Lead migration from contaminated sites : Door County, Wisconsin. [DNR-013] 1989

Wiersma, James H.; Stieglitz, Ronald D.
Madison, Wisconsin: Wisconsin Department of Natural Resources, 1989

https://digital.library.wisc.edu/1711.dl/DJHC4ZAB3LLUB8C

Wisconsin Groundwater Management Practice Monitoring Project

No. 14

GROUNDWATER
Wisconsin's
buried treasure

Wisconsin Department of Natural Resources

FINAL REPORT:

LEAD MIGRATION FROM CONTAMINATED SITES--DOOR CO., WI.

SUBMITTED TO THE WISCONSIN DEPARTMENT OF NATURAL RESOURCES

FROM THE UNIVERSITY OF WISCONSIN-GREEN BAY, DEPARTMENT OF NATURAL AND APPLIED SCIENCES

BY: JAMES H. WIERSMA and RONALD D. STIEGLITZ, COPRINCIPAL INVESTIGATORS

SIGNED: James H Wiersma
Ronald D. Stieglitz

DATE SUBMITTED: 30 AUGUST, 1989

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES continued

I. Executive Summary

One of 35 sites potentially contaminated with lead and arsenic containing pesticides was subjected to an intensive investigation. The site investigated was located in northern Door Co., about three miles north of the city of Sturgeon Bay. The site is presently used for cherry processing and was used in the past as a pesticide mixing site. Levels of contaminants at the site were measured in both the soils and the groundwater.

The site investigated is located in an area with thin soils and underling fractured dolomite. Solution features have been mapped near the site in other investigations and were found to exist on the site in this study. Rain and snowmelt on the site either infiltrate into the soils (dominate route) or runoff from the site. No surface water runs onto the site.

Surface soil samples were collected from a 50 ft sampling grid established on the site. Analysis of these samples revealed that a relatively small area of surface soils in the immediate vicinity of the former mixing area was found to be highly contaminated with lead, arsenic and copper. The maximum lead, arsenic, and copper levels found in the soil samples were 12,000, 2,040, and 23,200 mg/kg respectively. The high copper value was associated with a soil sample from 5 to 10 centimeters below the surface. The contaminated area displayed a "plume" type pattern with levels generally decreasing as one moves away from the area of highest contamination, the area presumed to have been used as a former mixing site.

Soils that contained more than 500 mg/kg lead and 300 mg/kg copper were essentially all found in the same area. Soils in an area of approximately 14,000 ft^2 were found to contain lead and copper above these levels. The area of soil contaminated with arsenic above 50 mg/kg level is approximately 50 percent larger.

Soils in the contaminated area were also sampled vertically. The vertical distribution of metals in the soils indicated that metal contamination was restricted to the upper soil layers. There was little downward migration of the metal contaminants into deeper soil layers even though the site was contaminated several decades earlier. This observation is similar to that of other investigators (Veneman, 1983, and Blancar, 1977) who studied lead/arsenic contamination problems in orchards in other regions. Contamination by lead and arsenic was limited to the top 20 to 25 centimeters (8 to 10 inches). If soils containing above 500 mg/kg lead is used to define contaminated soil, then approximately 430 yds^3 of contaminated soil are on the site.

Leaching contaminated soils from the study site with distilled water indicated that lead can become soluble and thus under the right conditions could move with groundwater. Aqueous lead levels were found to increase with increasing lead content in the soil sample. The solubility of lead from lead containing soils after 24 hours of mixing could be approximated by the equation:

$$\text{Log Aqueous Pb (ug/l)} = 1.01\text{Log Pb Matrix Conc (mg/kg)} - 0.76$$

Sorption studies of aqueous lead onto fresh dolomite surfaces indicated that dolomite was very efficient at removing lead from solution. The aqueous lead solutions were obtained by leaching contaminated soils. After two days of contact between dolomite cuttings and a lead contaminated aqueous phase, lead levels were reduced by approximately 500 fold to below 10 ug/l lead even with the most contaminated soil leachate sample.

Lead levels were measured in groundwater sampled from three monitoring wells constructed on the site for this study. Six of 39 samples from the down-gradient wells were found to contain lead; the remainder of the samples were below the analytical detection limit for lead of 2 ug/l. The six positive detections for lead were low, ranging from 2.0 to 6.5 ug/l lead. Lead levels never exceeded the present drinking water standard for lead of 50 ug/l.

Measurement of water levels in the monitoring wells and chemical analysis of water samples from these wells indicated that groundwater was continually exchanging. The groundwater levels were found to respond quickly to recharge events.

One of the down-gradient monitoring wells has been abandoned, the other down-gradient well has had a 3-level piezometer installed in it after sampling was completed for this study. The up-gradient well remains as it was originally constructed. The Wisconsin Geologic and Natural History Survey is continuing to monitor the water levels at the site a part of another study and has assumed the responsibility for abandoning the two remaining well installations at the completion of an on-going study.

II. Introduction

Problem Overview

Door County, WI has been a major cherry and apple producing area since the late 1880s. Until World War II lead arsenate and several related inorganic compounds were the sole insecticides used to protect the cherry and apple crops. Copper sulfate and lime-sulfur preparations were also used as fungicides. After World War II organic pesticides were introduced and the use of lead arsenate declined to the point where it was no longer used by about 1960.

The sheer size of the cherry and apple producing orchards meant that large quantities of pesticides were bought, stored, mixed and applied to orchards as part of the industry. Problems associated with the intended practice of spraying pesticides included spillage, overflow of mixing tanks, cleaning spraying equipment and disposal of unusable caked or hardened pesticides. These activities resulted in soil contamination at a number of sites throughout Door County.

Sites of soil contamination were first observed by the WDNR in mid 1983. A simple grab sample testing program by the WDNR verified that elevated levels (tens of thousands of milligrams per kilogram or parts per ppm) of lead and arsenic were present at a number of sites (Reyburn, 1986). Subsequent investigations revealed that up to forty such sites could be identified based on the location of past major orchard operations. Additional testing of private water supplies found some wells that were contaminated with lead in the 3-3300 parts per billion (ppb) range. Further-more, the contaminated wells appeared to be geographically correlated to the contaminated sites (Stoll, 1986). Extraction Procedure (EP) toxicity tests run for the WDNR showed the soil at a number of the sites would be classified as hazardous material.

After further investigation by the WDNR, 35 potential sites suspected to have serious soil contamination problems were chosen for more detailed evaluation. Thirty four of the sites were sampled and surveyed in more detail by Residuals Management Technology, RMT, an engineering and environmental management firm from Madison, WI. Their report on these 34 sites was submitted in May 1987. One site where heavy contamination was suspected was excluded from the RMT studies and was chosen for an intensive investigation by scientists from UW-Green Bay. This report details the results of that intensive investigation for lead and arsenic contamination at the Door County Fruit Growers Incorporated (formerly called Chico Enterprises) site, located about 3 miles north of the city of Sturgeon Bay, WI.

This investigation examined in detail a number of variables for which there was no background information. Reported herein are the vertical and horizontal distributions of lead and arsenic in the soils and studies of the leachability of the contaminated soils. Results of an extended groundwater monitoring program at the site are given. These results are based on groundwater samples collected at three monitoring wells constructed on the site. Studies on the sorption of lead on dolomitic materials have also been completed. Initial investigations revealed that significant quantities of copper were also present in the soils. Although copper was not initially a 'parameter of interest', its level was determined in most of the soil samples analyzed.

Chemistry of Lead and Arsenic

An extensive literature exists concerning the environmental chemistry of lead and arsenic. Specific studies of lead arsenate contamination in orchards which are the most relevant for this report are: Elliott et. al., 1986; Veneman et. al. 1983; and Hess and Blanchar, 1976. The environmental chemistry of arsenic has recently been reviewed in two different extensive reports (Eisler, 1988 and National Resource Council of Canada, 1978). The more important points concerning the chemistry of lead and arsenic are discussed in the following paragraphs.

Lead contamination of the environment can occur through inorganic and organic lead compounds. The chemistry of organo-lead compounds is complex and distinct from the chemistry of inorganic lead chemistry. Organo-lead compounds were not used as pesticides in Door County and thus are not of direct concern in this study. The chemistry of inorganic lead centers around the chemistry of its +2 salts. Most of the +2 lead compounds are very insoluble; two major exceptions being lead nitrate and lead acetate.

Most lead compounds are very insoluble under the conditions likely to be present in soils and the carbonate bedrock in both the saturated and unsaturated zones (Barnum, 1982.) Values as low as 3×10^{-6} parts per billion (ppb) can be calculated for the dissolution of galena (PbS) (Stumm and Morgan, 1981). For lead arsenate, [$Pb_3(AsO_4)_2$], in aqueous solution at pH 7 and in contact with atmospheric carbon dioxide (0.0003 atmospheres), the soluble lead concentration is calculated to be 3.1 x 10^5 ppb (Sadiq 1983). This values indicates that lead and arsenic are sufficiently soluble to be of concern in a simple aqueous systems. While lead arsenate was likely the most commonly used pesticide, other formulations were also likely used and thus solubility values for lead and arsenic would vary. Calcium aresenate and copper containing arsenic salts were also used as pesticides.

The values reported in the literature for the solubility of lead compounds also do not address the complex nature of "equilibrium" in the environment. Ionic strength, pH, common ion effects, redox conditions, soil type and temperature are some of the possible complicating factors that make predicting the solubility of lead in the environment under a particular set of condition nearly impossible.

Studies of lead arsenate in contaminated orchard soils (Veneman, 1983, and Hess and Blanchar, 1976) and in soils of varying composition (Elliot, 1986), show that lead is very immobile and unlikely to migrate as a soluble species. Clays and insoluble organic matter are thought to be responsible for immobilizing lead. If carbonates and or phosphates are present, the solubility of lead can be reduced by up to 3 orders of magnitude (Lindsay, 1979). The addition of phosphate salts or lime both would be expected to reduce the mobility of lead as a soluble species.

Lead has been shown to adsorb onto carbonates such as limestone and even more tightly onto dolomite. Once adsorbed onto these carbonate rock materials, lead remains tightly bound and requires severe leaching conditions to remobilize the lead as a soluble species (Pickering, 1972). The most probable migration pathways for lead are considered to be as suspended material in runoff, as spray drift, or by wind erosion.

Arsenic is a semimetal (metalloid) and can form both inorganic and organic compounds. The most common forms of arsenic found in environmental samples are listed in Table 1 below. The organic forms are usually referred to as organo-arsenicals. Nearly all (97%) of the arsenic compounds including the organo-arsenicals manufactured begin with arsenic trioxide; arsenic that originated as a by-product of copper smelting. Arsenic and its compounds are used in pesticides, glass ceramics, paints, dyes, and hide preservation.

