse effect on the zwitterionic surfactant than on the other extractants.

By far the most efficient extraction system consisted of a chelating agent in conjunction with an anionic surfactant (Figure 6-4). Without the chelating agent, extraction efficiency dropped to less than ten percent, regardless of whether the surfactant concentration was above or below the CMC level (Figure 6-5). It is hypothesized that, since the surfactant and the contaminant are both carrying negative charges, it is probable that the amount of contaminant that was extracted from the soil was largely due to ionic displacement of the arsenical oxyanion by the anionic surfactant.

In contrast, the extraction efficiency can approach 100% if the chelator/surfactant solution to soil ratio were high enough. For the Bt horizon soil samples, essentially 100% extraction efficiency was achieved using 30 mM SDS with a

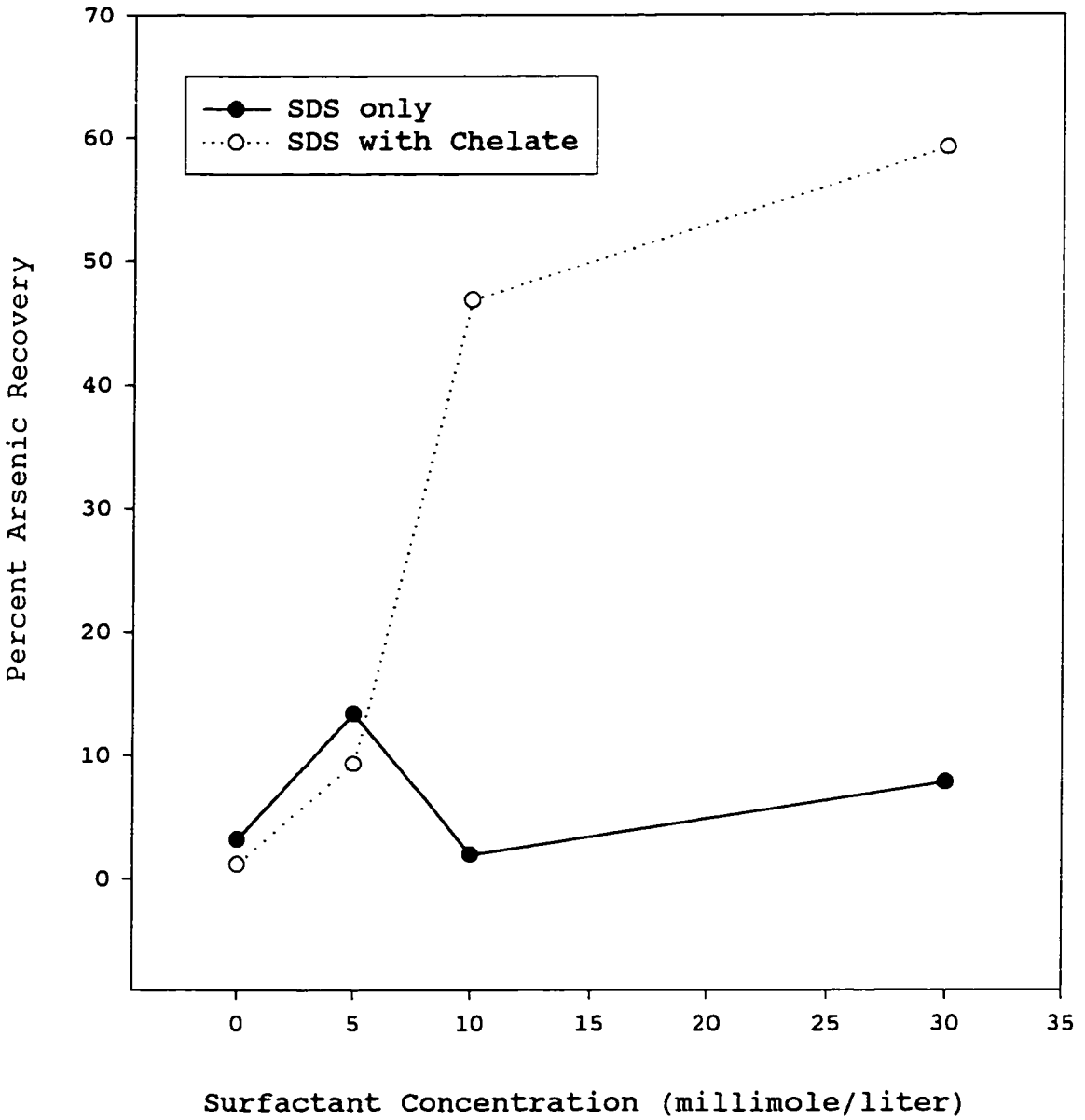

Figure 6-5. Comparison of extraction efficiency for the "Bt" horizon of Payne's Prairie Bison Pen vat soil using sodium dodecylsulfate (NaSDS) with and without the chelating agent [16-pyrimidinium crown-4]$^{4+}$.

chelator to soil weight(g) ratio equal to 150 (Figure 6-6). A lower rate of chelating agent to soil was required for the E horizon soil sample (Figure 6-7). Indeed, a very low ratio of 0.6 g chelator/g soil removed 100% of the arsenic found in the E horizon soil samples.

To ascertain whether the maximum extraction efficiency was attained in the allotted time for shaking, a timed trial was done. It is apparent that the maximum extraction was definitely obtained within a 24-hour shaking time (Figure 6-8). In fact, analysis of the data by the student's t-test revealed that the extraction efficiency from 1- through 24-hour shaking times were essentially equivalent. Since the maximum extraction efficiency for both Bt and E horizon soil samples was reached at equivalent shaking times, the implication is that the extraction kinetics were not diffusion limited for the time length examined for these soil samples and, thus, were not dependent on effective particle size below 2 mm. The surficial adsorption of arsenic was not completely unexpected, since observation of a nodule by scanning electron microprobe analysis using a Joel Superprobe 733 model revealed a lack of As in the cracks and fissures of the nodule. The As appeared to be located on the clay fraction that surrounded the nodule. This observation has been made by other investigators as well.[18] It has been shown that the silt, clay and humus fraction of soil contains a significant portion

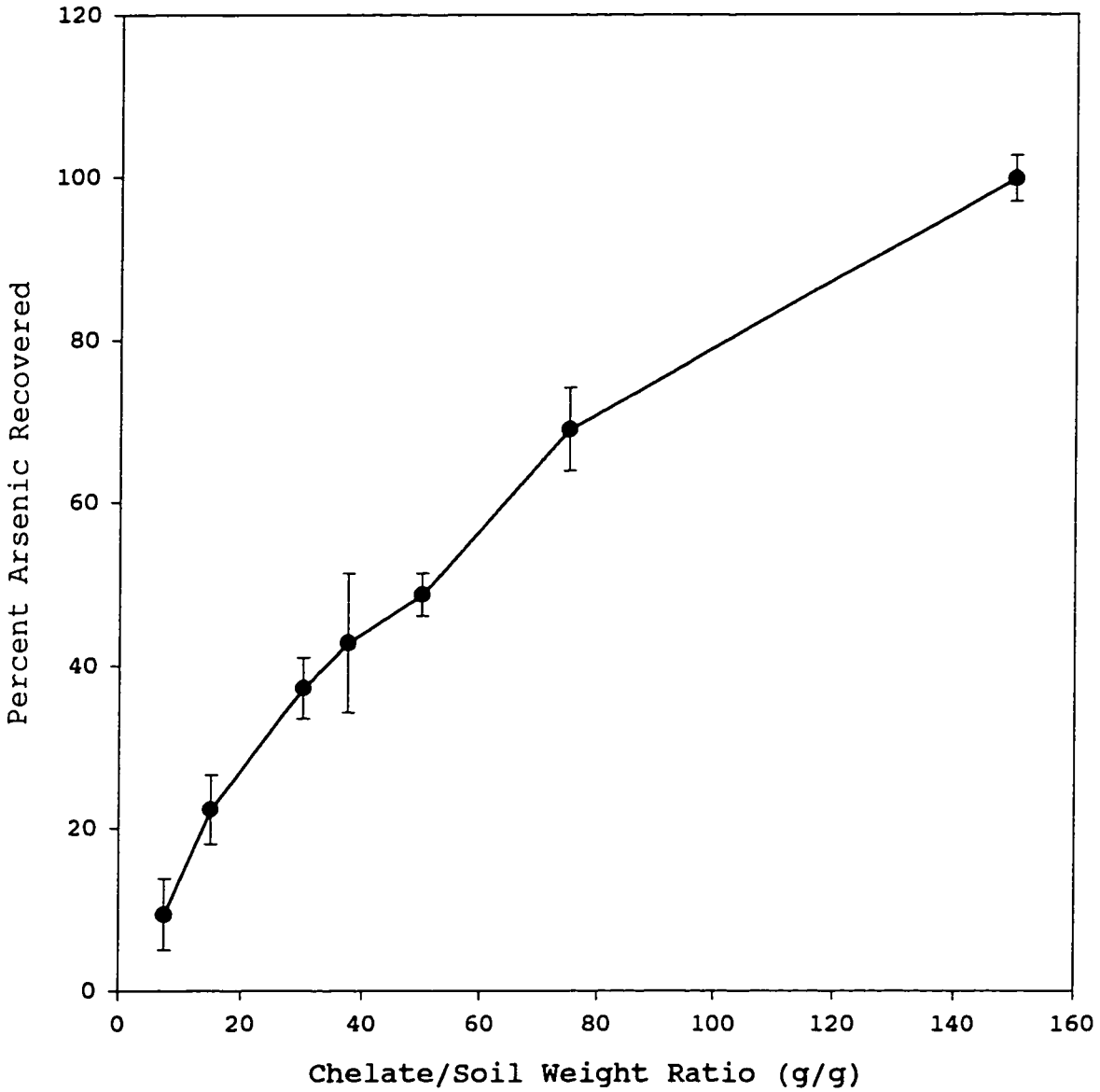

Figure 6-6. Effect of chelate to soil weight ratio on the extraction of arsenic from Payne's Prairie Bison Pen "Bt" soil samples using 30 mM sodium dodecylsulfate.

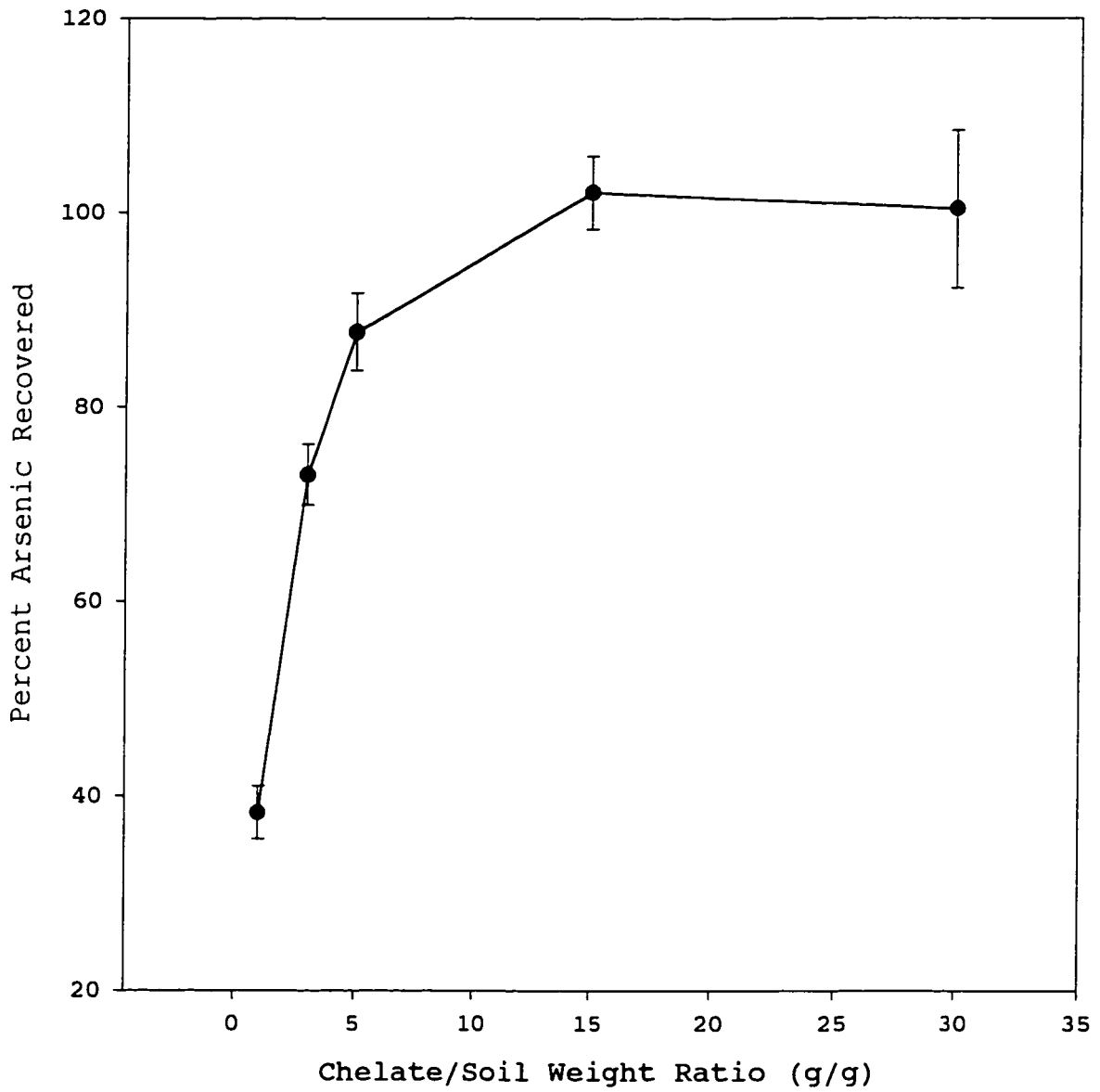

Figure 6-7. Effect of chelate to soil weight ratio on the extraction of arsenic from Payne's Prairie Bison Pen vat "E" soil samples using 30 mM sodium dodecylsulfate.

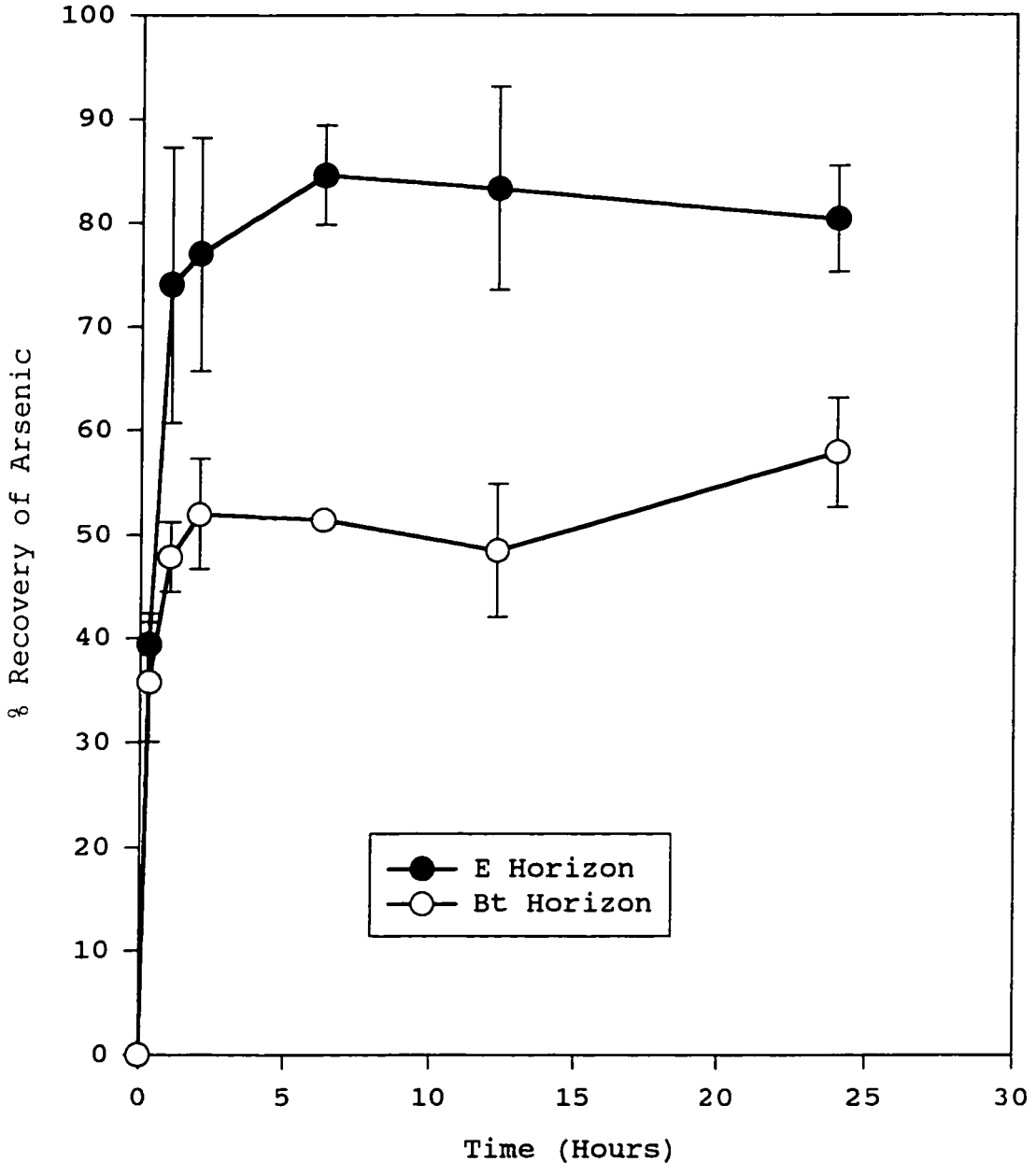

Figure 6-8. Timed trial study of chelate/SDS extraction of arsenic from Payne's Prairie Bison Pen vat site soil samples.

of the contaminants, regardless of whether the contaminants are metals (e.g. As, Zn, Cd, Cr, Cu, Pb) or organics (e.g. acetone, chlorobenzene, xylene, anthracene, and pentachlorophenol). If the medium to fine sand portion (<2 mm size fraction) is removed in the soil washing, then more than 90% of the contaminants are simultaneously removed.[94] For the soil fraction smaller than 2 mm in size, the surfactant/chelation technique was found to be a suitable method for the remediation of arsenical contamination in soil.

Conclusions

For samples from the "E" horizon of the Payne's Prairie Bison Pen vat site, the anionic surfactant/chelation system of sodium dodecylsulfate with [16-pyrimidinium crown-4]$^{+4}$ proved the most effective in removing As from soil. The cationic surfactant, hexadecyltrimethylammonium bromide (HdtABr), did not have as high an extraction efficiency as the zwitterionic surfactant, 3-[3-cholamidopropyl)-dimethyl ammonia)-1-propane sulfonate (CHAPS).

For soil samples from the Bison Pen vat site "Bt" horizon, the cationic and zwitterionic surfactants were essentially equivalent in their low recovery of As. It was also found that NaSDS alone could not effectively remove As from a contaminated soil. However, the anionic surfactant/chelator system of NaSDS with a high positively charged macrocycle proved to be much more efficient than the other surfactant

systems tested. In fact, if the soil weight to surfactant/chelate weight ratio were adjusted, it is possible to achieve 100% extraction efficiency for both the "E" and the "Bt" horizon soils from the Bison Pen vat site. A timed trial using the surfactant/chelate system revealed that there was no significant difference between mixing times of one hour and twenty-four hours.

Although the extraction efficiency is not a problem with the surfactant/chelate system, several issues need to be resolved before it is implemented on a commercial scale. First, the cost of the macrocycle will be high, since it is not yet commercially available. Secondly, biodegradability of the surfactant/chelate mixture must be demonstrated. Lastly, removal of the surfactant and chelating agent from the waste stream has yet to be worked out.

CHAPTER 7
CONCLUSION

The presence of more than 3400 cattle dipping vats in Florida was considered to be a cause of concern. The primary reason for the concern was because these vats were expected to be emptied yearly onto the soil as raw waste or as a precipitated iron complex. Considering that the tick eradication program ran from 1906 to the early 1960s, there was considerable anthropogenic introduction of As into the Florida environment. This contamination occurred in fourteen other states as well.

Overall, the U.S. demand for As products increased by ten percent from 1971 to 1991, even though the tick eradication program ended ten years earlier. The toxicity of these As compounds is highly dependent on the speciation and may range from an LD_{50} of 4.5 mg kg^{-1} for arsine to more than 10,000 mg kg^{-1} for arsenobetaine. Although there is such a great range in toxicity, the U.S. government has set a maximum limit of 50 $\mu g\ L^{-1}$ total As in drinking water, regardless of species. For soil, there currently is no limit on As concentration other than for soil leachate. As determined by the U.S.E.P.A. toxic contaminant leaching procedure, the leachate must contain less than 5 mg L^{-1} for the soil to be considered as non-hazardous

waste. Arsenic in soil may be present as the chemically stable species such as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^=$, and As_2O_3. The effect of the biota on As in soil means that the species may be present as an organo-complex or even a gaseous compound.

The problems presented by such a large number of potentially hazardous sites and the complexity of the chemistry, as well as the biochemistry, of As requires a far-reaching approach. This dissertation may be summarized by categorizing these problems into four objectives.

The first objective was to evaluate the extent of the arsenic contamination at selected cattle dipping vat sites. Before this evaluation could take place, the vats had to be located. The tick eradication program terminated more than thirty years ago and, since no formal record of vat locations had been made, it was found that personal anecdotes were the primary source for locating these vats. A secondary problem with these investigations was engendered by the question of liability. Although the operation of these vats and the disposal of the waste were mandated by both the federal and state governments, there are currently no laws allocating funds for the remediation of these sites. This meant that the vast majority of the vats that were found were sited on government property, since few private owners would admit to having a vat site where the remediation costs could be quite prohibitive.

There were ninety-four vats located in Alachua County, Florida. This dissertation documents the location of approximately ten percent of the total vats in this county. The conditions of these vats ranged from virtually intact to almost total excavation, with only loose rubble left to mark the vat location.

The second objective of this dissertation is closely related to the first. The second goal was to assess the physical and chemical properties that affect arsenic at these sites. The amount of As contamination found in the soil at these vat sites depended on the area's hydrology and on the soil's ability to retain the arsenic. It was found that, in general, As was accumulated in soil with high clay or organic matter content. An uncoated Quartzipsamment soil retained little As, and the location of arsenic at the sites with these soils remained a mystery. Argillic horizons, on the other hand, could retain As in the top several centimeters of the horizon at some sites. At these sites, the topography of the argillic horizon determined the shape of the contaminant plume. At other sites, where the hydrology differed, As was found to have moved vertically as well as horizontally.

To facilitate the mapping of these plumes, three essential basics were proposed for the field protocol. First was prior knowledge of field conditions by study of soil survey and topographical maps; second was on-site inspection to confirm soil and water conditions; and lastly, the use of

the quick field test for arsenic. The latter was based on the Merck "Arsenic Quant Test for Water". Its usage in the field would allow for faster delineation of plume parameters by cutting down on lab "turn-around" time required to show the presence of the contaminant. It should be noted that the field test was actually more sensitive than the laboratory analysis of the soils. There are several possible explanations for the elevated concentrations. First, the weight of the soil used in the field test was estimated by the field operator and could have been more than the expected amount. Secondly, the scale used for field results was initially devised for water, not soil. Thirdly, the presence of volatile As compounds in the soil has been confirmed, and transport back to the laboratory, with the necessary lag time before digestion, may have resulted in the loss of some As. A fourth possibility is that the digestion procedure used in the laboratory, which is defined as "Total Recoverable Metals" by the U.S.E.P.A., in no way can be construed to mean total metals present in the soil. However, even with all of these problems, the field test for arsenic should be considered as a valid, semi-quantitative measure of the contamination and can be used to shorten the amount of field work required to delineate a contaminant As plume in soil.

Plume shape in the soil depended not only on soil properties, such as amounts of silt, sand, clay and organic matter as well as hydrologic properties of the site, but

biological activities, whether by micro- or macro-organisms, could also influence the transport and movement of As.

A third objective was to elucidate the factors that may influence As release from a contaminated soil. This study was done predominantly using column studies. It was found in all aqueous and oxic conditions that the application of phosphate anion was more effective at displacing As than either nitrate or chloride. For eluviated or argillic horizon soil columns, iron was released prior to or during the elution of arsenic. This implied that As anion was associated to some extent with iron compounds. Only in soil columns containing an argillic horizon or a relatively high organic matter soil was aluminum observed to be eluted in noticeable amounts. In general, more As was released under low oxic conditions than under high oxic conditions for any given soil.

In an attempt to compare binding properties of a surface soil for arsenate compared to phosphate, log-log isotherms were constructed. At the concentrations studied, it was observed that generally less arsenate was sorbed than phosphate for any given concentration, although it should be noted that, at the highest concentration of 2000 μg/mL, there was no significant difference. The implication is that arsenate binds less tightly to soil (lower amount sorbed) than phosphate. Since it has already been demonstrated that phosphate can displace arsenate from soil, this was not wholly unexpected.

Another column study that was performed involved an attempt to simulate flow and concentration conditions found when a cattle dipping vat solution was dumped onto a typical Florida soil. It was found that under these conditions, a simple one-dimensional transport model that employed equilibrated sorption as defined by the Freundlich relationship could be used to predict, within ten percent of the correct pore volume, the break-through of arsenate from the soil column.

The fourth objective was directly related to the third goal, in that the removal of As from soil was the main thrust. Both biological volatilization and direct chemical extraction methods were investigated. Fungi, bacteria, and actinomycetes are capable of volatilizing As. The studies described herein are the first to document that a *Fusarium* species can accomplish this feat. *Fusarium* is a wide-spread soil fungi, so it may be quite common that one method of transporting As from the immediate environment is by volatilization. It has been shown that, at the two vat sites where subsurface probes were installed, a volatile As species was being produced. It is interesting to note that, at the two vat sites where a surface gas collection box was utilized, there was no detectable As being emitted from the soil surface. This implied that the volatile As was being converted to a less labile form before reaching the surface. The laboratory experiments designed to explore this hypothesis were not

conclusive. One possible explanation is that the post-reactor soil columns had failed to maintain biotic viability. It was also found that low oxic conditions for the *Fusarium* liquid medium tended to produce more gaseous As than high oxic conditions. The appearance of a floating fungal mat under low oxic conditions was postulated as the reason for the lower conversion of gaseous As to other non-volatile species.

Although volatilization is one method of removing As from soil, it must be considered a rather hazardous means of remediation, considering the toxicity of the compounds generated. A safer method of removing As from soil is by direct chemical extraction. Several surfactant studies were initiated to determine the feasibility of removing As from soil by this procedure.

It was found that 100% of the arsenic in argillic or eluviated soil horizon samples could be removed by an anionic surfactant, sodium dodecylsulfate, after complexation of the arsenic with highly-charged macrocycle cation, [16-pyrimidinium crown-4]$^{4+}$. Far less effective were the cationic surfactant, hexadecyltrimethylammonium bromide, and the zwitterionic surfactant, 3-[(3-cholamidopropyl)-dimethylammonia]-1- propane sulfate. It should be noted that there are potential problems with using the surfactant/chelator system for remediating soils. The first potential problem was the cost effectiveness of this method. Although the macrocycle chelator was synthesized from vitamin

B1, it was not a commercially available product. Second, the ratio of surfactant/chelate to soil weight was not the most favorable. Third, the biodegradability of the macrocycle is still largely unknown. This latter area is one that needs further research before commercial feasibility can be determined.

Other areas that need further study include: 1) locating and assessing the remaining vat sites (>80 in Alachua County alone); 2) evaluation of the risk to humans and livestock; and 3) resolution of the question of liability should a problem be found. The task of locating vats alone is immense. This is particularly true considering the following facts: 1) that Florida had 3400; 2) that fourteen other states have the same problem and 3) that other countries, such as Australia and South Africa, were known to use cattle dipping vats as well. Overall, resolution of the problems arising from arsenic contamination via cattle dipping vat waste will not be laid to rest easily.

APPENDIX A
RAW DATA FOR CONFIRMED VAT SITES

This appendix contains elevation and metal analysis for the transects that were performed on the Alachua County cattle dipping vat sites by John E. Thomas.

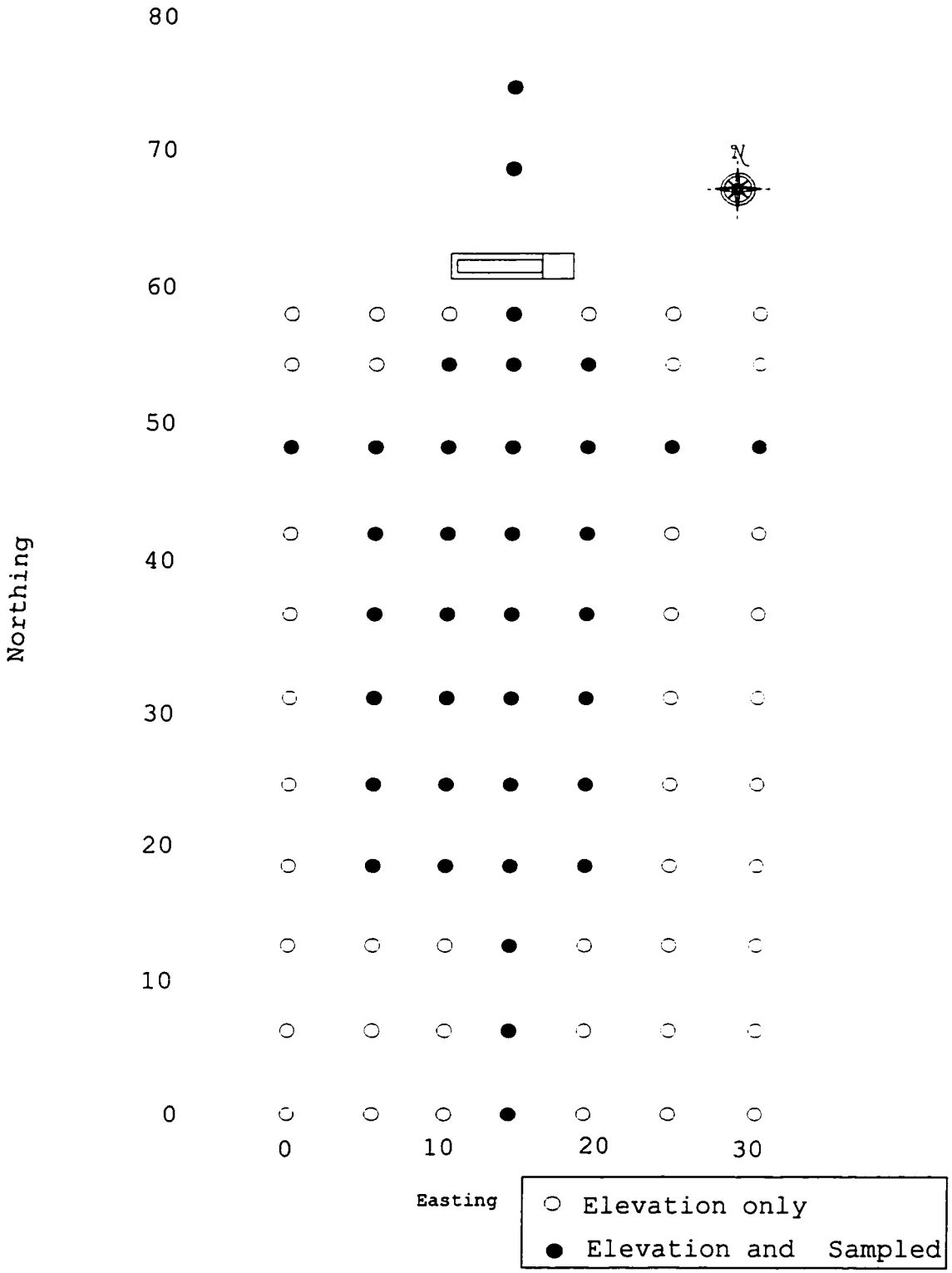

Figure A-1. Sampling map for Payne's Prairie Bison pen vat site. All distances are in meters.

Table A-1. Selected site data for Payne's Prairie Bison Pen cattle dipping vat.