In the soil environment, arsenic can be found in both the inorganic and the organic forms listed in Table 1. The form of arsenic found in the soil environment depends on soil pH, organic content, and the Eh (Oxidizing-Reducing) condition present in the soil. Under conditions with oxygen present (high Eh), alkaline pH, and low levels of organic material, arsenic in the form of arsenate is favored. As conditions change toward lower Eh and pH values and toward higher organic content, the arsenite form is favored. Under anaerobic conditions arsenate is reduced to arsenite which in turn can be methylated or dimethlyated by microorganisms to form methylarsinic acid or dimethylarsenic acid. Further methylation results in the formation of volatile tri- or dimethyl arsine, a route that allows arsenic to escape to the atmosphere. Normally, warm, flooded organic soils where oxygen is absent would be required for complete reduction of arsenic compounds to the volatile arsenic forms. When organic forms of arsenic are released into an oxygenated environment, they are oxidized to the more stable arsenite and arsenate forms. Arsenic is somewhat mobile but does not accumulate in air, plant and water phases of the soil environment. Arsenic, however, can accumulate in soil when heavily applied (Woolson 1975). In oxygenated soils the arsenate form would be expected to behave similiar to phosphate ion in soil. As such it would bind tightly to soil particles, especially clays.

Table 1. Chemical Forms of Arsenic Found in Environmental Samples

NAME	STRUCTURE	OXIDATION STATE
INORGANIC FORMS		
Arsenate	AsO_4^{3-}	+5
Arsenite	AsO_3^{3-}	+3
Arsine	AsH_3	-3
ORGANIC FORMS		
Methanearsonic Acid Monomethyl Arsonic Acid	$CH_3AsO(OH)_2$	+3
Hydroxydimethyl Arsine Oxide Dimethyl Arsenic Acid Cacodylic Acid	$(CH_3)_2AsOOH$	+1

The specific mixtures of lead and arsenic used in Door County are unknown and even if they were known, they probably varied over time. Mixtures probably were lead arsenate compounds or mixtures containing lead +2 species as well as an arsenic (III) (arsenite) or (V) (arsenate) anion. Also, compounds such as calcium arsenate, either $Ca_3(AsO_4)_2$ or $CaHAsO_4$, were used at some locations. Copper containing mixtures, Paris Green and Bordeaux Mix, were also popular in orchard operations. Paris Green is usually considered to be copper aceto-arsenite, $(CH_3COO)Cu\cdot 3Cu(AsO_2)_2$. Bordeaux mixture is $CuSO_4\cdot 3Cu(OH)_2\cdot H_2O$. The Bordeaux mixture was used for its fungicidal properties.

Overview of the Toxicology of Lead and Arsenic

Exposure to lead can come through a number of different mechanisms. The air a person breaths and the food and nonfood substances ingested by an individual all contribute to the total exposure to lead. Children are considered to be more sensitive to exposure to lead than adults. One of the reasons is that young children are believed to adsorb lead more efficiently than adults. The currently excepted levels of maximum exposure to lead by children are in the range of 100-150 ug Pb/day. Children living in an urban environment are exposed to the highest levels of lead. They often display pica, the eating of nonfood items, and consume lead-containing materials including lead-based paint chips, urban dusts, and soil. While atmospheric lead levels are higher in urban environments, air polluted by lead is thought to contribute only about 3 ug/day directly to the total lead burden of a child. However, indirectly air polluted by lead results in contaminated soils and dusts which do further add to the total exposure to lead. A child consuming 1 gram per day of urban dust would ingest from 100-10,000 ug of lead. These values show that only very small amounts of urban dust need to be consumed by a child to exceed the recommended daily intake of lead for children.

Absorption of lead through the gastrointestinal tract is the major route of exposure. Factors that influence the rate of absorption include the physical and chemical form of lead, dietary factors, the presence of other pollutants, and the state of health of an individual child. Lead associated with dusts and soils is thought to be absorbed by an individual with about 30% efficiency.

Lead absorbed by an individual is distributed among the blood, bone and soft tissues. The residence time for lead in blood and soft tissues is on the order of four to six weeks whereas in bone, residence times are as long as thirty years. While lead in the skeletal system is physiologically inactive, lead in the soft tissues and blood has effects on the hematopoietic system. Ultimately an anemia occurs which is similar to iron deficiency. Lead decreases red blood cell survival and inhibits the synthesis of heme. Lead also inhibits a number of enzyme systems (delta-aminolevulinic acid dehydratase, and ferrochelatase) which are important to good health.

The central nervous system is also affected by high blood lead levels. Concentrations of 80-100 ug Pb/dL cause acute encephalopathy. Children surviving these high levels have demonstrated irreversible effects such as seizures, behavioral changes, and mental retardation. At low levels of exposure, subtle changes such as irritability, and lack of coordination have been observed. The subclinical effects of lead also have drawn considerable attention. Decreased IQ, hyperactivity, and mental retardation have been reported but many of the studies suffer from serious experimental design problems (Smith, 1985). At present it is not possible to attribute any of these effects to exposure to low levels of lead.

Other effects associated with exposure to lead include: kidney insufficiency, colic, constipation, and other effects on the gastrointestinal tract. Effects of lead on the reproduction reported include: sterility, abortion, stillbirths, and neonatal deaths.

The toxicity of arsenic is highly dependent upon the chemical species to which an organism is exposed. Arsenicals are readily absorbed by ingestion but most of the arsenic is excreted in urine within a few days to a week. This fairly rapid turnover of arsenic by most organisms suggests that long-term (chronic) effects would likely require repeated exposure to arsenic. The general consensus among scientists is that arsenic compounds listed in order from most toxic to least toxic conform to the following order: arsines > inorganic arsenites > organic trivalent compounds > inorganic arsenates > organic plus 5 compounds > arsonium compounds > elemental arsenic. Inorganic trivalent arsenic is toxic through reactions that make it an enzyme inhibitor. While many of the biochemical pathways for the toxicity of arsenic have been elucidated, there also exists some evidence in animal studies, that it may be required as a trace nutritional requirement.

Epidemiological evidence shows that exposure to inorganic forms of arsenic increases the risk of cancer of the skin, lung, lymph and hematopoietic (blood) systems in humans. Inorganic arsenicals are weak inducers of chromosomal changes and thus are considered as weak mutagens. Arsenic is known to cause teratogenic effects in some invertebrates and has been implicated as a cause of birth defects in humans.

Arsenic has been shown to become concentrated in a number of different plant species, especially algae. There is, however, little evidence that arsenic bioaccumulates up the food chain to a significant degree. Bioconcentration factors determined experimentally for aquatic systems tend to be low except for algae. Animals that consume contaminated plants tend to excrete arsenic quite rapidly thus it does not reach high levels in organisms at the top of the food web (chain).

In summary, the toxicological properties of lead and arsenic bring one to the conclusion that chronic exposure of organisms to lead should be of greater concern than chronic exposure to arsenic compounds. Lead has a much longer residence time in organisms and causes disruption of a number of biological functions. In addition there exist in today's society, a number of routes of exposure that contribute to the total body burden of lead. Since, children are more susceptible than are adults to the harmful effects of lead, every effort should be made to reduce their exposure. The acute effects of exposure to high levels of either lead and arsenic will cause serious impairment of the health of individuals.

III. Site Description

Geology and Hydrogeology

The Door County Fruit Growers Association site investigated in this study is located approximately 3 miles (4.5 kilometers) north of the city of Sturgeon Bay in Northern Door County, Wisconsin (See Figure 1). The site is and has been used to process cherries. It is located on the northeast corner of the intersection of CTH HH with Martin Road in the township of Sevastopol (NE 1/4, NW 1/4, Section 20, T 28 N, R26 E).

The Door Peninsula of northeastern Wisconsin extends into Lake Michigan to form Green Bay. The peninsula is a cuesta with a west facing scarp and an eastward dipping back slope. The site is on a plateau 20 to 40 ft (6 to 12 meters) above the surrounding area; the topography in the immediate vicinity of the contaminated area is of low relief (approximately 10 feet--3 meters). The Niagara Escarpment forms the western boundary of the plateau approximately 0.3 miles (0.5 kilometers) west of the study site.

Work by Thwaites and Bertrand (1957) and later by Schneider (1981) indicates that the northern portion of the Door Peninsula was last glaciated during the Late Wisconsin Age Port Huron Advance. The Green Bay lobe expanded in a southeasterly direction out of the present day Green Bay Basin, down preglacial stream valleys, and finally across the entire Peninsula. A thin till unit named the Liberty Grove Member of the Horicon Formation was deposited on the Silurian dolomites of northern Door County.

The bedrock beneath the thin veneer of glacial till is fractured and solution modified by solution dolomite of the Manistique Formation. Solution features or "karst" features are potential conduits to drain surface water to the aquifers with little filtration or attenuation of contaminates. Near the study site, surface karst features are abundant and some have been mapped in

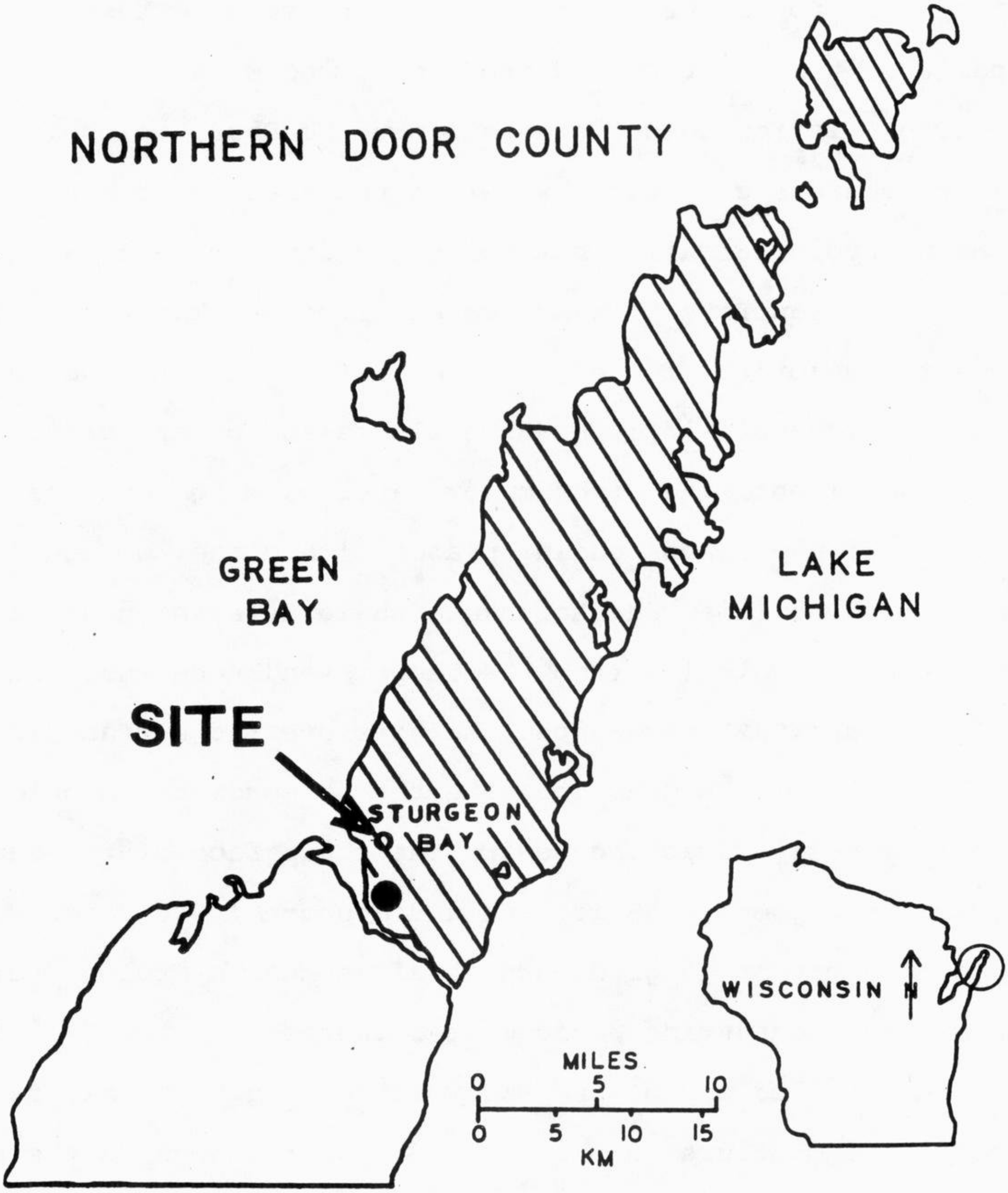


Figure 1. Study Site Location.