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Arsenic (mg/kg)	Aluminum (mg/kg)
0	67.06	2.554	-1.417		
0	60.96	2.426	-1.544		
0	54.86	2.283	-1.347		
0	48.76	2.222	-1.277		
0	42.66	1.939	-1.361		
0	36.56	1.756	-1.291		
0	30.46	1.536	-1.277		
0	24.36	1.323	-1.080		
0	18.26	1.079	-0.954		
0	12.61	0.707	-0.911		
0	6.1	0.381	-0.883		
0	0	0.055	-0.799		
4.57	67.06	2.566	-1.375		
4.57	60.96	2.576	-1.403		
4.57	54.86	2.240	-1.333	<0.7	436.7
4.57	48.76	2.082	-1.319	<0.7	171.8
4.57	42.66	1.935	-1.235	<0.7	145.5
4.57	36.56	1.701	-1.263	<0.7	482.2
4.57	30.46	1.490	-1.122	<0.7	953.8
4.57	24.36	1.289	-1.122	<0.7	517.8
4.57	18.26	1.045	-1.066		
4.57	12.61	0.695	-1.080		
4.57	6.1	0.424	-1.080		
4.57	0	0.079	-1.066		
9.14	67.06	2.932	-1.199		
9.14	60.96	2.356	-1.165	1.41	572.2
9.14	54.86	2.228	-1.188	32.97	924
9.14	48.76	2.100	-1.245	22.15	427.7
9.14	42.66	1.841	-1.188	<0.7	301.4

Table A-1. – continued

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Arsenic (mg/kg)	Aluminum (mg/kg)
9.14	24.36	1.631	-1.154	7.13	178.7
9.14	18.26	0.933	-0.973		
9.14	12.61	0.677	-0.950		
9.14	6.1	0.421	-0.871		
9.14	0	0.101	-0.769		
13.71	67.06	2.542	-1.411		
13.71	60.96	2.268	-1.411	97.81	1008.8
13.71	54.86	2.057	-1.372	110.24	446.2
13.71	48.76	1.932	-1.411	12.19	1008.8
13.71	42.66	1.932	-1.295	25.77	786.6
13.71	36.56	1.695	-1.333	1.11	1088.5
13.71	30.46	1.439	-1.295		
13.71	24.36	1.186	-1.101	2.89	604.4
13.71	18.26	0.945	-0.946	<0.7	922.5
13.71	12.61	0.686	-0.907	<0.7	332.1
13.71	6.1	0.424	-0.907	<0.7	398.8
13.71	0	0.070	-0.635		
18.28	67.06	2.576	-1.384	19.56	770
18.28	60.96	1.948	-1.430	29.59	535.2
18.28	54.86	2.045	-1.197	8.28	729.8
18.28	48.76	1.841	-1.384	<0.7	450.8
18.28	42.66	1.783	-1.523	<0.7	409.9
18.28	36.56	1.536	-1.174	<0.7	337.6
18.28	30.46	1.350	-1.081	<0.7	385.5
18.28	24.36	1.109	-1.104	<0.7	445.8
18.28	18.26	0.872	-1.174		
18.28	12.61	0.604	-1.244		
18.28	6.1	0.320	-1.174		
18.28	0	0.055	-1.057		
22.85	67.06	2.460	-1.407		
22.85	60.96	2.195	-1.430	17.86	691.9

Table A-1. – continued

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Arsenic (mg/kg)	Aluminum (mg/kg)
22.85	36.56	1.591	-1.547		
22.85	30.46	1.390	-1.453		
22.85	24.36	1.122	-1.477		
22.85	18.26	0.802	-1.407		
22.85	12.61	0.604	-1.314		
22.85	6.1	0.317	-1.290		
22.85	0	0.101	-1.267		

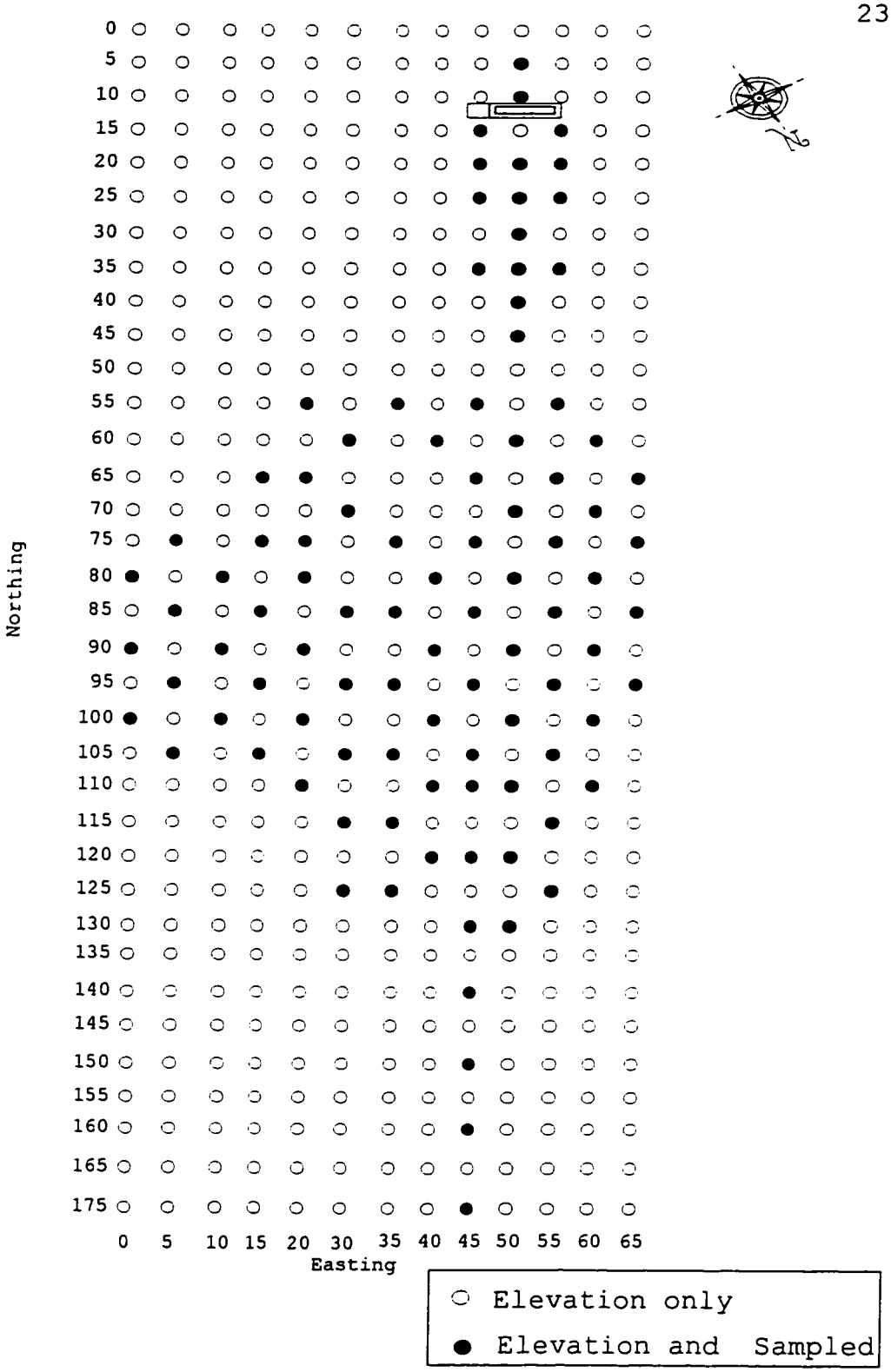

Figure A-2. Sampling map for 10205 S.W. Williston Road vat site. All distances are in meters.

Table A-2. Selected site data for 10205 S.W. Williston Road cattle dipping vat.

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Argillic Arsenic Concentration (mg/kg)		Argillic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
30	0	2.003						
35	0	1.960						
40	0	2.015						
45	0	2.060						
50	0	2.100						
55	0	2.198						
30	5	1.914						
35	5	1.920						
40	5	1.939						
45	5	2.015	-1.397	0	0	2780	11600	0
50	5	2.045						
55	5	2.045						
30	10	1.832						
35	10	1.939						
40	10	2.051						
45	10	2.112						
50	10	2.094						
55	10	2.100						
40	15	2.042	-1.448	1.25	0.11	1190	27100	1
45	15	2.009						
50	15	2.006	-1.549	3.75	0.59	608	26600	1
55	15	2.054						
40	20	1.939	-1.499	1.25	1.24	470	4100	0
45	20	1.878	-1.499	1.25	12.4	610	4300	0
50	20	1.856	-1.626	1.25	8.36	3450	10000	0
55	20	1.890	-1.397	0.625	1.37	1300	7400	0
40	25	1.945	-1.372	12.5	3.46	910	6500	1
45	25	1.628						
50	25	1.704	-1.397	1.25	0	5910	33700	1
55	25	1.695						
40	30	1.347						
45	30	1.359	-1.118	1.25	12.5	1480	11400	0

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Argillic Arsenic Concentration (mg/kg)		Argillic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
55	30	1.670						
40	35	1.698	-1.194	1.25	0.95	3560	30000	1
45	35	1.268	-1.041	3.75	0	2010	12900	0
50	35	1.524	-1.270	3.75	0.54	3900	22000	1
55	35	1.676						
40	40	1.448						
45	40	1.237						
50	40	1.472						
55	40	1.576						
40	45	1.158						
45	45	1.198	-1.397	3.75	0.57	1440	11800	1
50	45	1.362						
55	45	1.426						
40	50	1.027						
45	50	1.152						
50	50	1.170						
55	50	1.210						
15	55	0.972						
20	55	0.994	-1.397	1.25	0	3950	30200	1
25	55	0.951						
30	55	0.927	-1.295	8.75	0	2740	22400	1
35	55	0.988						
40	55	0.988	-1.321	6.25	1.69	5020	37400	2
45	55	1.109						
50	55	1.128	-1.575	21.2	0.88	2920	23600	1
55	55	0.981						
15	60	0.792						
20	60	0.683						
25	60	0.823	-1.321	6.25	2.55	2460	23100	1
30	60	0.671						
35	60	0.628	-0.940	21.2	4.44	3000	28900	1
40	60	0.863						
45	60	0.930	-1.295	3.75	5.33	210	2800	3

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Argillic Arsenic Concentration (mg/kg)		Argillic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
20	65	0.494	-0.965	3.75	3.99	8280	52000	4
25	65	0.457						
30	65	0.445	-1.118	12.5	5.2	2930	22800	2
35	65	0.512						
40	65	0.695	-1.422	3.75	9.22	2940	25400	1
45	65	0.835						
15	70	0.335						
20	70	0.207						
20	70	0.421						
25	70	0.341	-0.991	12.5	3.77	3640	26600	5
35	70	0.808						
40	70	0.866						
45	70	1.006	-1.397	31.2	6.18	2020	18400	2
5	75	0.372	-1.143	1.25	0.46	3900	30900	2
15	75	0.293	-1.168	1.25	0	2440	24300	2
20	75	0.265	-1.143	12.5	3.87	2860	24200	3
30	75	0.207	-1.067	15	4.85	7440	26800	2
25	75	0.262						
35	75	0.643						
40	75	0.677	-1.245	31.2	6.43	730	8500	0
45	75	0.762						
0	80	0.238	-1.041	1.25	0.04	4230	31200	2
5	80	0.396						
10	80	0.116	-1.016	12.5	0	2090	20900	13
15	80	0.280						
20	80	0.171	-0.940	12.5	3.87	3920	32600	4
20	80	0.122						
25	80	0.189						
35	80	0.485	-1.118	17.5	8.17	3130	29100	2
40	80	0.518						
45	80	0.570	-0.864	37.5	99.6	1640	13100	0
0	85	0.177						
5	85	0.085	-0.572	15	7.21	11800	68400	2

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Argillic Arsenic Concentration (mg/kg)		Argillic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
20	85	0.049						
25	85	0.055	-0.864	37.5	33.1	4180	29400	1
25	85	0.058						
35	85	0.506						
40	85	0.445	-0.914	37.5	28.1	2160	16300	1
45	85	0.445						
0	90	0.104	-0.711	2.5	0.4	1010	6800	0
5	90	0.158						
10	90	0.134	-0.800	21.2	12.1	7220	55200	1
15	90	0.067						
20	90	0.055	-0.965	2.5	0.39	3870	29900	1
25	90	0.006						
30	90	0.485						
35	90	0.503	-0.864	37.5	26.2	2670	23600	1
40	90	0.451						
45	90	0.469	-0.889	37.5	65.1	2160	16900	0
0	95	0.085						
5	95	0.146	-0.762	18.7	13.8	5270	31200	1
10	95	0.091						
15	95	0.085	-0.813	6.25	1.32	2040	18800	0
20	95	0.058						
25	95	0.049	-0.787	18.7	4.01	2450	23300	1
30	95	0.491	-0.864	21.2	7.73	2530	31000	1
35	95	0.491						
40	95	0.436	-1.041	2.5	5.18	2340	23100	1
45	95	0.494						
0	100	0.116	-0.787	1.25	0	2700	16100	1
5	100	0.171						
10	100	0.079	-0.813	3.75	0	2740	25800	0
15	100	0.067						
20	100	0.055	-0.508	37.5	9.21	6170	34000	1
25	100	0.073						
30	100	0.454						

Table A-2. — continued

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Argillic Arsenic Concentration (mg/kg)		Argillic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
45	100	0.427	-0.965	21.2	16.9	1400	11100	0
5	105	0.116	-1.029	1.25	1.36	4840	36200	2
15	105	0.073	-1.105	1.25	0.37	2200	20200	1
20	105	0.067						
25	105	0.037	-0.737	15	3.85	2300	21300	0
30	105	0.448	-0.864	12.5	5.35	1280	12600	0
35	105	0.436						
40	105	0.366	-0.940	21.2	8.96	1010	8900	0
45	105	0.390						
20	110	0.064	-1.118		0.41	6200	41600	1
25	110	0.018						
30	110	0.411						
35	110	0.393	-0.940	17.5	4.12	2020	16100	0
40	110	0.341	-0.838	2.5	3.28	2350	20100	1
45	110	0.390	-0.914	2.5	7.95	2000	22900	1
25	115	0.034	-0.914	3.75	1.72	2670	26200	1
30	115	0.430	-0.838	1.25	0.39	1200	13500	1
35	115	0.363						
40	115	0.347						
45	115	0.396						
25	120	0.000						
30	120	0.424						
35	120	0.338	-0.914	1.25	0.69	4890	35800	1
40	120	0.347	-0.813	2.5	2.8	2280	18200	1
45	120	0.390	-0.889	1.25	5.97	2910	24400	1
25	125	0.018	-1.016	1.25	1.54	3920	38300	1
30	125	0.472						
40	130	0.287	-0.991	0	0.22	1050	10900	0
45	125	0.378						
40	135	0.317						
45	130	0.351	-0.864	0	0.25	1720	18800	1
40	140	0.299						
40	125	0.341						

Table A-2. — continued

Easting	Northing	Surface Elevation (meters)	Argillic Depth (meters)	Argillic Arsenic Concentration (mg/kg)		Argillic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
50	80	0.552						
50	85	0.491	-1.105	37.5	14.7	1830	17500	1
50	90	0.475						
50	95	0.469	-0.864	6.25	12.1	2640	21900	1
50	100	0.421						
50	105	0.415	-0.838	5	3.85	1400	14200	1
50	110	0.411						
50	115	0.396	-0.940	12.5	0	1120	11000	0
50	120	0.408						
50	125	0.390	-1.041	1.25	0.52	5140	25500	2
55	65	0.792						
55	70	0.683	-1.092	1.25	0.03	3470	27500	2
55	75	0.600						
55	80	0.500	-0.902	8.75	2.36	2640	23900	2
55	85	0.475						
55	90	0.475	-0.635	12.5	2.21	1270	10800	1
55	95	0.479						
55	100	0.439	-0.584	3.75	1.11	2790	27400	1
55	105	0.466						
55	110	0.427	-0.965	0	0	3520	26200	1
60	65	0.844						
60	70	0.668						
60	75	0.549	-0.991	0	0	3470	25900	2
60	80	0.500						
60	85	0.472	-0.914	0	0	2440	16600	1
60	90	0.491						
60	95	0.463	-0.889	1.25	0	11000	67400	3