nearby fields and ditches (Stieglitz and Johnson, 1986). Fracture traces of 0.3 miles (0.5 kilometers) in length exist on and near the site. These features which are observable on air photos are interpreted to be buried joints or joint sets. These joints are capable of transmitting and storing ground water.

The Silurian dolomites that form the Door Peninsula are the primary sources of potable water in the area and can be divided into two hydrologically interconnected aquifers--the Niagaran and Alexandrian Aquifers. These two aquifers are karstic aquifers because the majority of the groundwater flow and storage is in the solution widened joints, bedding planes and other voids. Sherrill (1978) has identified eight major water bearing zones associated with solution-widened bedding planes within the two aquifers. The subjacent Ordovician age Maquoketa shale acts as an aquitard and separates the dolomite from the deeper sandstone aquifers below.

Howard (1982) has mapped the piezometric surface identified by Sherrill. These data indicate that groundwater should flow in a southwesterly direction toward the scarp face of the nearby Niagara Escarpment. Stieglitz and Johnson (1986), however, have found that potential gradients at sites near hydrologic divides can be reversed during periods of recharge.

A detailed map of the study site is shown in Figure 2. The topographic contours on the map and observations on the site indicate that during precipitation events or snow melt, drainage is away from the contaminated zone (the area immediately east of the building) in both north and south directions. There was no flow of water onto the region of high contamination. During periods of

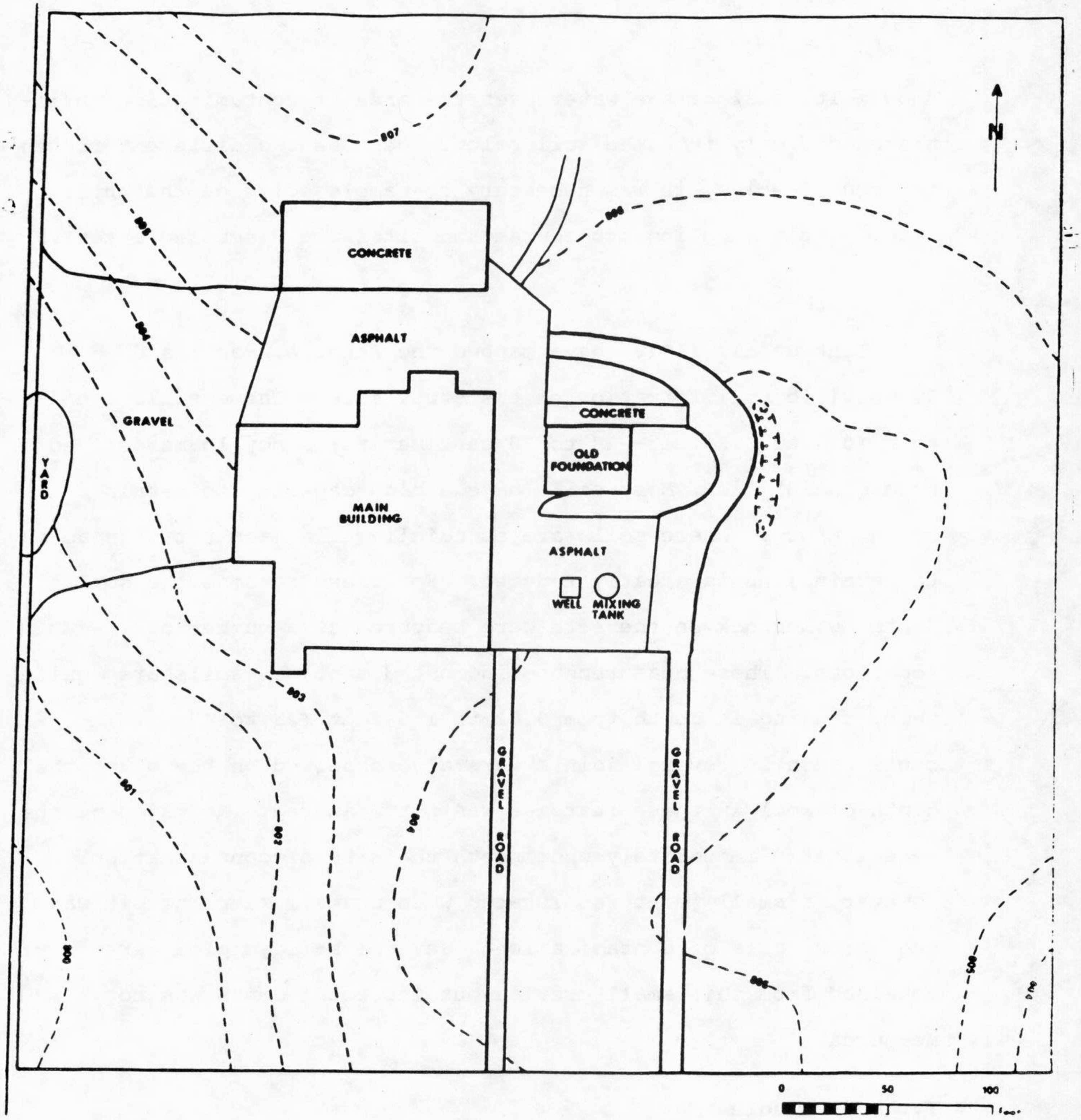


Figure 2. Map of Study Site with Elevations.

snow melt, most of the water over the area of contamination infiltrated directly into the soil below. Because two different routes for runoff exist, it was necessary to sample soils on the entire site. (Soil sampling procedures and sites are discussed later).

Soil Depths:

Link et al. (1978) have mapped the Longrie, Namur and Summerville soil formation on the study site. These soils are thin (0.7 to 2.3 feet--20 to 70 centimeters) sandy loams derived from glacial till. Most soils have a high capacity to retain contaminants. Where soils are especially thin, the total capacity to retain ions is greatly reduced. For these reasons the soil depth to bedrock on the site were measured at a number of locations. These measurements indicated that the soils are quite thin, ranging in depth from 0.82 to 1.5 feet (25 to 45 centimeters). Several joints were also observed on the site; the depth of soil in these features was not measured. No major joints were located immediately underneath the site of contamination. However, a small joint was located when a small sampling pit was dug in the area of contamination. Several soil samples were obtained from this small crevice but its total depth was not measured.

IV. Soil Studies

Surface Soil Sample Collection

An initial investigation of the site was made on 19 May, 1986. A series of twenty nine surface soil samples were collected at various points around the site on this date. Analysis of samples collected during this survey revealed that a zone east of the building contained high levels of metals. The initial survey also revealed that the soils on the site had been disturbed in a number of locations. Because of the high levels of metals found in the initial investigation and the presence of disturbed soils, it was decided that a regular sampling grid would be the best method to sample the untilled soils around the site. The grid used 50 foot (15.2 meter) intervals for sample collection points. The specific grid locations where surface soil samples were collected are shown on Figure 3. Surface soil samples were collected by digging approximately 10 cm deep with a shovel and placing 100-200 grams of sample into sterile Whirl-pak bags. The sample bags were immediately sealed, transported to the laboratory and stored at room temperature until the acid digestion procedure was initiated. Surface soil samples were collected from these locations on 10 June, 1986 and 20 June 1986. A total of 57 soil samples was collected at different points on the grid.

Soil Profile Samples Collected

Two different sampling efforts were conducted to obtain information on the vertical distribution of metals in the soils on the site. On 3 July, 1986 three pits, hand dug to bedrock in the zone of high contamination were samples at 2.0 inch (5 centimeter) intervals. Samples from these small pits were designated P-1, P-2, and P-3. The location of these three sampling points are shown on Figure 3. A description of soils found at 5 cm intervals in the pits is found in Appendix I.

On 10 October an additional 13 sites were sampled by

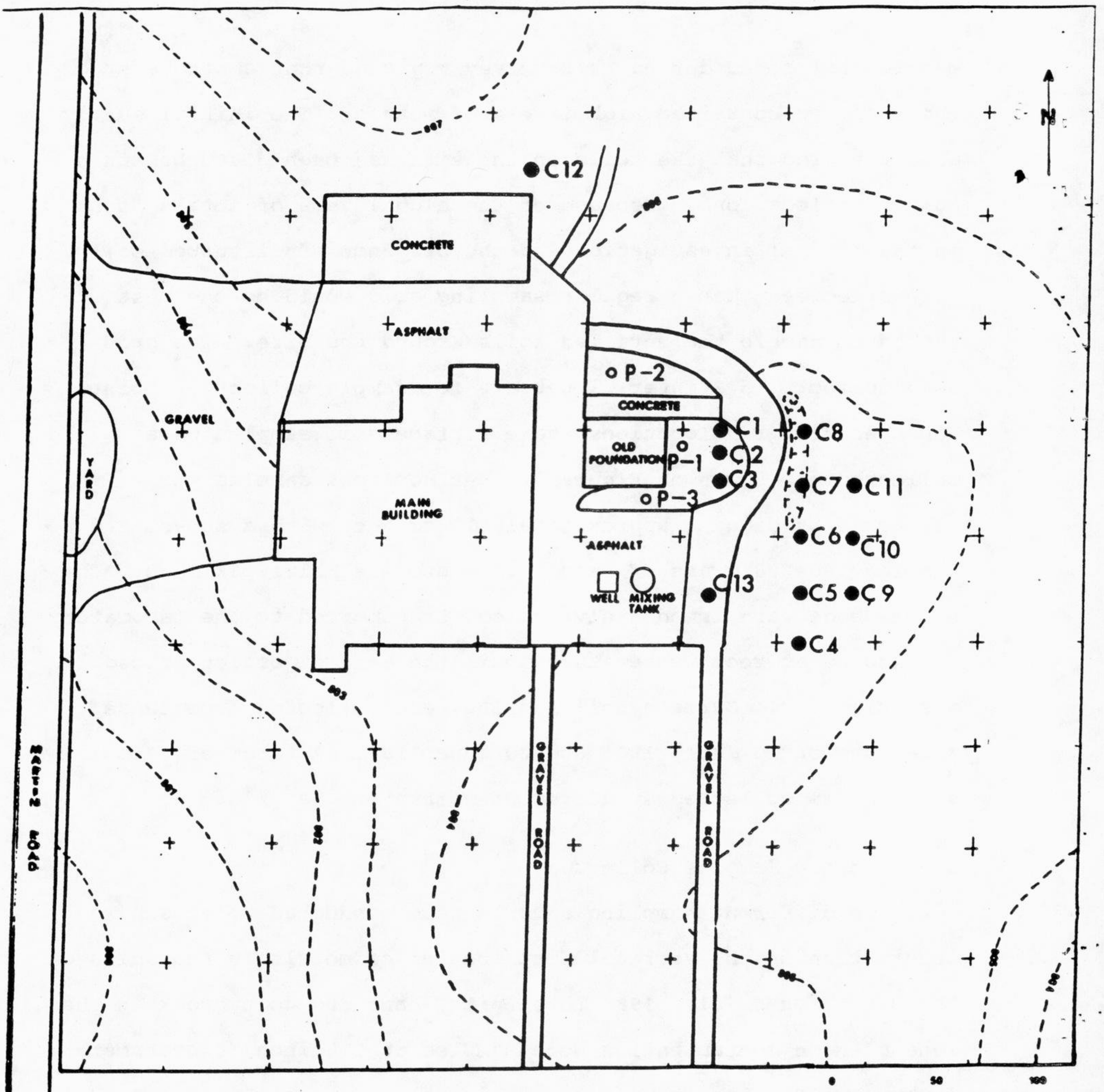


Figure 3. Location of Surface Soil Sample Collection Points (Grid Intersections) Vertical Pit Samples (P Series), and Core Samples (C Series).

collecting soil cores. The location of the sampling points for the core samples are also shown in Figure 3 and are designated by the letter "C" followed by the core number. A trailer mounted hydraulic coring apparatus was used to obtain the cores. In every case, cores were taken to bedrock. The cores were removed from the core barrels and wrapped in plastic. The soil cores were sectioned into 2.0 inch (5 centimeter) sections. Selected sections of selected cores were subjected to chemical analysis. Descriptions of the soil cores are found in Appendix I.

Methods of Soil Analysis

Soil samples were digested by weighing between 1-5 grams of sample into a 100 ml beaker. Five mls of 6 M HNO_3 and 5 mls of distilled water was added to each beaker. The samples were then digested on hot plates for two hours. Watch glasses were placed on each of the beakers to prevent splattering. After 2 hours, the watch glasses were removed, rinsed with distilled water into the samples, and then the sample volume allowed to evaporate to approximately 8 ml. The samples were then vacuum filtered through Whatman GF/A 2.1 cm glass fiber mats held in Gooch filtering crucibles. The filtrate collected in the vacuum filter flask was quantitatively transferred to a 100 ml volumetric flasks, diluted to volume, and then thoroughly mixed. The filtrates were then transferred to clean plastic bottles, and then tightly sealed with screw caps. Two blank controls were also carried through the procedure. The first blank control consisted of distilled water and 5 ml of 6 M HNO_3 diluted to a final volume of 100 ml. The second blank control used the same quantities of acid used to digest the soil samples, but the sample was carried through all steps in the procedure including the filtration steps. The acid filtrates and the blanks were transported to the Plant and Soil Analysis Laboratory of the University of Wisconsin-Extension. This laboratory used an Inductively Coupled Plasma (ICP) emission spectrometer to determine the levels of metals in the acid filtrates.

At the same time that soil samples were weighed for the acid digestion procedure, a second subsample of approximately 5 grams was weighed into a metal can. The samples were dried overnight at 110 degree Celsius and reweighed to determine the amount of moisture lost. The weight loss of the sample was used to adjust the weight of the acid digested samples to a dry weight basis. All results of metal content in soils in this report are total metal content on a dry weight basis.

Distributions of Metals in Surface Samples:

The lead content of surface soils collected from the sampling grid were found to range widely from a maximum value of 10,800 mg/kg Pb to a minimum value of 45 mg/kg Pb. A background soil sample from a wood lot across from the study site had a value of 41 mg/kg Pb. Burau, 1982, states that average concentrations of lead range between 15 to 25 mg/kg. The highest levels of lead were found east of the building where pesticides were mixed in the past. (An old elevated pesticide mixing tank is located immediately to the south of the area with the highest lead levels.)

The distribution of lead in surface soil samples is shown in

Figure 4. Included on Figure 4 is a 500 mg/kg isopleth for lead. The results show that a plume of higher lead content has spread east into the edge of an agricultural field located just east of the gravel road indicated on the east edge of the mapped area. During the summer of 1986 this field was planted with corn and the corn plants in the plume area were stunted. The number of plants affected, however was very small.

The most heavily contaminated area (See Figure 5) is found immediately adjacent to an old foundation and floor slab. The building once located on this foundation was likely used for pesticide storage as green stains are visible on the remaining concrete floor. Soils next to the foundation would have received runoff from it and the asphalt pad next to the mixing tank. It is not known whether high concentrations of lead exist in the soils beneath the asphalt pad. (The asphalt pad is of fairly recent construction--perhaps 10 years old.) One isolated value for lead exceeded the 500 mg/kg level; this sample was located in the northwest corner of the sampling grid.

Arsenic levels in the soils also varied widely in the samples collected from the sampling grid. The maximum value for arsenic in the soil samples was 2040 mg/kg As. However, a higher value was found, 8000 mg/kg As, in a small grab sample with green stained materials. The distribution of arsenic in the surface soil samples on the study site are shown in Figure 6. Arsenic values at the perimeter of the site are in the range one would expect for background levels in soils. Ganje and Rains, 1982, state that virgin soils contain between 0.2 to 40 mg/kg arsenic

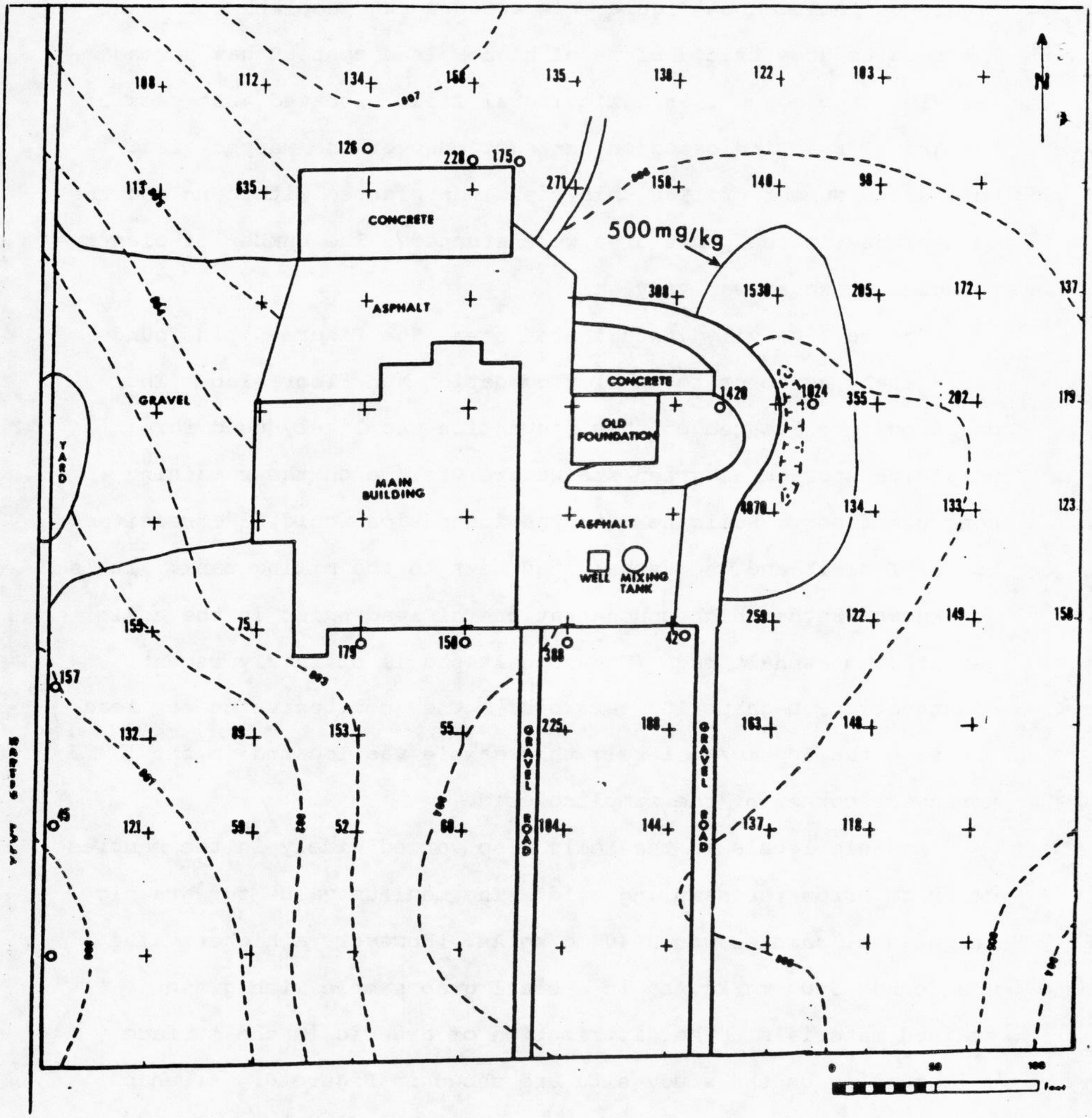


Figure 4. Distribution of Lead (mg/kg) in Surface Soil Samples. (Off grid sample locations are indicated with an "O.")