Table A-2. — continued

Easting	Northing	Surface Elevation (meters)	Surface or Spodic Horizon Depth (meters)	Horizon's Arsenic Concentration (mg/kg)		Surface or Spodic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
45	0	2.060						
50	0	2.100						
55	0	2.198						
30	5	1.914						
35	5	1.920						
40	5	1.939						
45	5	2.015	-0.889	0.62	0.4	180	2600	0
50	5	2.045						
55	5	2.045						
30	10	1.832						
35	10	1.939						
40	10	2.051						
45	10	2.112						
50	10	2.094						
55	10	2.100						
40	15	2.042	-1.219	16.2	2.08	1190	8600	4
45	15	2.009						
50	15	2.006	-1.143	1.25	0.07	760	4400	1
55	15	2.054						
40	20	1.939	-1.168	16.2	0.69	210	1800	1
45	20	1.878	-1.118	31.2	1.24	230	1400	1
50	20	1.856	-1.245	0.62	0.42	340	2200	2
55	20	1.890	-1.168	1.25	0	80	1200	0
40	25	1.945	-1.041	21.2	5.04	380	3200	0
45	25	1.628						
50	25	1.704	-0.991	1.25	0.02	1250	9400	3
55	25	1.695						
40	30	1.347						
45	30	1.359	-0.914	12.5	12.4	580	2600	0
50	30	1.512						
55	30	1.670						

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Surface or Spodic Horizon Depth (meters)	Horizon's Arsenic Concentration (mg/kg)		Surface or Spodic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
40	35	1.698	-0.864	3.75	5.97	2330	17700	3
40	40	1.448						
45	40	1.237						
50	40	1.472						
55	40	1.576						
40	45	1.158						
45	45	1.198	-0.902	6.25	8.87	290	3500	2
50	45	1.362						
55	45	1.426						
40	50	1.027						
45	50	1.152						
50	50	1.170						
55	50	1.210						
15	55	0.972						
20	55	0.994	-1.067	1.25	0	990	4300	1
25	55	0.951						
30	55	0.927	-0.991	6.25	1.2	980	6400	1
35	55	0.988						
40	55	0.988	-1.194	2.5	0.74	520	3000	3
45	55	1.109						
50	55	1.128	-1.067	2.5	1.38	2800	8100	8
55	55	0.981						
15	60	0.792						
20	60	0.683						
25	60	0.823	-0.483	1.25	0	520	1400	5
30	60	0.671						
35	60	0.628	-0.432	1.25	0	1030	2800	3
40	60	0.863						
45	60	0.930	-0.495	0.625	0.69	220	600	2
50	60	0.835						
55	60	0.774	-0.254	0	0	1790	3700	5

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Surface or Spodic Horizon Depth (meters)	Horizon's Arsenic Concentration (mg/kg)		Surface or Spodic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
15	65	0.494	-0.229	0	0	970	1700	56
20	65	0.494	-0.152	1.25	0	760	2400	4
40	65	0.695	-0.381	0	0.23	600	1200	16
45	65	0.835						
15	70	0.335						
20	70	0.207						
20	70	0.421						
25	70	0.341	-0.203	1.25	0.29	370	2100	66
35	70	0.808						
40	70	0.866						
45	70	1.006	-0.381	0	0.69	1030	2300	16
5	75	0.372	-0.102	1.25	0.43	1670	6300	4
15	75	0.293	-0.102	0	0.21	1550	8200	7
20	75	0.265	-0.152	2.5	1.37	1230	4900	2
30	75	0.207	-0.152	12.5	3.27	4310	7100	40
25	75	0.262						
35	75	0.643						
40	75	0.677	-0.254	16.2	10.7	1120	4900	6
45	75	0.762	-0.406	31.2	14.6			
0	80	0.238	-0.076	2.5	1.66	2020	11900	38
5	80	0.396						
10	80	0.116	-0.127	12.5	2.71	2330	9200	16
15	80	0.280						
20	80	0.171	-0.127	2.5	2.2	1050	5300	10
20	80	0.122						
25	80	0.189						
35	80	0.485	-0.178	21.2	1.89	980	6700	8
40	80	0.518						
45	80	0.570	-0.254	37.5	60.1	450	4500	1
0	85	0.177						
5	85	0.085	-0.102	12.5	3.59	3080	9500	1

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Surface or Spodic Horizon Depth (meters)	Horizon's Arsenic Concentration (mg/kg)		Surface or Spodic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
10	85	0.171						
15	85	0.146	-0.127	3.75	1.7	890	7400	4
30	85	0.098	-0.127	37.5	10.8	2520	6000	24
35	85	0.506						
40	85	0.445	-0.152	37.5	13.8	1080	3600	22
45	85	0.445						
0	90	0.104	-0.102	1.25	0.21	3380	5500	1
5	90	0.158						
10	90	0.134	-0.102	1.25	0.36	2220	8400	16
15	90	0.067						
20	90	0.055	-0.076	18.7	7.75	1480	7600	25
25	90	0.006						
30	90	0.485						
35	90	0.503	-0.152	12.5	7.45	3820	4900	33
40	90	0.451						
45	90	0.469	-0.127	37.5	13.8	640	2700	5
0	95	0.085						
5	95	0.146	-0.127	1.25	0.33	2420	6700	1
10	95	0.091						
15	95	0.085	-0.102	5	2.46	1250	7600	4
20	95	0.058						
25	95	0.049	-0.102	6.25	4.22	1450	5500	16
30	95	0.491	-0.127	37.5	14.7	2440	6400	17
35	95	0.491						
40	95	0.436	-0.178	2.5	8.3	1100	4400	4
45	95	0.494						
0	100	0.116	-0.127	0	0.14	1330	2700	3
5	100	0.171						
10	100	0.079	-0.152	3.75	0	450	3300	0
15	100	0.067						
20	100	0.055	-0.127	6.25	3.92	1600	7900	20

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Surface or Spodic Horizon Depth (meters)	Horizon's Arsenic Concentration (mg/kg)		Surface or Spodic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
25	100	0.073						
30	100	0.454						
35	100	0.430	-0.127	15	5.37	1810	4300	3
40	100	0.402						
15	105	0.073	-0.127	0	0.42	1370	4400	1
20	105	0.067						
25	105	0.037	-0.102	6.25	3.11	1780	3700	4
30	105	0.448	-0.127	6.25	2.28	1540	4700	5
35	105	0.436						
40	105	0.366	-0.165	37.5	13.8	730	4100	0
45	105	0.390						
20	110	0.064	-0.102	1.25	0	780	2200	2
25	110	0.018						
30	110	0.411						
35	110	0.393	-0.102	15	2.69	1740	3500	2
40	110	0.341	-0.114	12.5	5.31	1940	3700	3
45	110	0.390	-0.254	5	0.23	390	1700	1
25	115	0.034	-0.127	1.25	0.74	1430	3600	0
30	115	0.430	-0.076	1.25	2.19	3900	5900	45
35	115	0.363						
40	115	0.347						
45	115	0.396						
25	120	0.000						
30	120	0.424						
35	120	0.338	-0.102	12.5	4.17	1430	4400	1
40	120	0.347	-0.127	10	3.46	1040	1400	2
45	120	0.390	-0.203	0	0.23	620	2000	0
25	125	0.018	-0.076	1.25	0.74	970	2700	4
30	125	0.472						
40	130	0.287	-0.127	12.5	3.61	1410	2100	4
45	125	0.378						

Table A-2. – continued

Easting	Northing	Surface Elevation (meters)	Surface or Spodic Horizon Depth (meters)	Horizon's Arsenic Concentration (mg/kg)		Surface or Spodic Horizon		
				Field Results	Laboratory Analysis	Iron (mg/kg)	Aluminum (mg/kg)	Manganese (mg/kg)
40	135	0.317						
45	130	0.351	-0.178	1.25	0.22	820	1500	0
40	140	0.299						
40	125	0.341						
50	65	1.097	-0.356	0	0	800	1300	23
50	85	0.491	-0.203	21.2	13.6	620	3800	2
50	90	0.475						
50	95	0.469	-0.178	25	11.2	680	3900	1
50	100	0.421						
50	105	0.415	-0.152	6.25	5.5	980	2900	1
50	110	0.411						
50	115	0.396	-0.178	2.5	0.23	570	1800	1
50	120	0.408						
50	125	0.390	-0.178	0	0	1520	2200	1
55	65	0.792						
55	70	0.683	-0.154	0	0.14	460	4200	35
55	75	0.600						
55	80	0.500	-0.305	0	1.01	440	10700	7
55	85	0.475						
55	90	0.475	-0.152	2.5	1.79	1300	5000	12
55	95	0.479						
55	100	0.439	-0.102	3.75	1.27	1230	4700	5
55	105	0.466						
55	110	0.427	-0.102	0	0.06	930	6600	1
60	65	0.844						
60	70	0.668						
60	75	0.549	-0.127	0	0.89	1940	10100	40
60	80	0.500						
60	85	0.472	-0.102	0	0.61	2090	9000	22
60	90	0.491						
60	95	0.463	-0.127	1.25	0.36	2550	7900	4

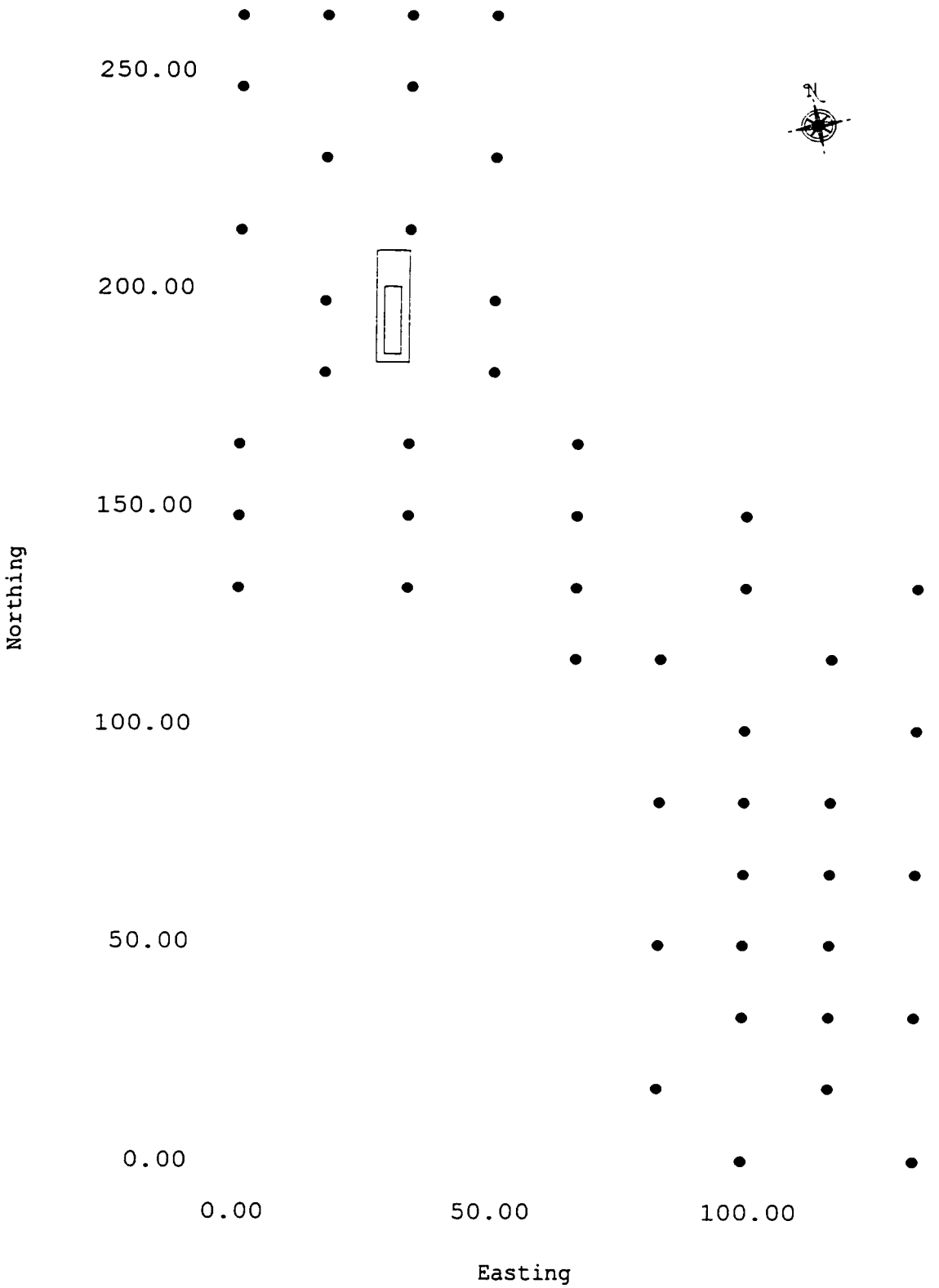

Figure A-3. Sampling map for Dudley Farm vat site.
All distances are in meters.

Table A-3. Selected site data for Dudley Farm cattle dipping vat.

Easting	Northing	0-5 cm Surface Arsenic (mg/kg)
131.23	0.00	0
98.43	0.00	1.9
114.83	16.40	1
82.02	16.40	0.2
131.23	32.81	4.5
114.83	32.81	4.3
98.43	32.81	4.2
114.83	49.21	10.3
98.43	49.21	6.1
82.02	49.21	0.6
131.23	65.62	6.3
114.83	65.62	17.7
98.43	65.62	43.5
114.83	82.02	3.6
98.43	82.02	0
82.02	82.02	0.2
131.23	98.43	2.5
98.43	98.43	7.7
114.83	114.83	3.1
82.02	114.83	2.2
65.62	114.83	1.4
131.23	131.23	0.6
98.43	131.23	0.5
65.62	131.23	3.1
32.81	131.23	1.3
0.00	131.23	0.9
98.43	147.64	0.6
65.62	147.64	19
32.81	147.64	1.4
0.00	147.64	0
65.62	164.04	0
32.81	164.04	0

Table A-3. – continued

Easting	Northing	Arsenic (mg/kg)
0.00	164.04	0.4
49.21	180.45	0.2
16.41	180.45	0
49.21	196.85	0.4
16.41	196.85	0.2
32.81	213.25	0.5
0.00	213.25	0
49.21	229.66	0.6
16.41	229.66	0
32.81	246.06	0.1
0.00	246.06	0.1
49.21	262.47	0.7
32.81	262.47	1.9
16.41	262.47	0.4
0.00	262.47	0

APPENDIX B
RAW DATA FOR REPORTED VAT SITES

This appendix contains sampling maps of arsenic analysis for other cattle dipping vat sites as performed by Woodward-Clyde Consultants for the Florida Department of Environmental Protection.[4]

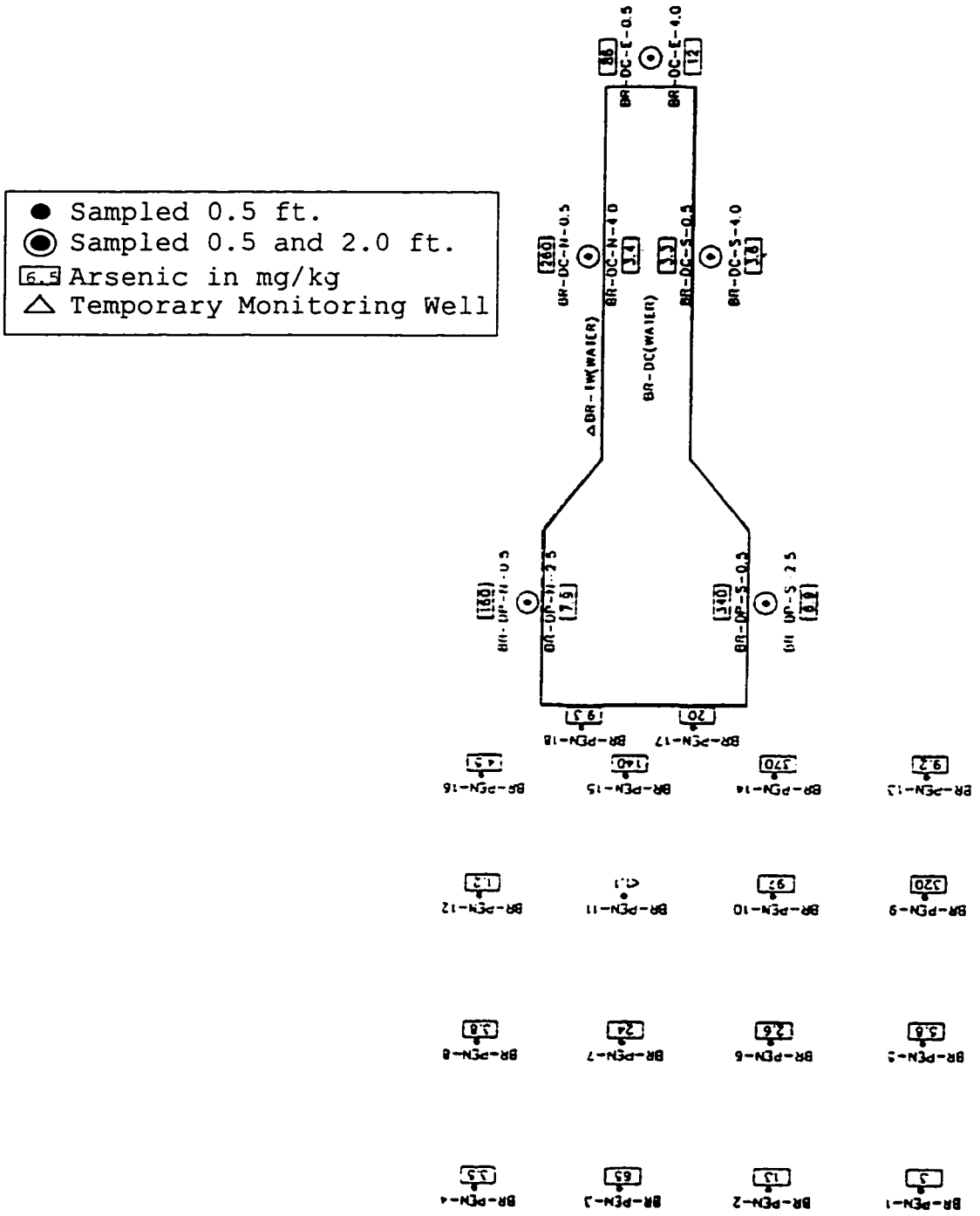

Figure B-1. Woodward-Clyde Consultants' arsenic survey map of Blackwater State Forest cattle dipping vat site.