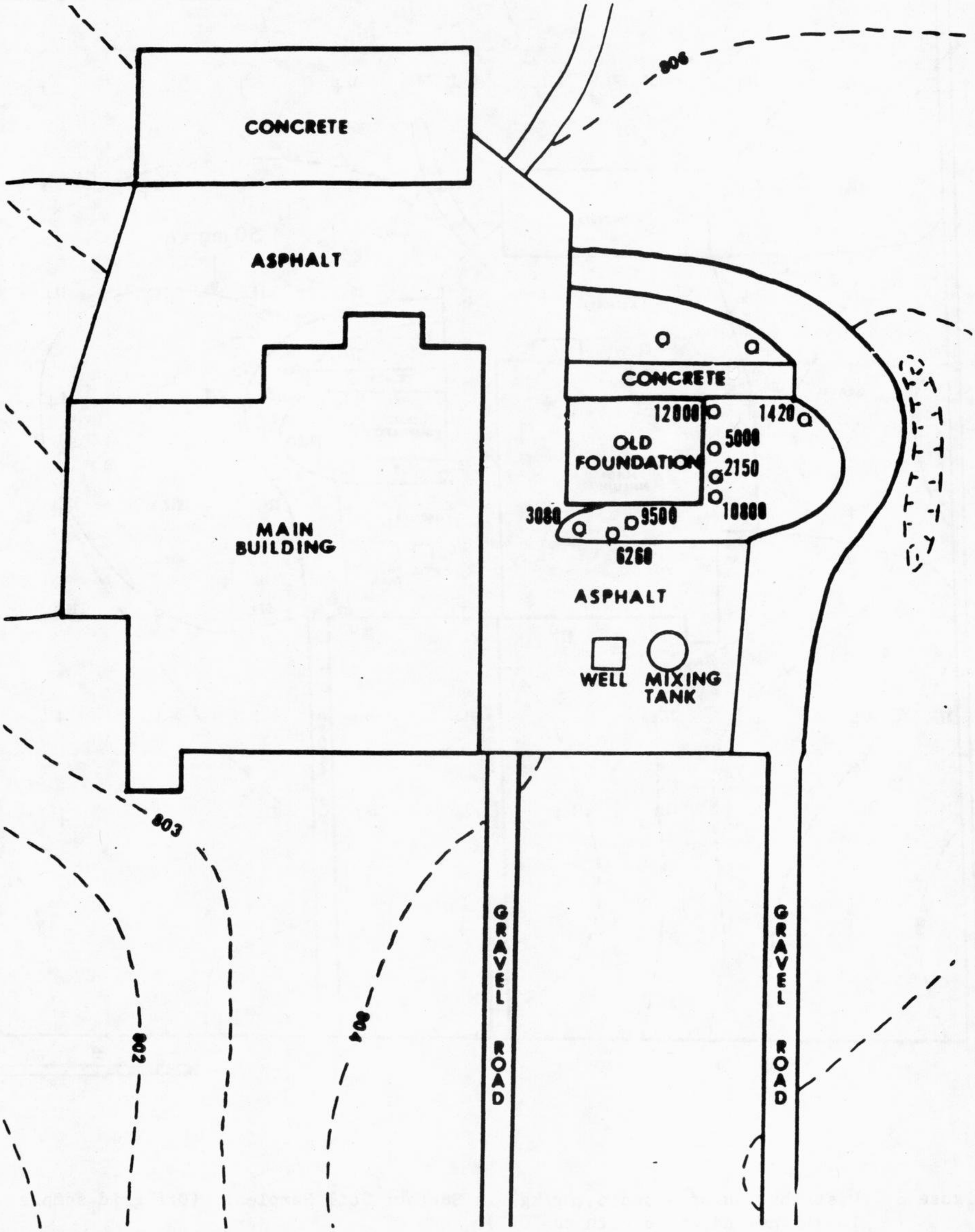


Figure 5. Lead Levels (mg/kg) in the Area of Highest Contamination.

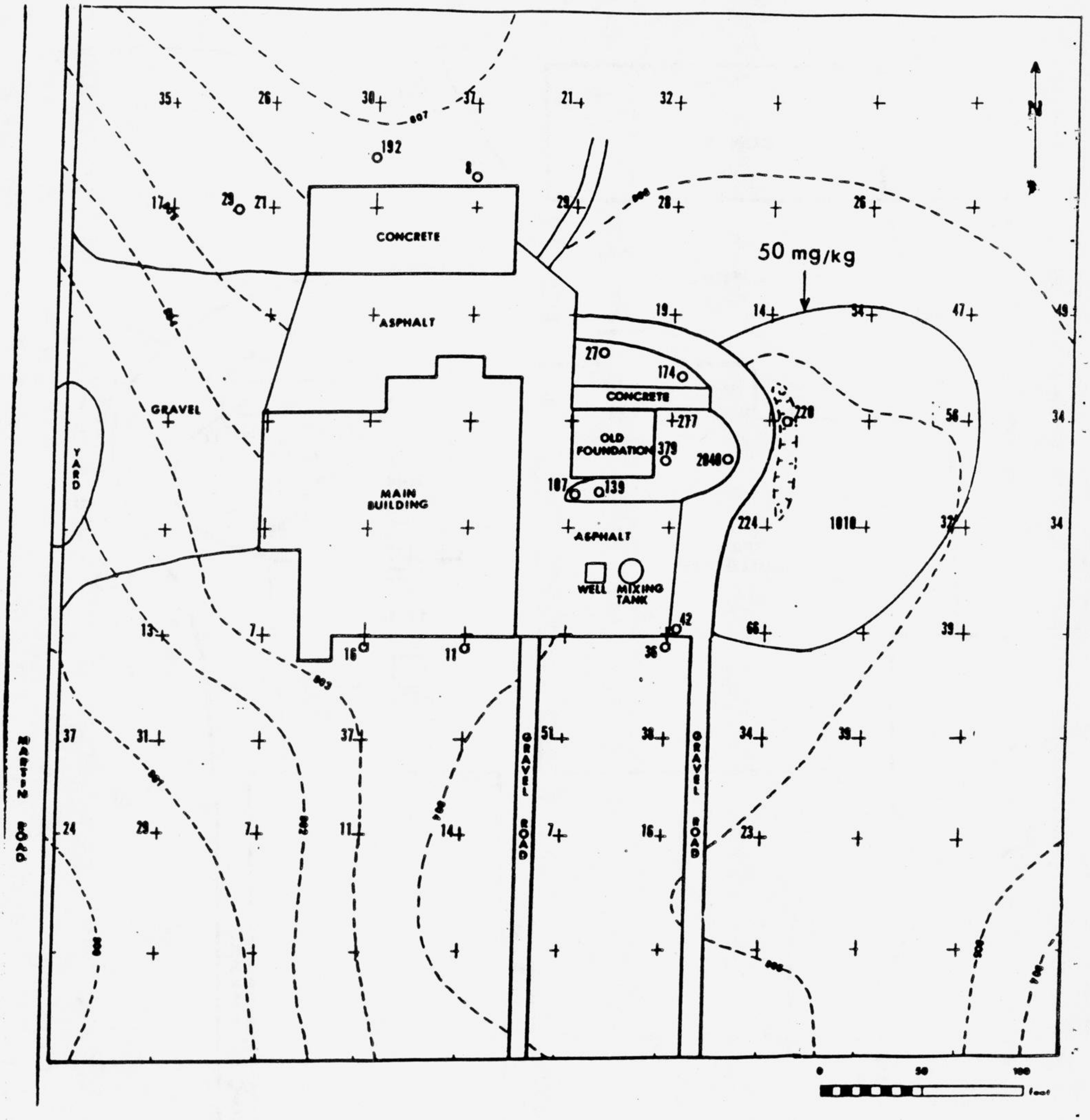


Figure 6. Distribution of Arsenic (mg/kg) in Surface Soil Samples. (Off grid sample locations indicated with an "O.")

with an average of 5 mg/kg. The distribution pattern of arsenic on the site is similar to that of lead. The estimated position of the 50 mg/kg arsenic isopleth has been placed on the map. Its position and shape is similar to the 500 mg/kg isopleth for lead. One isolated high level for arsenic, (192 mg/kg), was found north of the main building complex.

A large number of soil samples were also analyzed for copper content even though these analysis were not part of the initial proposal. Analytical methods for copper are easier than methods for lead and especially much easier than methods for arsenic. It seemed worthwhile to determine if high copper levels were indicative of high arsenic and high lead levels. If such a relationship existed, copper analysis could be used to determine if there was a potential for contamination.

The distribution of copper in surface soil samples is presented in Figure 7. The same soils that are contaminated with lead and arsenic, are also contaminated with copper. The 300 mg/kg Cu isopleth on Figure 7 approximately corresponds to the 500 and 50 mg/kg isopleths for lead and arsenic respectively. A small green-stained grab sample was found to contain 33,400 mg/kg Cu, the highest value found, while larger surface grab samples had a maximum value of 5600 mg/kg Cu. Two isolated soil samples not associated with the lead-arsenic plume showed copper levels in excess of 300 mg/kg. One sample is located immediately north of the zone of highest contamination and the other sample is located immediately adjacent to Martin Road in the southern part of the sample grid.