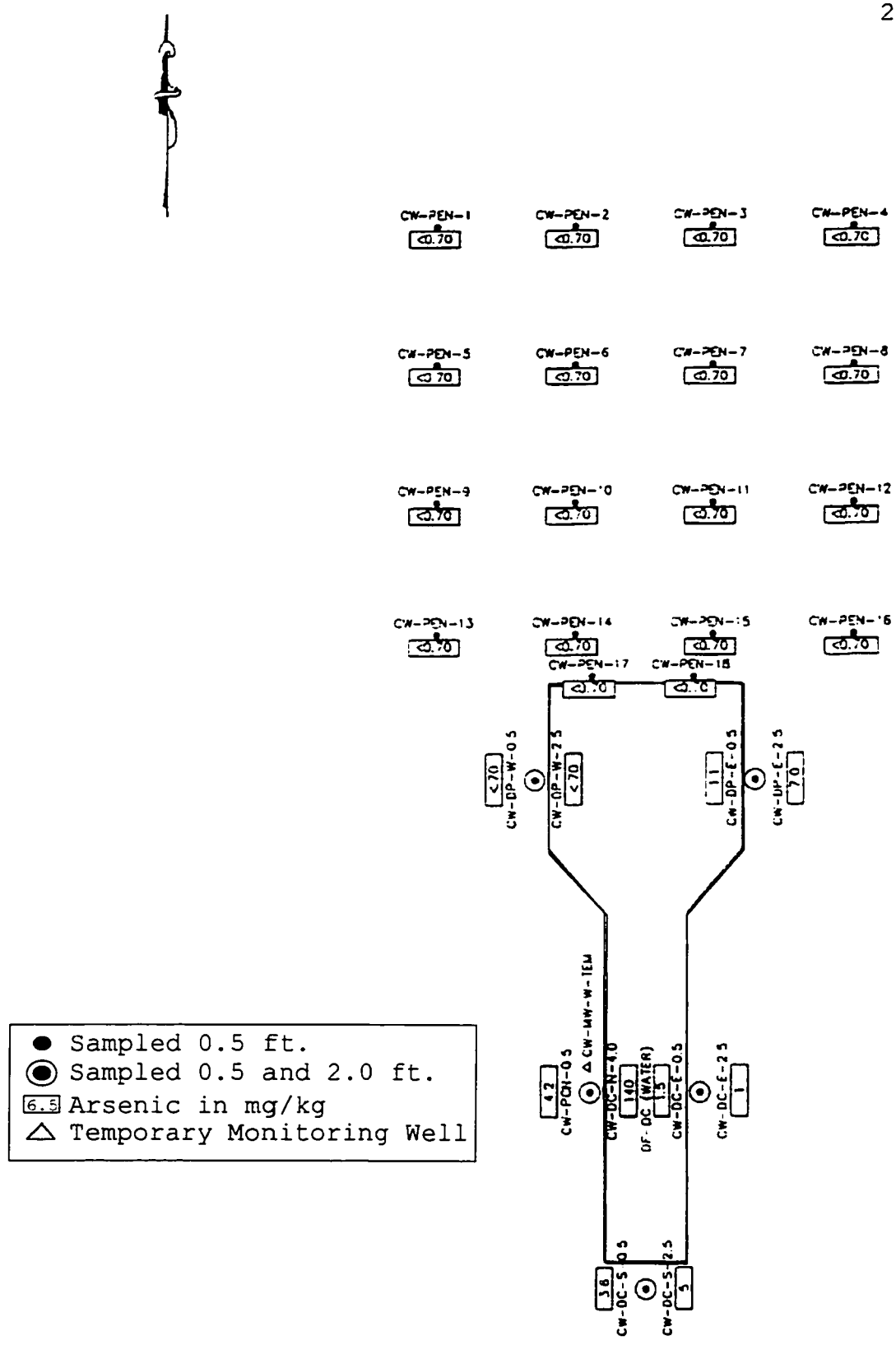

Figure B-2. Woodward-Clyde Consultants' arsenic survey map of Cecil Webb cattle dipping vat site.

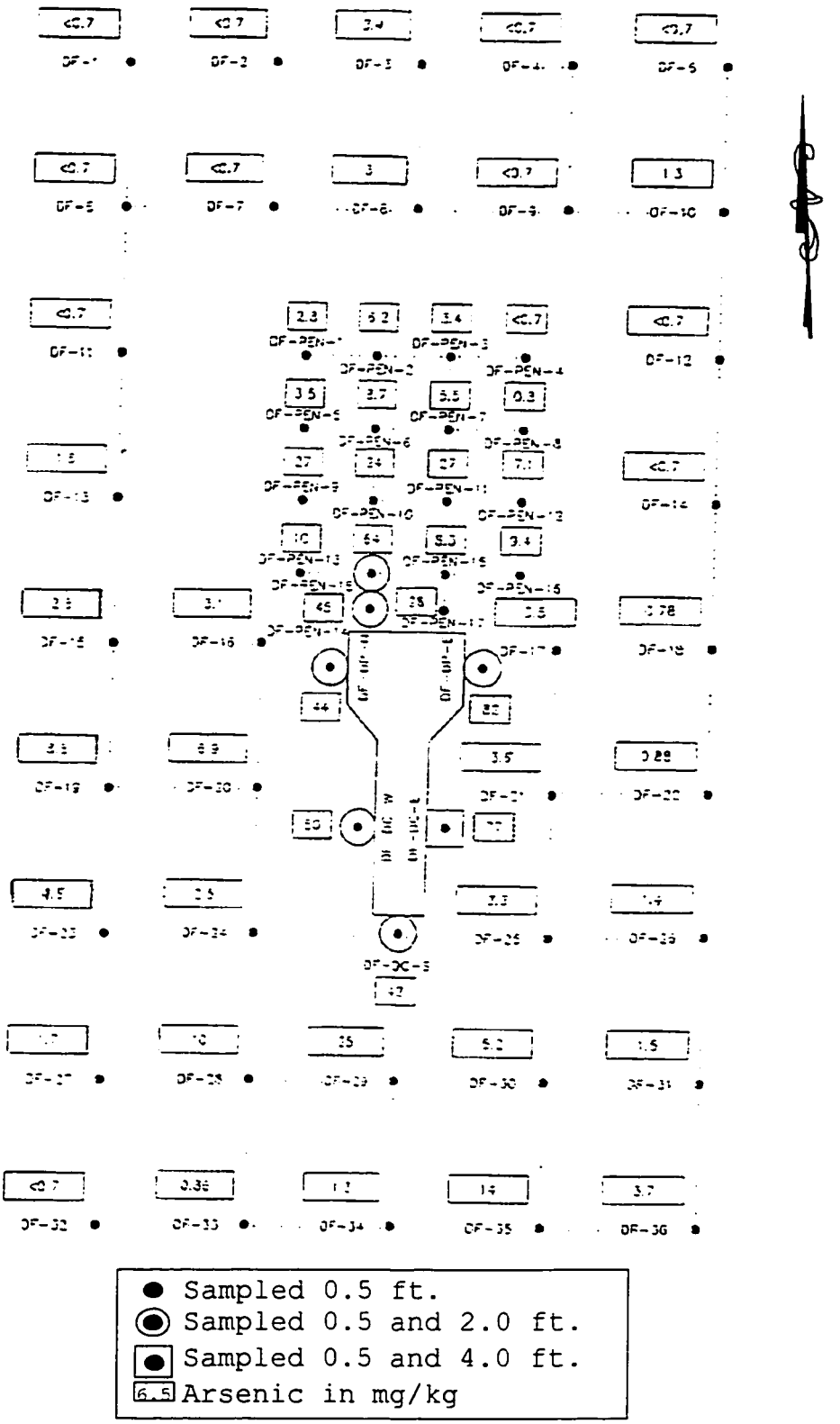

Figure B-3. Woodward-Clyde Consultants' arsenic survey map of Dudley Farm cattle dipping vat site. Arsenic detected in soil samples at 0-30 cm below surface.

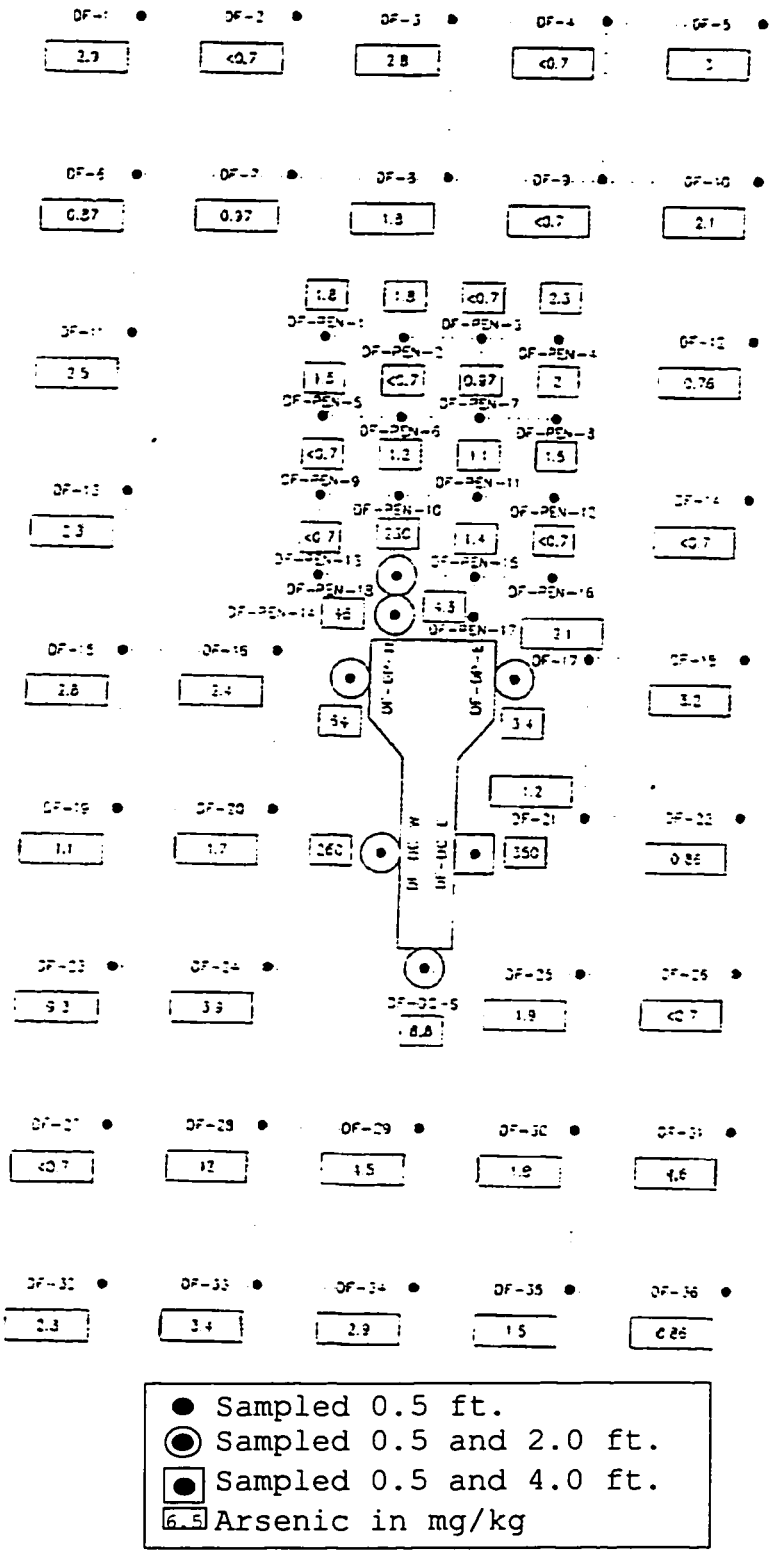

Figure B-4. Woodward-Clyde Consultants' arsenic survey map of Dudley Farm cattle dipping vat site. Arsenic detected in soil samples at 91-122 cm below surface.

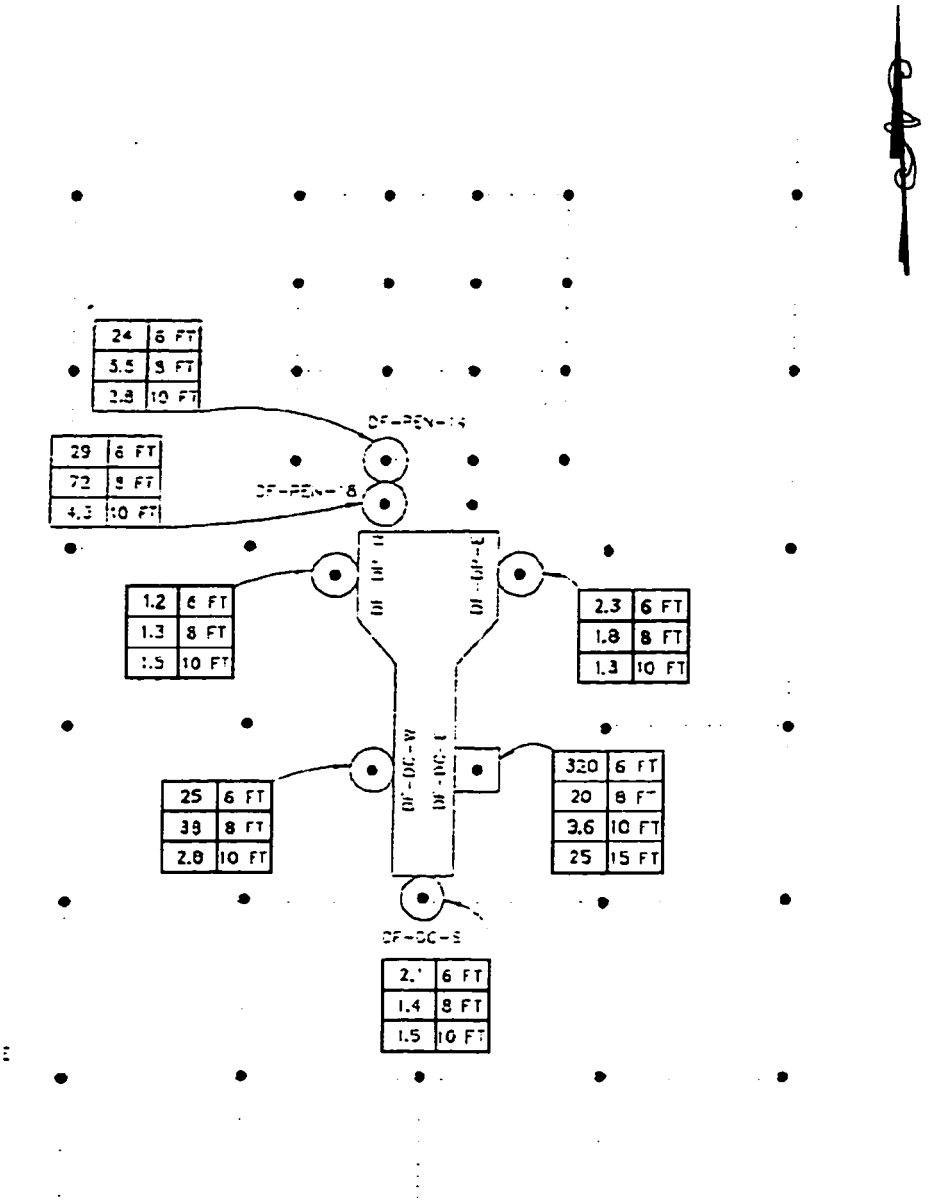

Figure B-5. Woodward-Clyde Consultants' arsenic survey map of Dudley Farm cattle dipping vat site. Arsenic detected in soil samples deeper than 122 cm below surface.