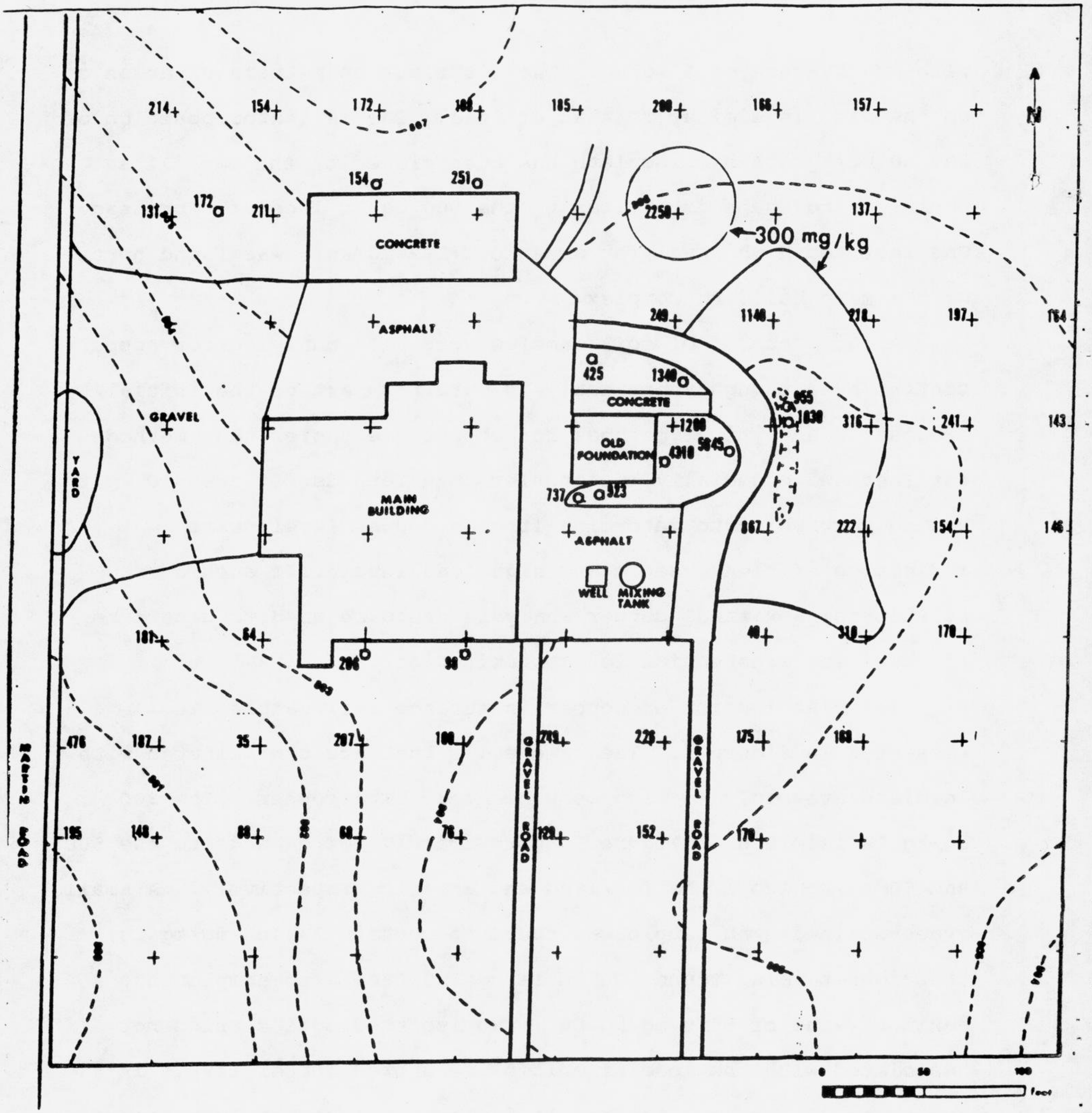


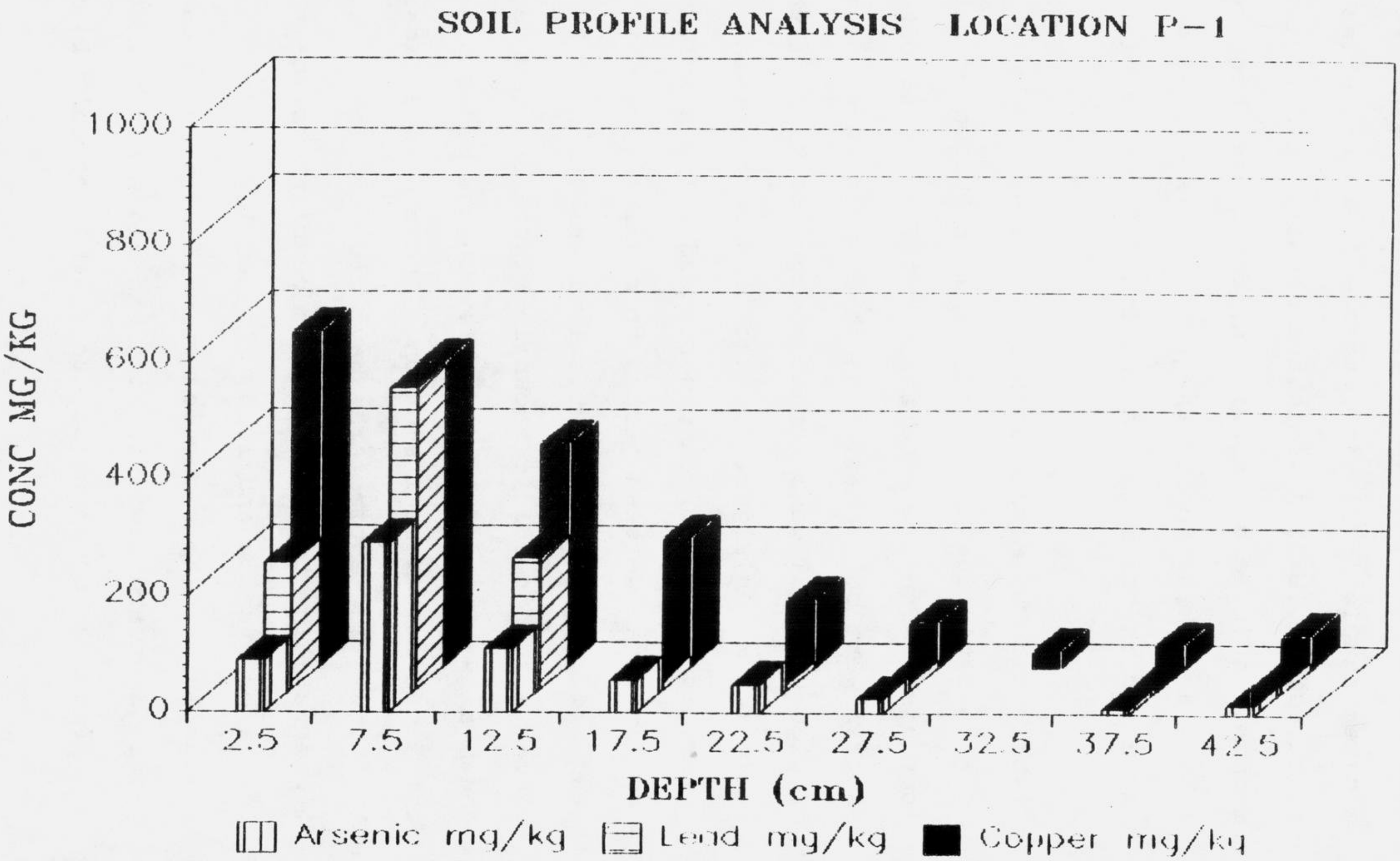
Figure 7. Distribution of Copper (mg/kg) in Surface Soil Samples. (Off grid sample locations are indicated with an "O.")

While the distribution of high lead, arsenic, and copper levels are similar, the ratios of metal concentrations are not consistent. The varying values for the ratios of metal content in a given sample likely indicates different sources (pesticide mixtures) of lead, arsenic and copper, or different distribution mechanisms (time of deposition) for these three substances. Most likely a combination of the two factors is the cause for the variation in the metal ratios found in the various soil samples.

Distribution of Metals in Soil Profiles

To determine the vertical distribution of metal contaminants in the soils on the site three small sampling pits and 13 core samples were collected. The three pits were located in the area of highest metal concentration; the location of the sampling pits is indicated on Figure 3. The pits were sampled at 5 centimeter intervals until bedrock was reached. The samples collected from each interval were subjected to chemical analysis for arsenic, lead and copper. The vertical distribution of these three elements in pit P-1 is shown in Figure 8. The depths indicated on the x-axis of this figure refer to the mid-depth measurement of the 5 centimeter soil section. These data indicate that the top 10 inches (25 centimeters) have elevated levels of all three elements. The top 6 inches (15 centimeters) have the highest levels of arsenic and lead. Copper levels decreased more gradually. In this section of soil it appears that there has been little downward migration of lead and arsenic in the soil profile.

Pit P-2 could be dug to a depth of only 10 inches (27



Missing values below detection limit

Figure 8. Vertical Distribution of Lead, Arsenic, and Copper in Sampling Pit P-1.

centimeters) before encountering bedrock. The levels of arsenic, lead and arsenic found in the soil profile at location P-2 are shown in Figure 9. It is important to note that the y-axis is not the same as that used in the previous figure, Figure 8. The soils sampled in this pit were the most highly contaminated soils found on the site. The section of soil between 5-10 centimeters was found to contain 23,200 mg/kg copper. Lead and arsenic levels were substantially lower but still at levels that indicate the soils have been contaminated. The levels of arsenic, lead, and copper found in each section of soil are given in Table 2. The bottom most sample, 25-27 cm, had higher levels of both arsenic and lead than the 10 cm of soil overlying this sample. It is possible that the dolomite directly in contact with the soil increases pH locally which in turn increases the soil's capacity to retain arsenic and lead.

Table 2. Metal Content of Soils in Pit P-2.

Depth	Metal Concentration (mg/kg)		
(cm)	As	Pb	Cu
0-5	331	1310	2630
5-10	998	2320	23200
10-15	790	2400	5960
15-20	266	1110	1100
20-25	148	455	
25-27	561	1660	382

Pit P-3 was dug to a depth of 29 inches (73 cm). Below a depth of 18 inches (45 cm) the soils sampled were removed from a

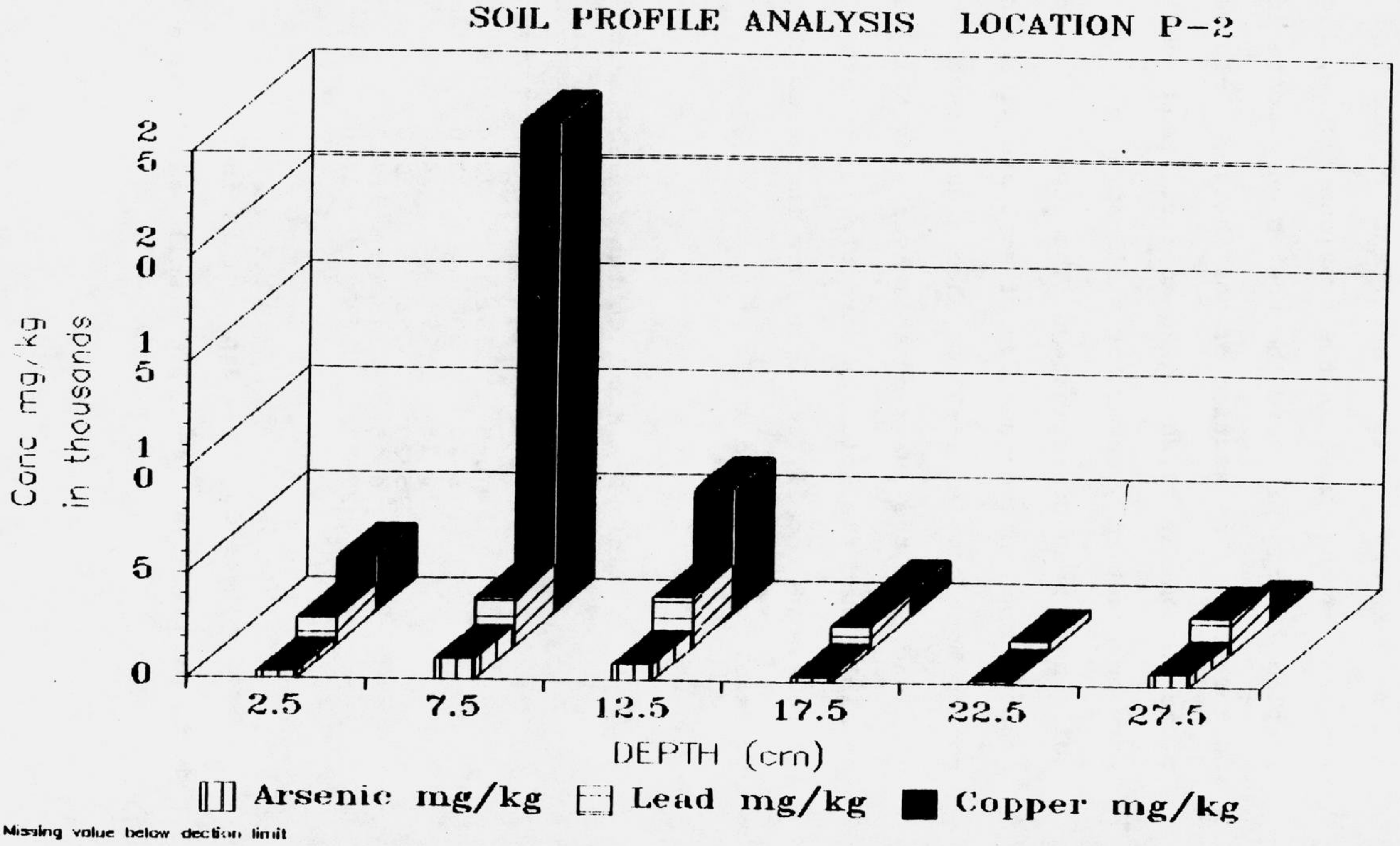


Figure 9. Vertical Distribution of Lead, Arsenic, and Copper in Sampling Pit P-2.