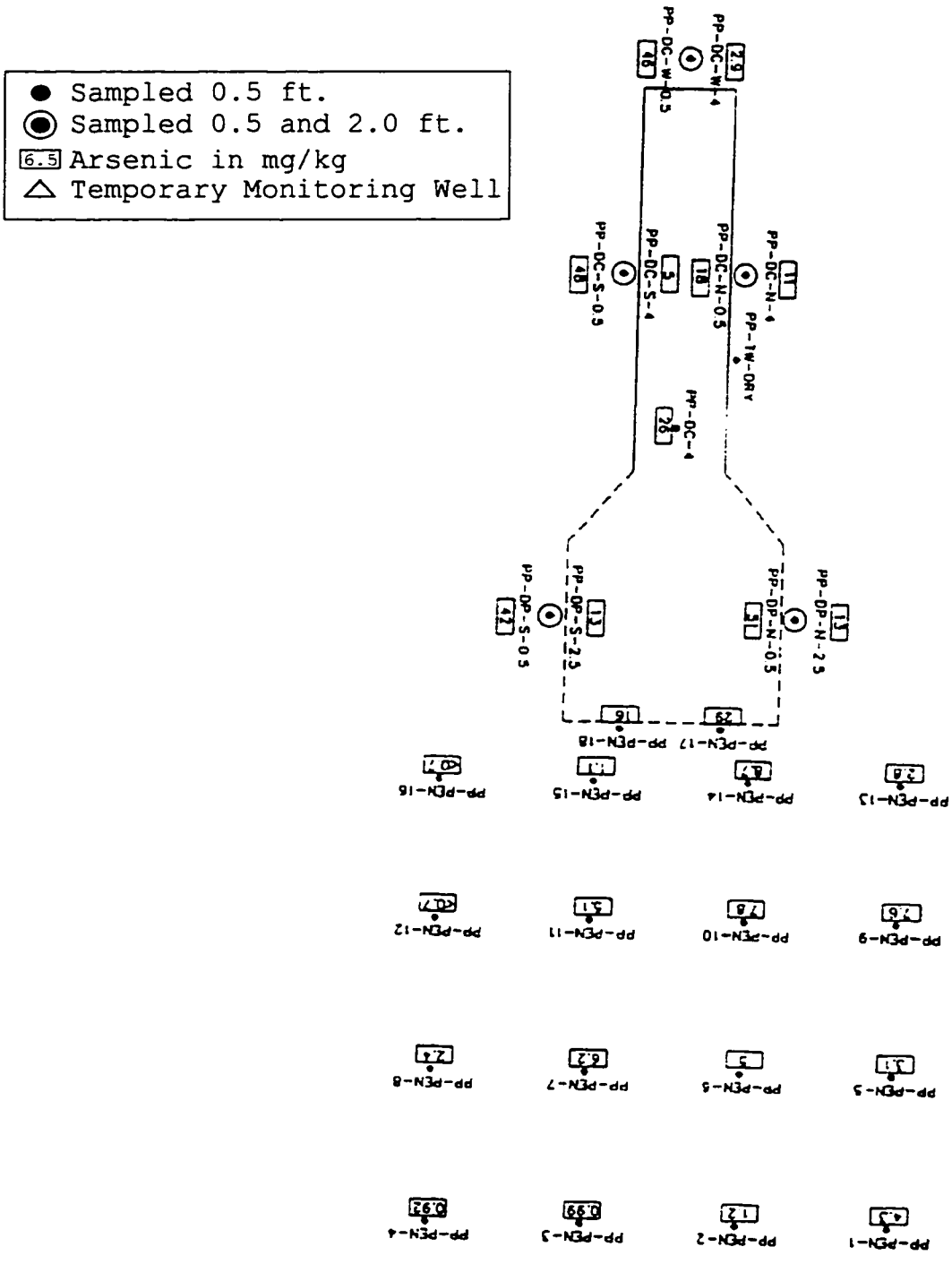

Figure B-6. Woodward-Clyde Consultants' arsenic survey map of Jackson's Gap cattle dipping vat site.

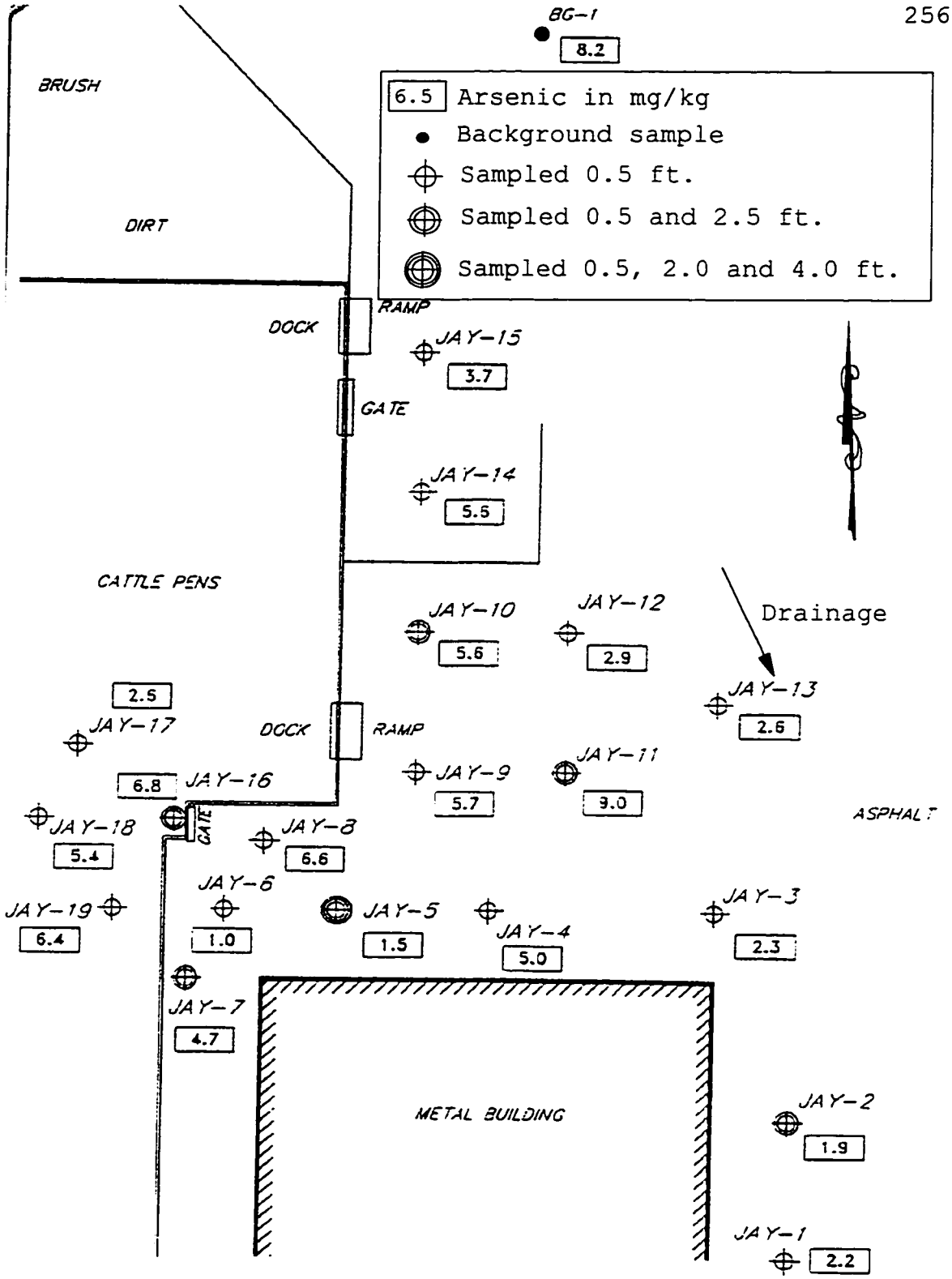

Figure B-7. Woodward-Clyde Consultants' arsenic survey map of Jay Livestock Market cattle dipping vat site. Arsenic detected in soil samples 0-30 cm below surface.

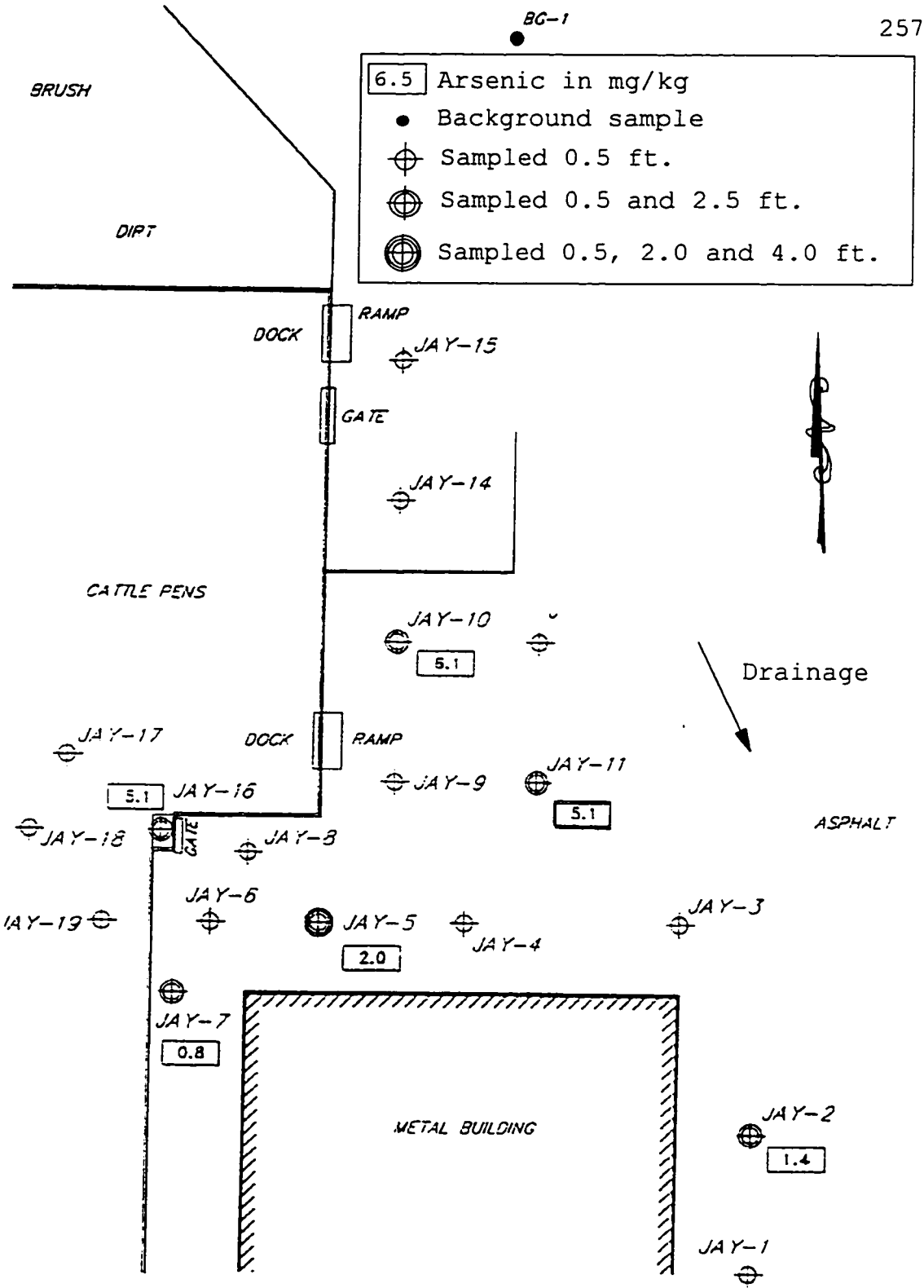

Figure B-8. Woodward-Clyde Consultants' arsenic survey map of Jay Livestock Market cattle dipping vat site. Arsenic detected in soil samples 61-76 cm below surface.

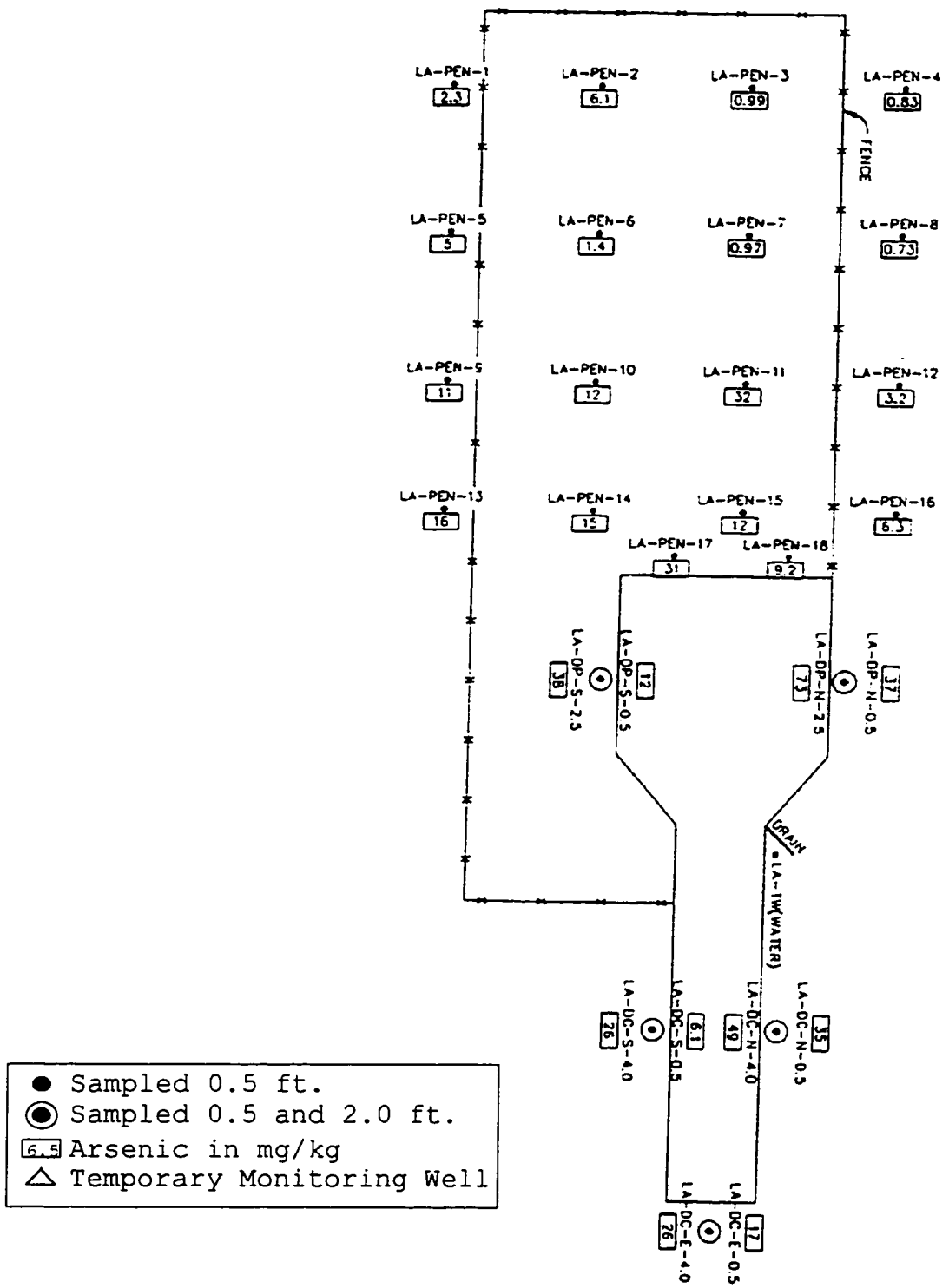

Figure B-9. Woodward-Clyde Consultants' arsenic survey map of Lake Arbuckle cattle dipping vat site.