crevice in the bedrock. The soils were only sampled to a depth of 65 cm. The levels of arsenic, lead and copper found in the soil profile at location P-3 are shown in Figure 10. The top 20 cm of soil was found to contain elevated levels of all three metals but not nearly as high as those found in pit P-2. In the middle section, 20-45 cm, the metal levels were essentially at background levels. The soil removed from the crevice, however, showed higher levels of copper as indicated in Figure 10. Arsenic and lead levels in soils removed from the crevice showed slight increases in concentration compared to soils that overlie the crevice. It is expected that water infiltrating through the soils would move directly through the soils in the crevice. Both the increased amount of water flowing through a crevice and the close proximity of the bedrock may cause features such as crevices to be sites of accumulation of metals. There appears to be only minimal downward migration of the metal contaminants in pit P-3 as was the case for Pit P-1. The soil in pit P-2 was to shallow to make an interpretation if metal ions were migrating downward.

To further elucidate the vertical distribution of metal contaminants in the soils on the study site, selected sections of core samples were analyzed. The location of the core sampling points is shown in Figure 3. Sixteen 5 cm core sections from 6 different cores were subjected to chemical analysis for arsenic and lead. The cores analyzed were C-1, C-3, C-6, C-10, C-12, and C-13. The core sections selected for analysis were primarily from samples within the plume of contamination with the exception of C-12. The results of these analysis are shown in Figures 11 to 16.

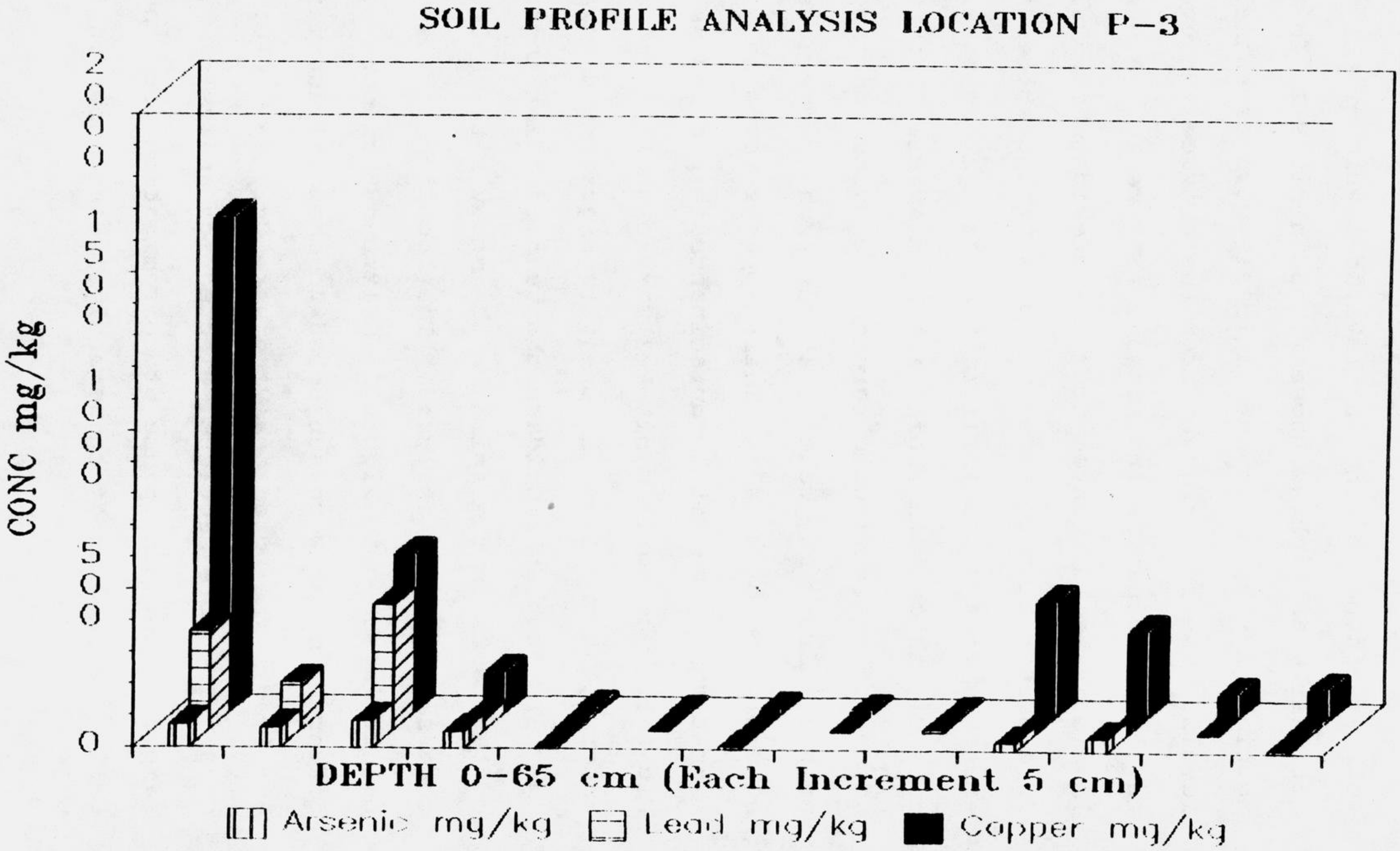


Figure 10. Vertical Distribution of Lead, Arsenic, and Copper in Sampling Pit P-3.

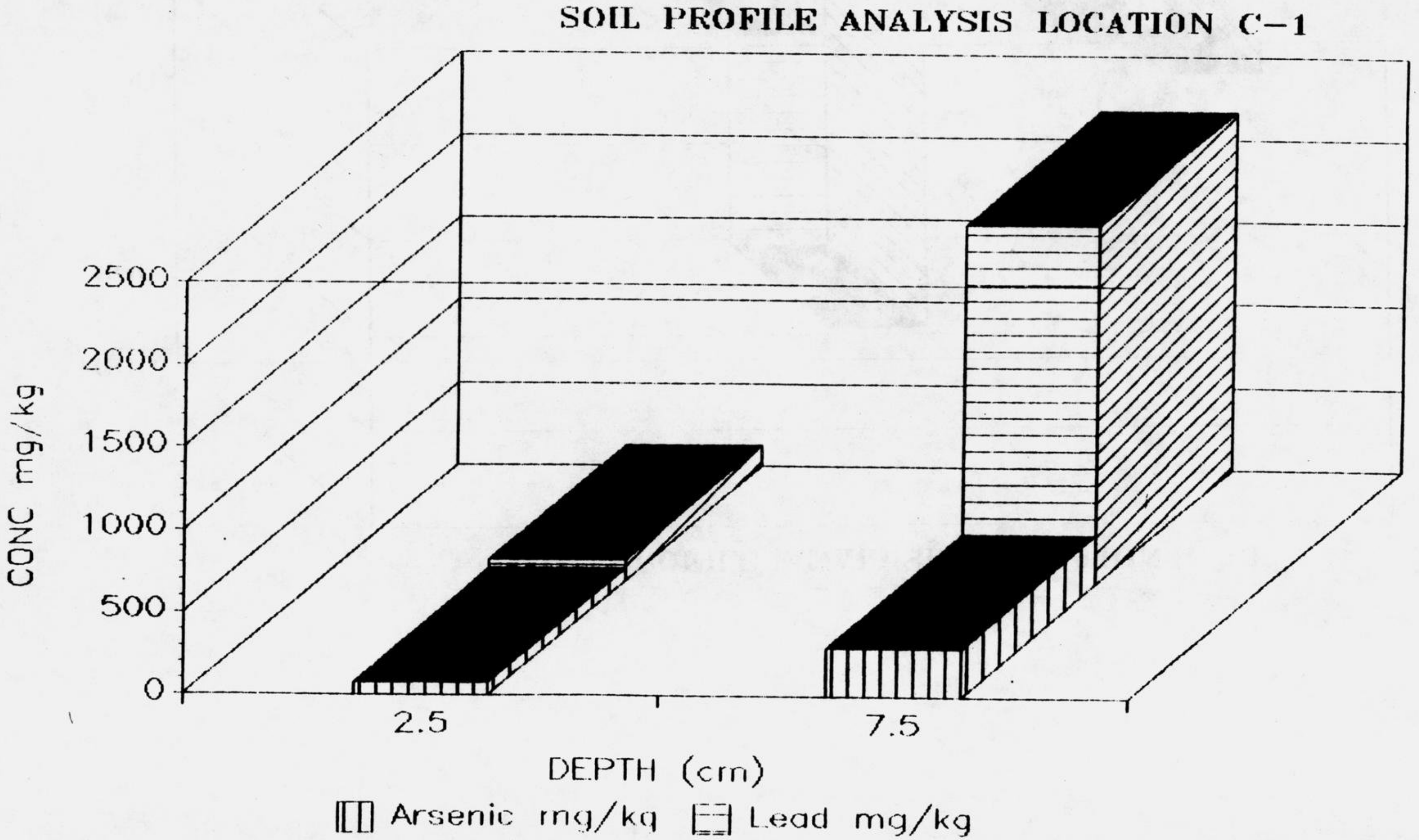
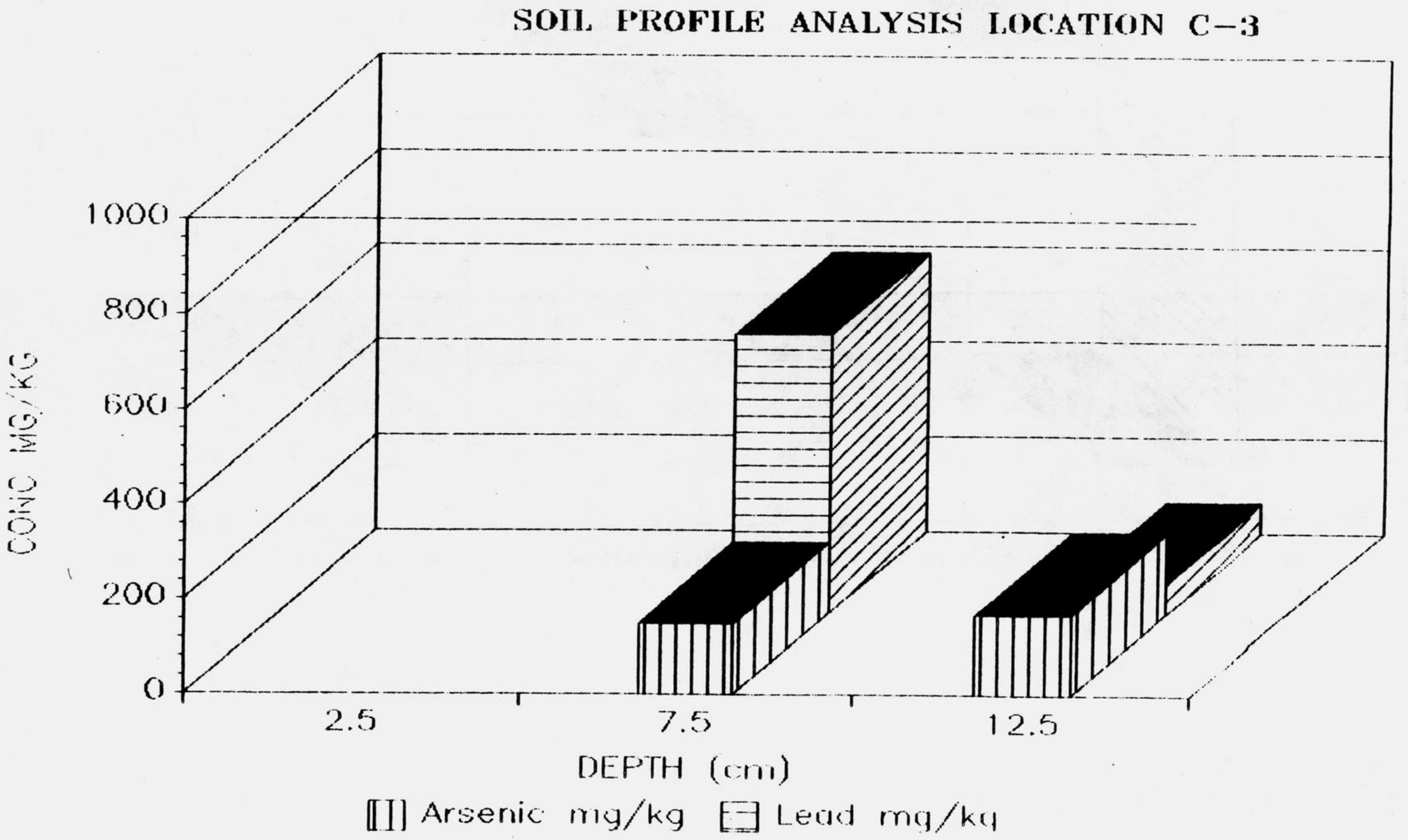