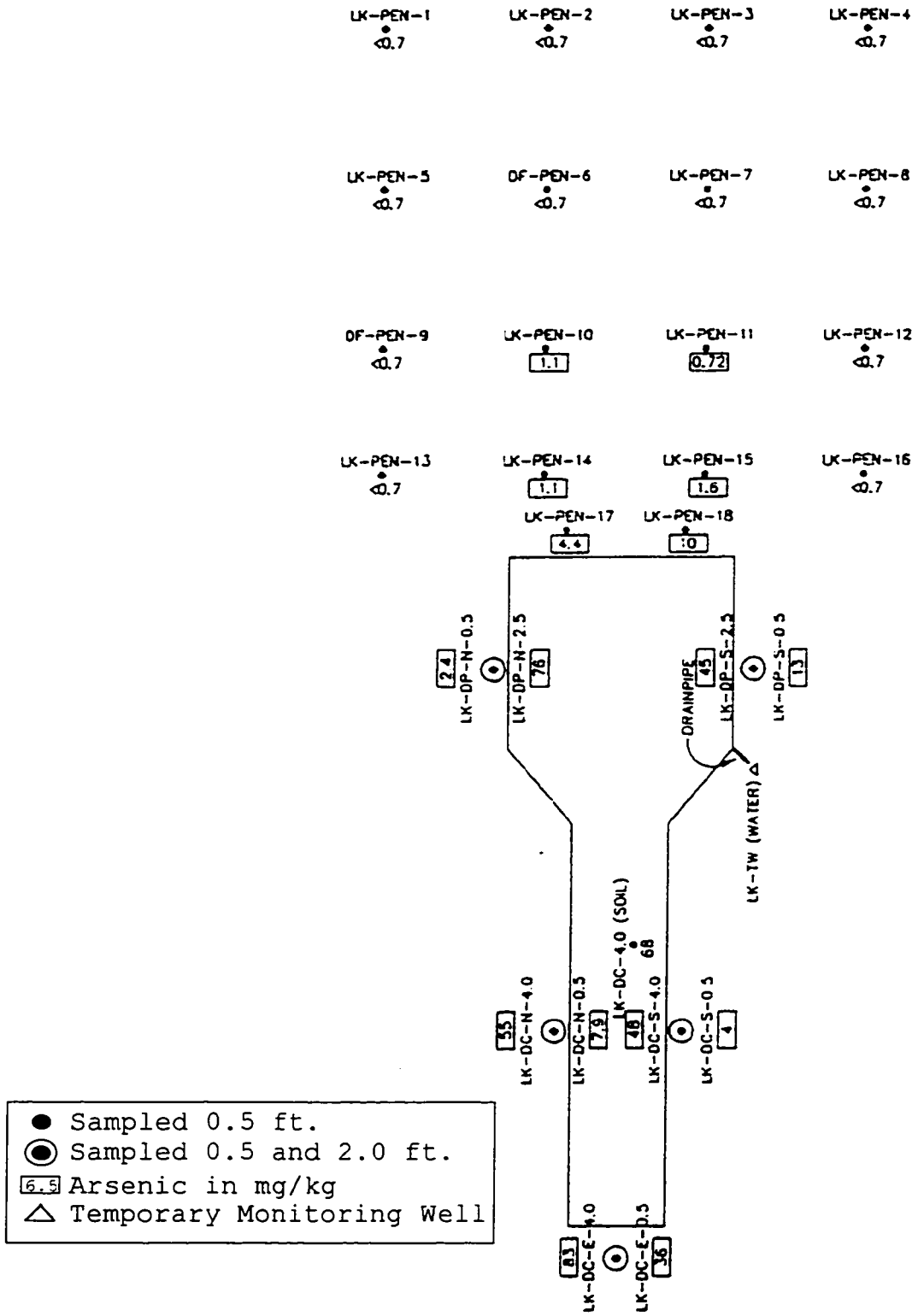

Figure B-10. Woodward-Clyde Consultants' arsenic survey map of Lake Kissimmee cattle dipping vat site.

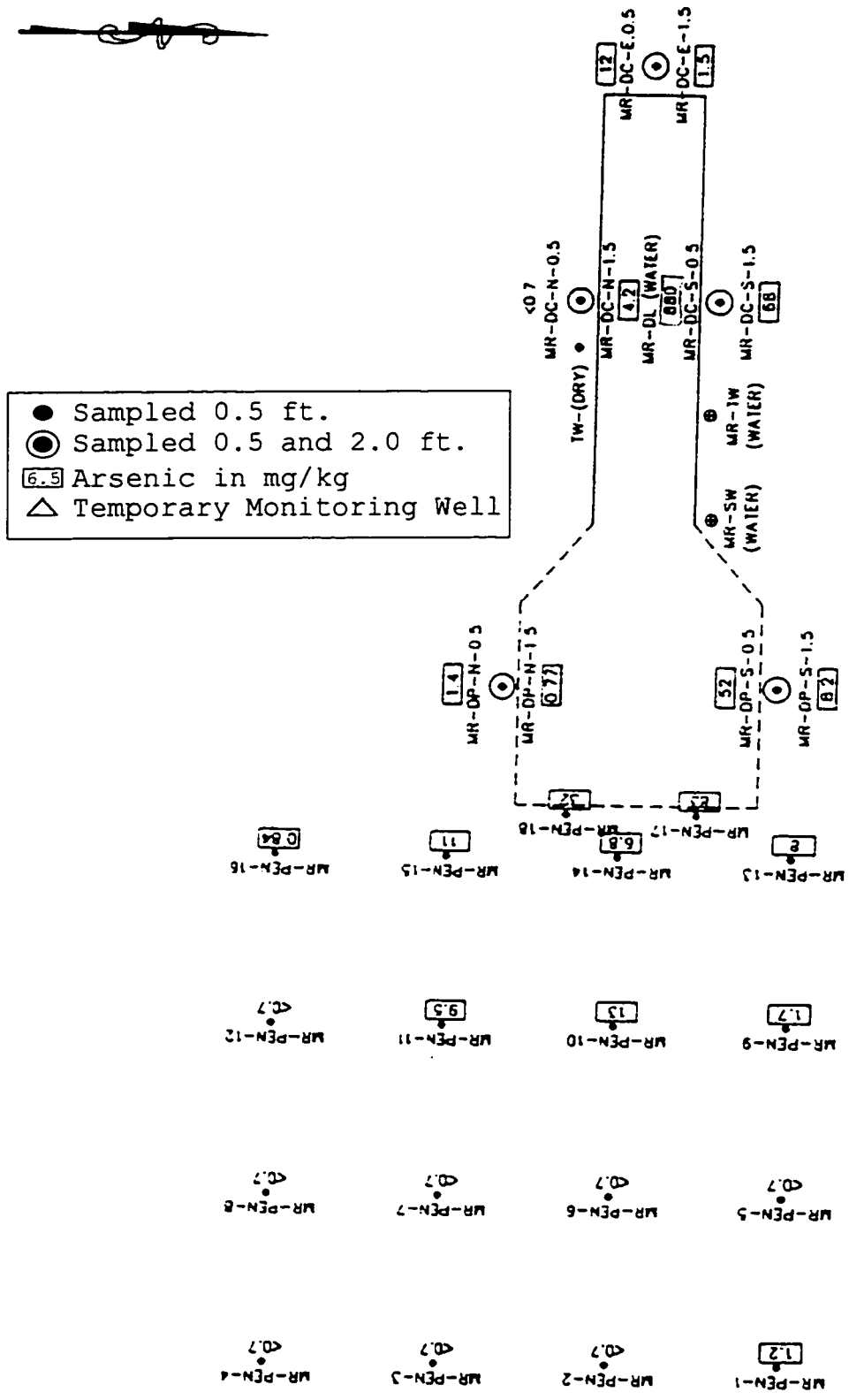

Figure B-11. Woodward-Clyde Consultants' arsenic survey map of Myakka River State Preserve cattle dipping vat site.

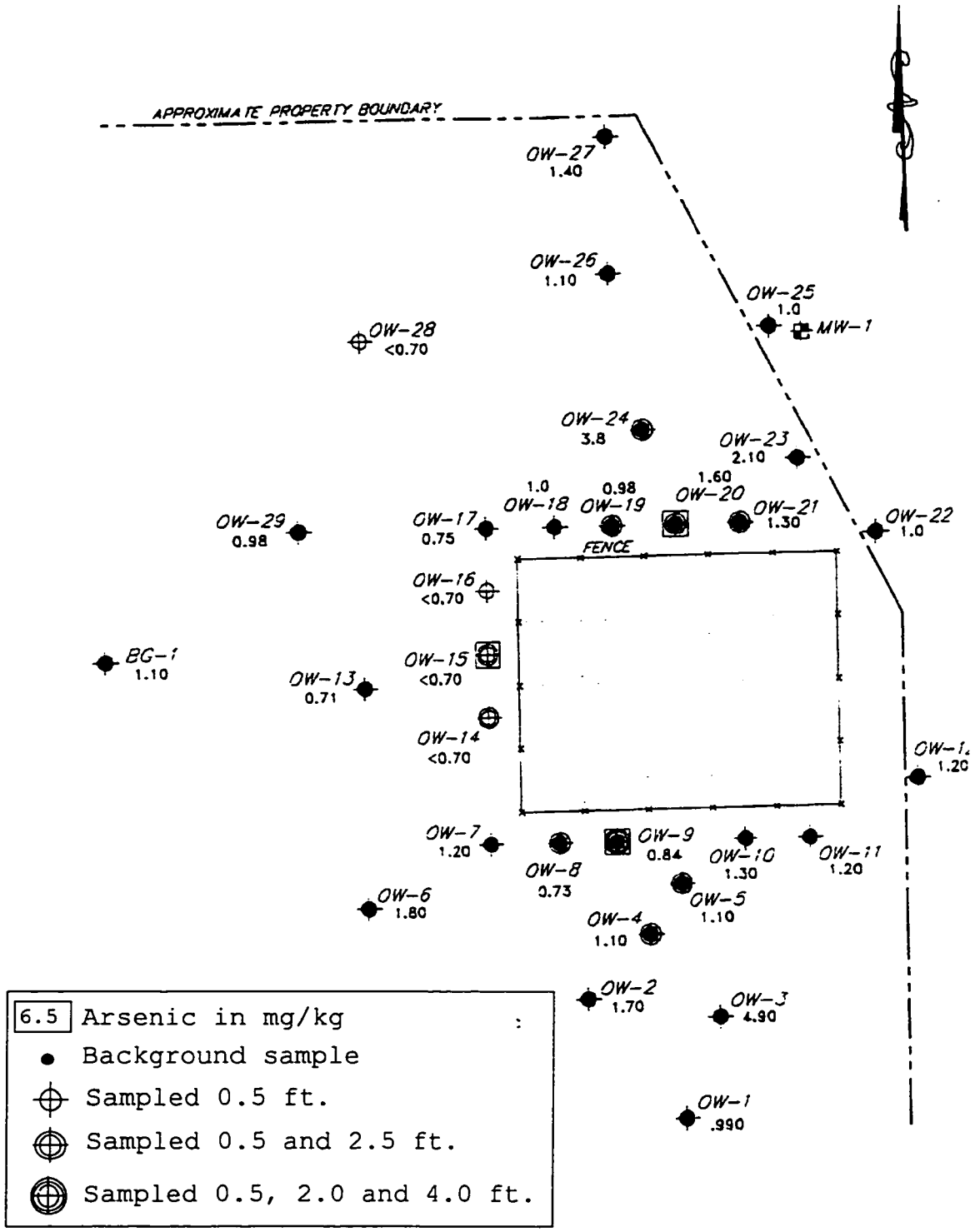

Figure B-12. Woodward-Clyde Consultants' arsenic survey map of Okaloosa-Walton Community College cattle dipping vat site. Arsenic detected in soil samples at 0-61 cm below surface.

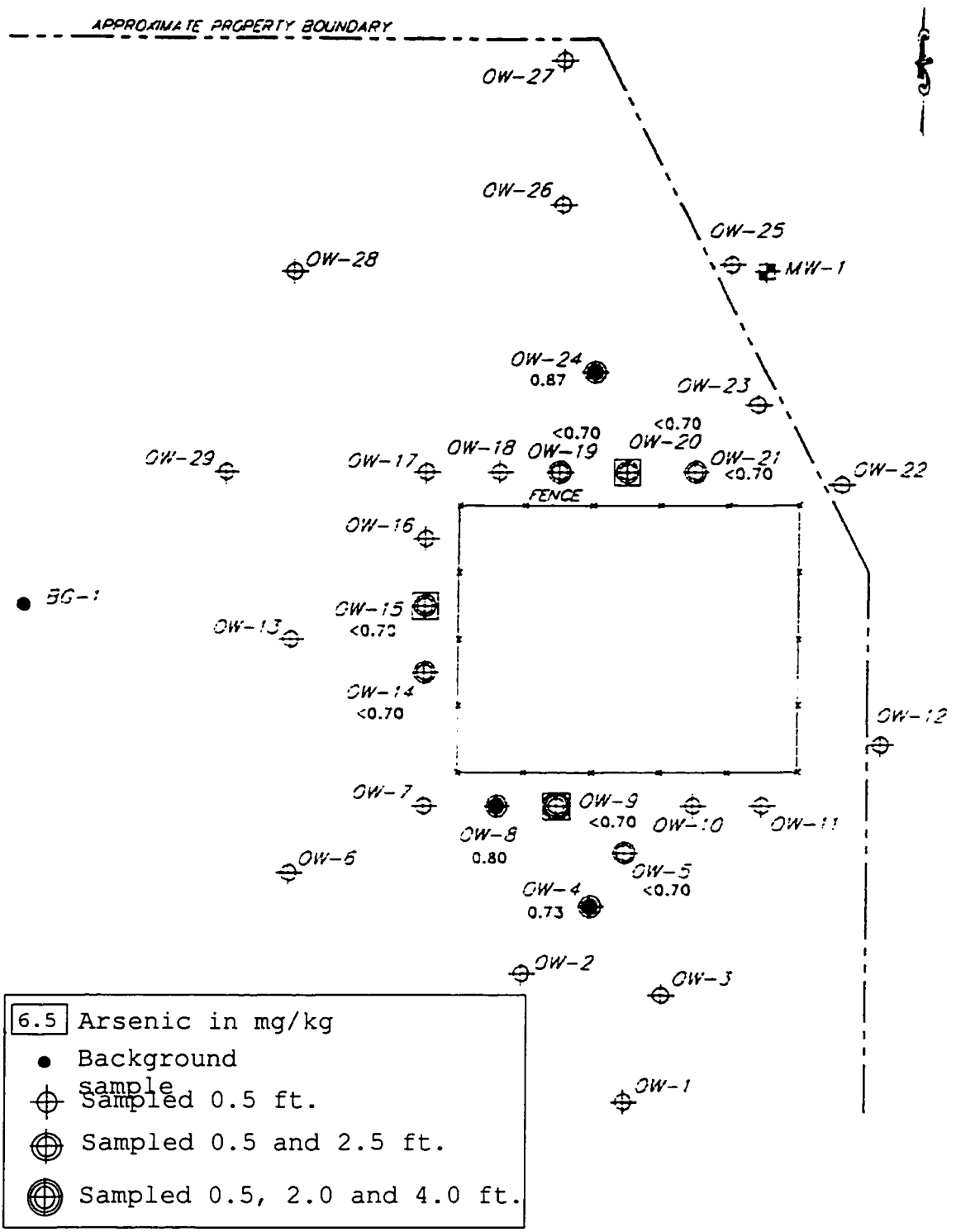

Figure B-13. Woodward-Clyde Consultants' arsenic survey map of Okaloosa-Walton Community College cattle dipping vat site. Arsenic detected in soil samples at 152-183 cm below surface.

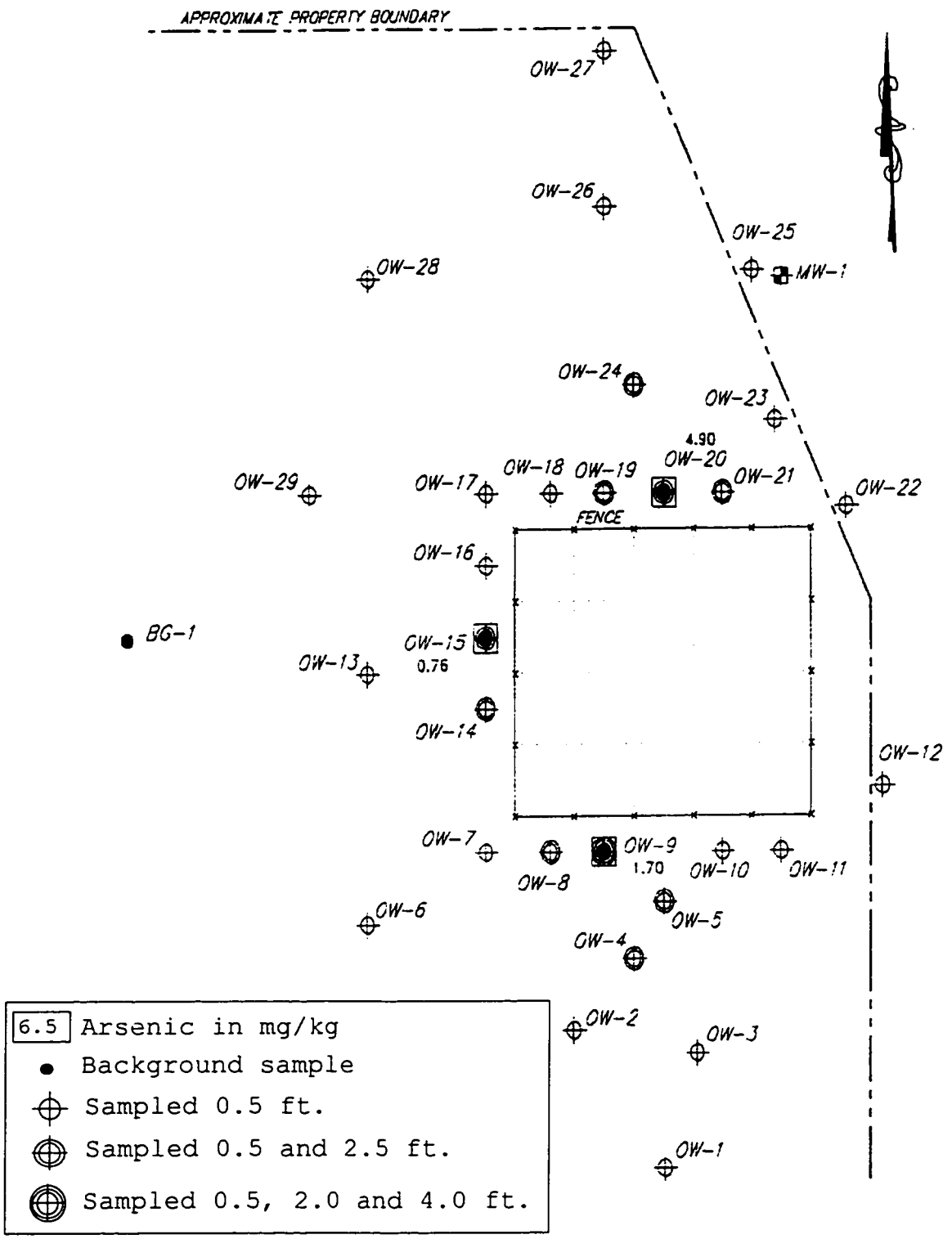

Figure B-14. Woodward-Clyde Consultants' arsenic survey map of Okaloosa-Walton Community College cattle dipping vat site. Arsenic detected in soil samples at 274-305 cm below surface.

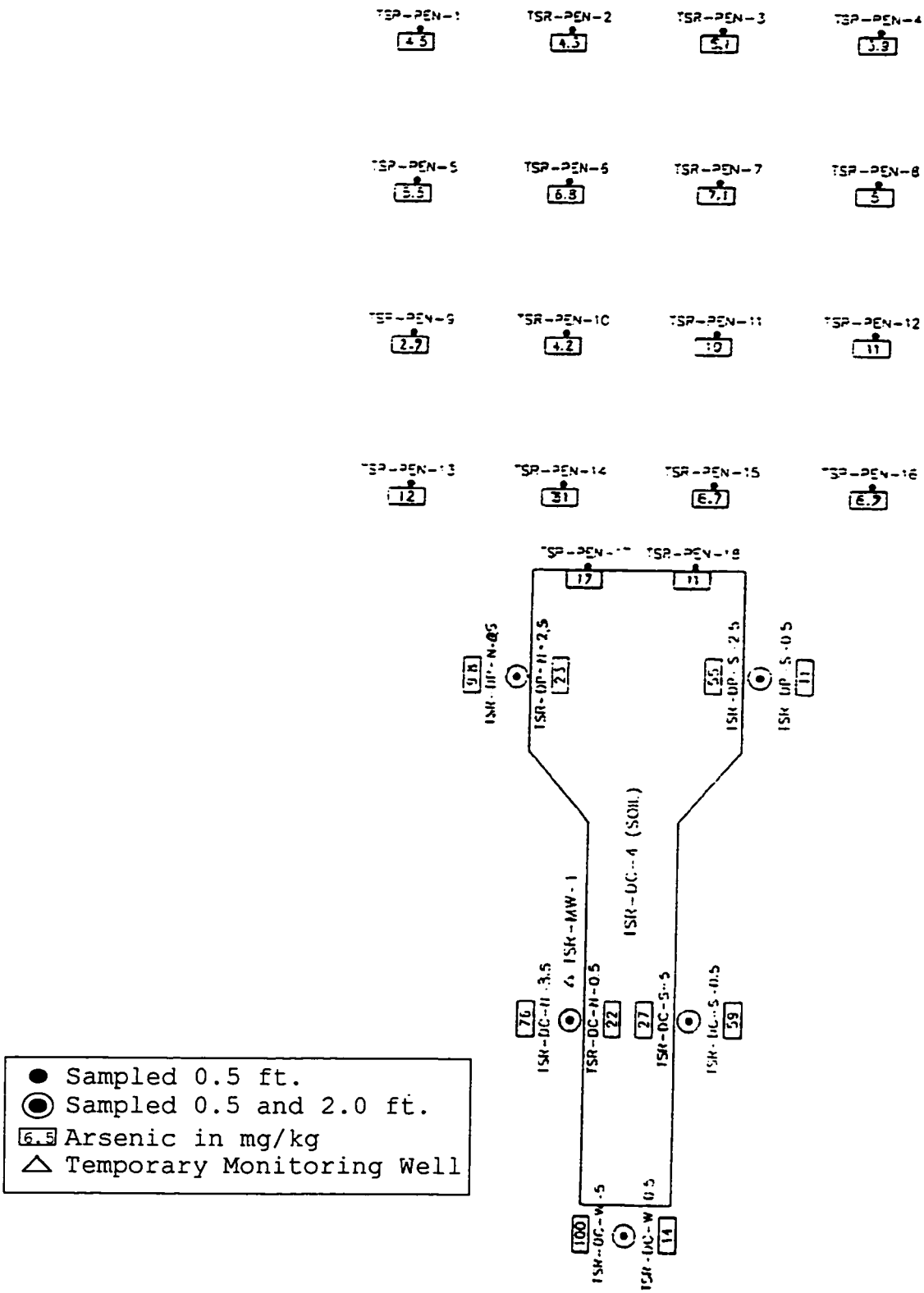

Figure B-15. Woodward-Clyde Consultants' arsenic survey map of Tosohatchee cattle dipping vat site.

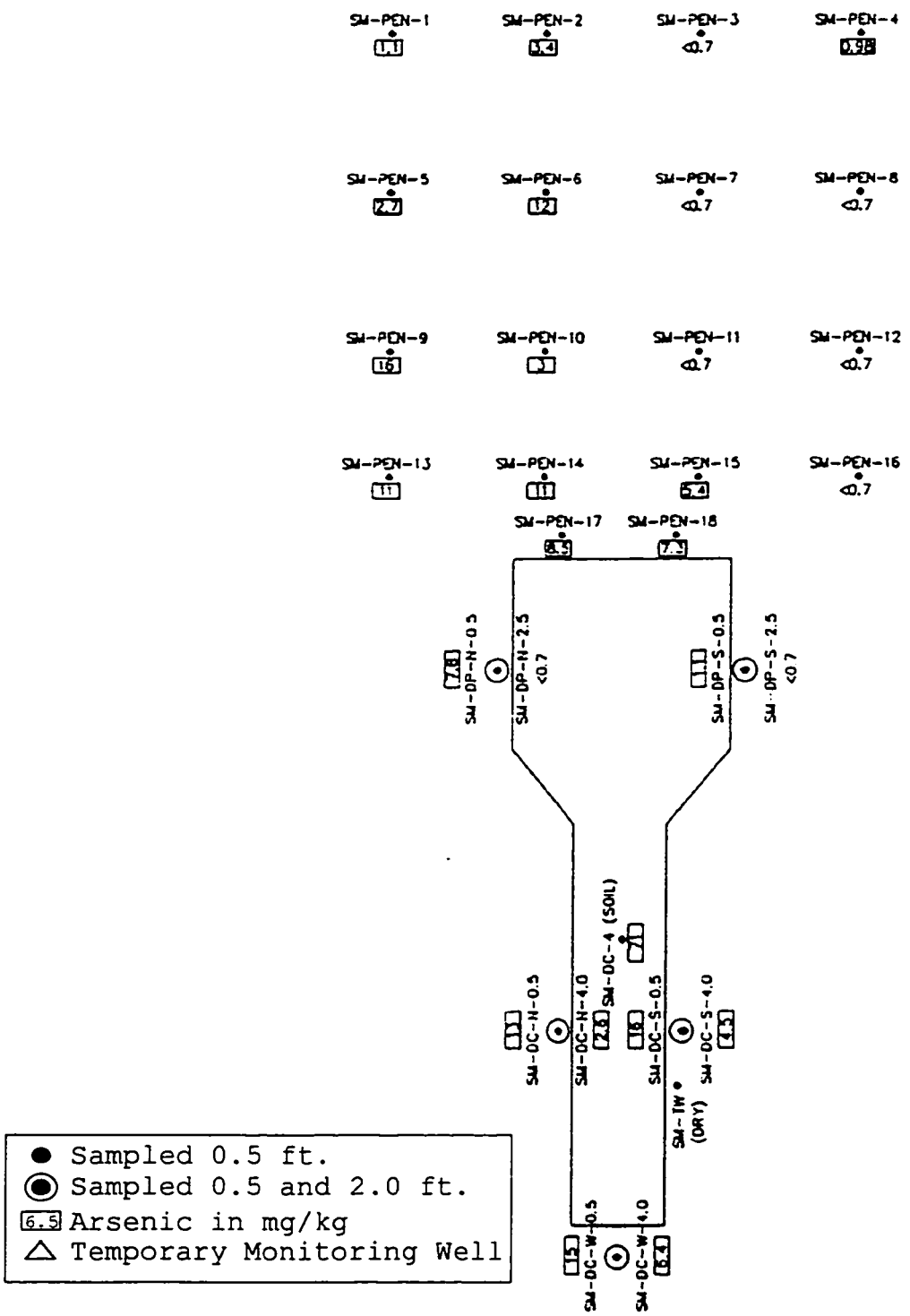

Figure B-16. Woodward-Clyde Consultants' arsenic survey map of St. Marks Wildlife Refuge cattle dipping vat site.

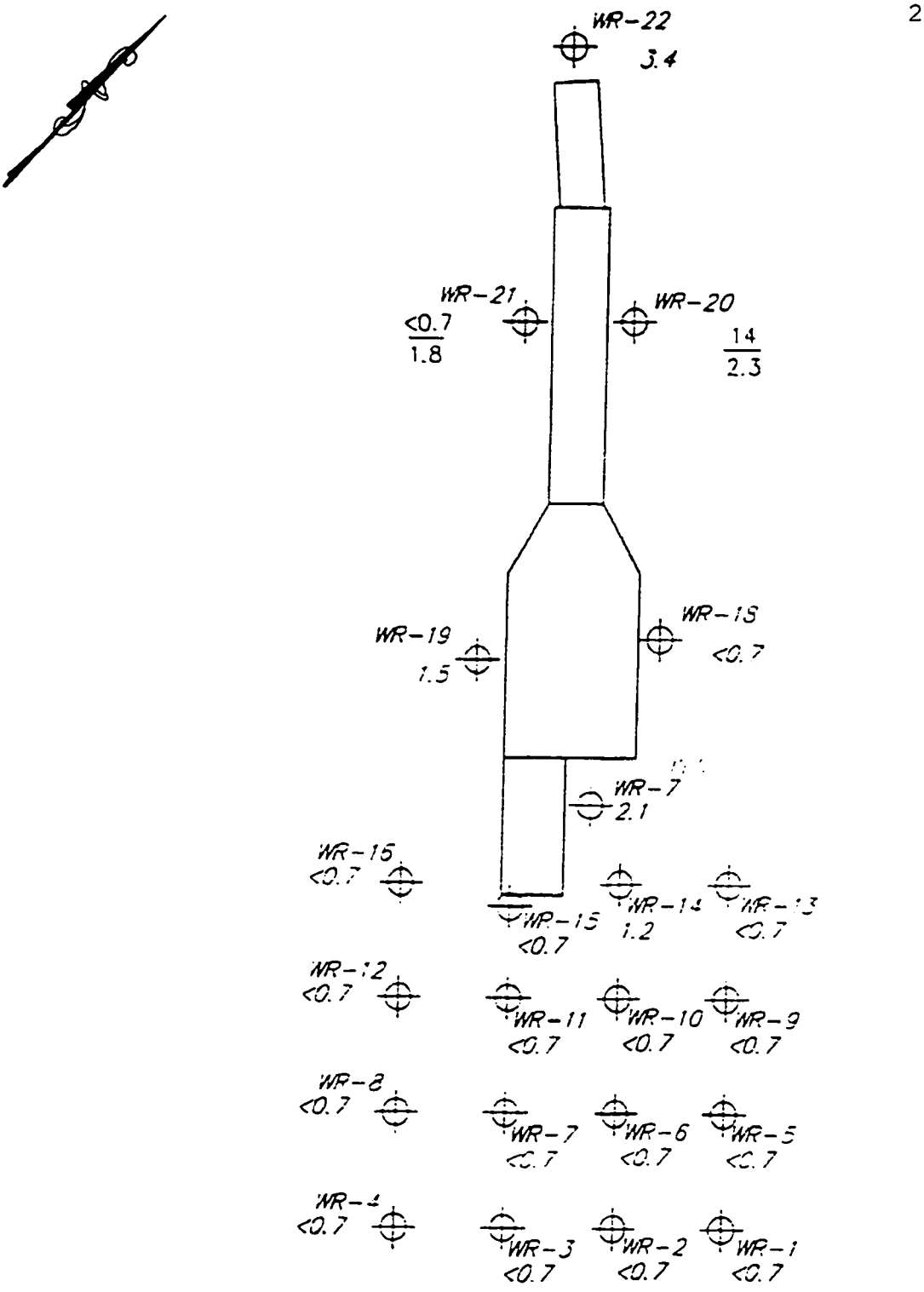

Figure B-17. Woodward-Clyde Consultants' arsenic survey map of Walker Ranch cattle dipping vat site.

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BIOGRAPHICAL SKETCH

John E. Thomas was born on August 16, 1952 in Paoli, PA. He graduated from Juniata College in Huntingdon, PA, with a B.S. in chemistry in 1973. His first project after graduation was on a newly developed automobile exhaust catalyst control with W.R. Grace, Inc. Following this experience, he returned to college and received a M.S. degree from the University of Florida's Department of Chemistry in 1978. His major area of study involved X-ray crystallographic structure determination of lanthanide and actinide complexes. In the following years, he worked for the U.S.D.A. on insect pheromone separation and synthesis; for Water and Air Research Co. as a private consultant; for the University of Florida (U.F.) Department of Food Science and Human Nutrition on registration of pesticide use for minor crops; for the U.F. Department of Agronomy on no-tillage systems; and, finally, for the U.F. Department of Soil and Water Science on projects ranging from metal transport in soil after sludge application to bioremediation of chemicals such as tetraethyllead, aldicarb, 1,3-dichloropropene, carbofuran, fenamiphos, and methyl bromide. In 1992, he started work on a Doctor of Philosophy degree under the direction of Dr. R. D. Rhue in the Soil and Water Science Department, investigating soil and groundwater arsenic

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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