Figure 11. Vertical Distribution of Metals in Core C-1.



No Data for First Section

Figure 12. Vertical Distribution of Metals in Core C-3.

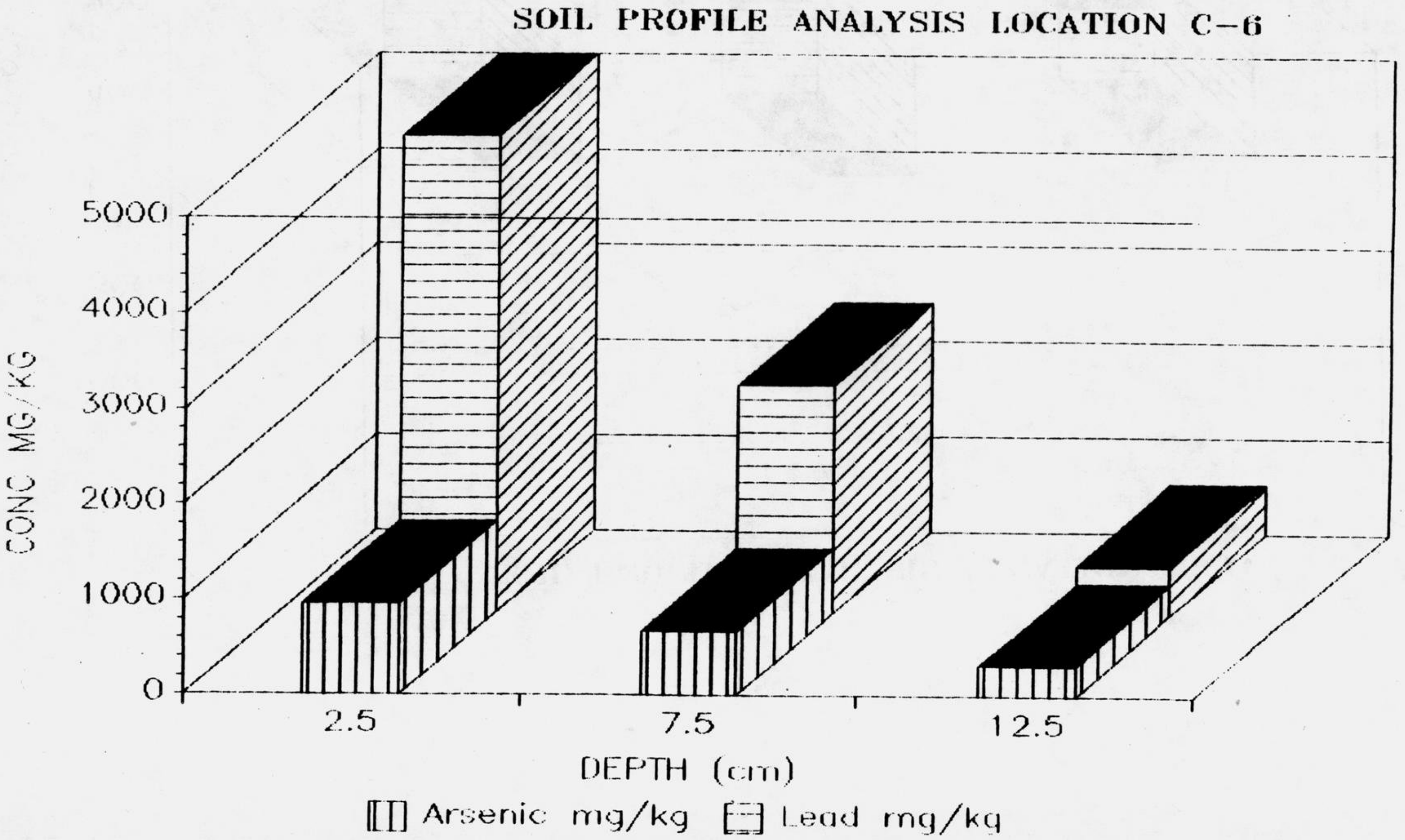


Figure 13. Vertical Distribution of Metals in Core C-6.

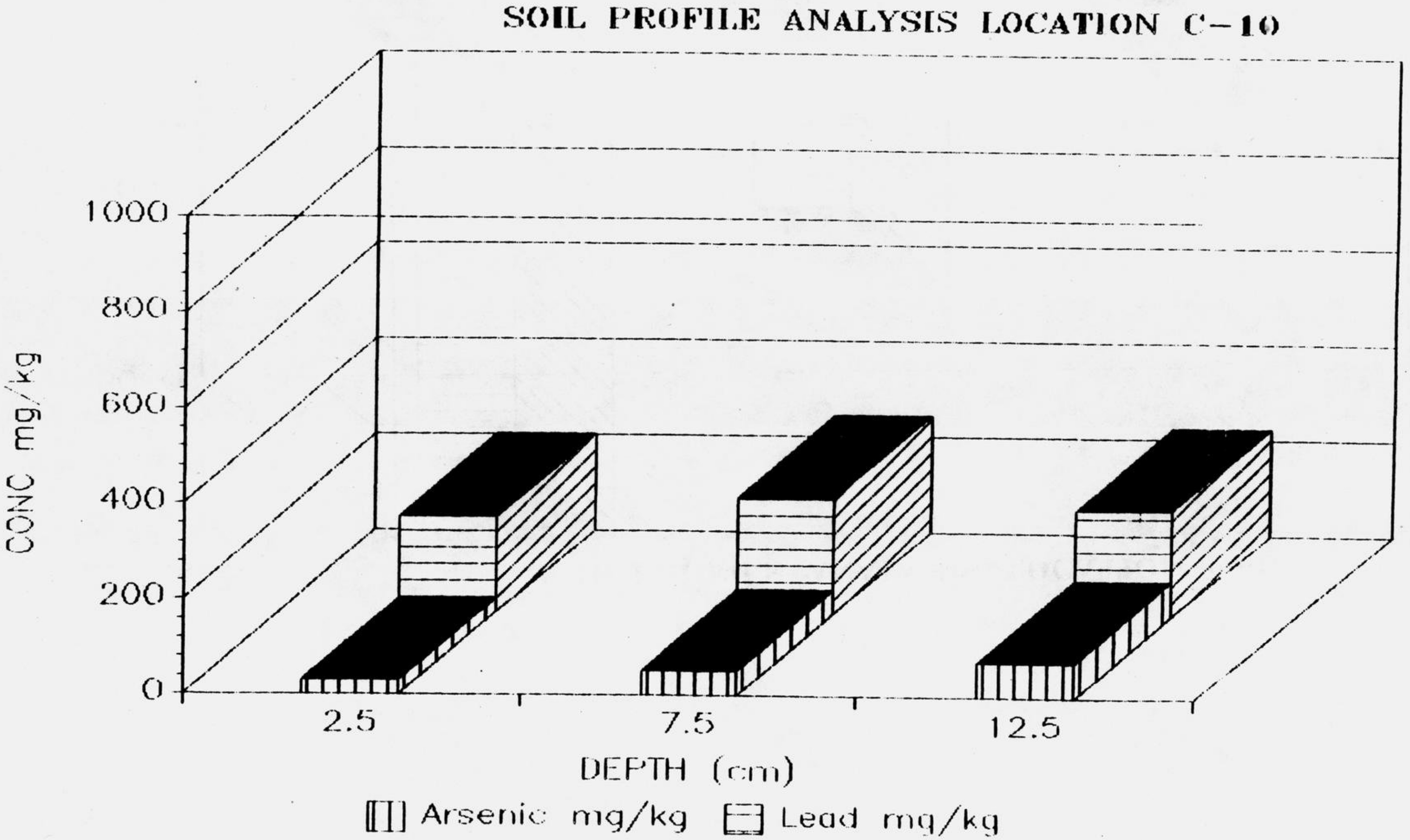


Figure 14. Vertical Distribution of Metals in Core C-10.

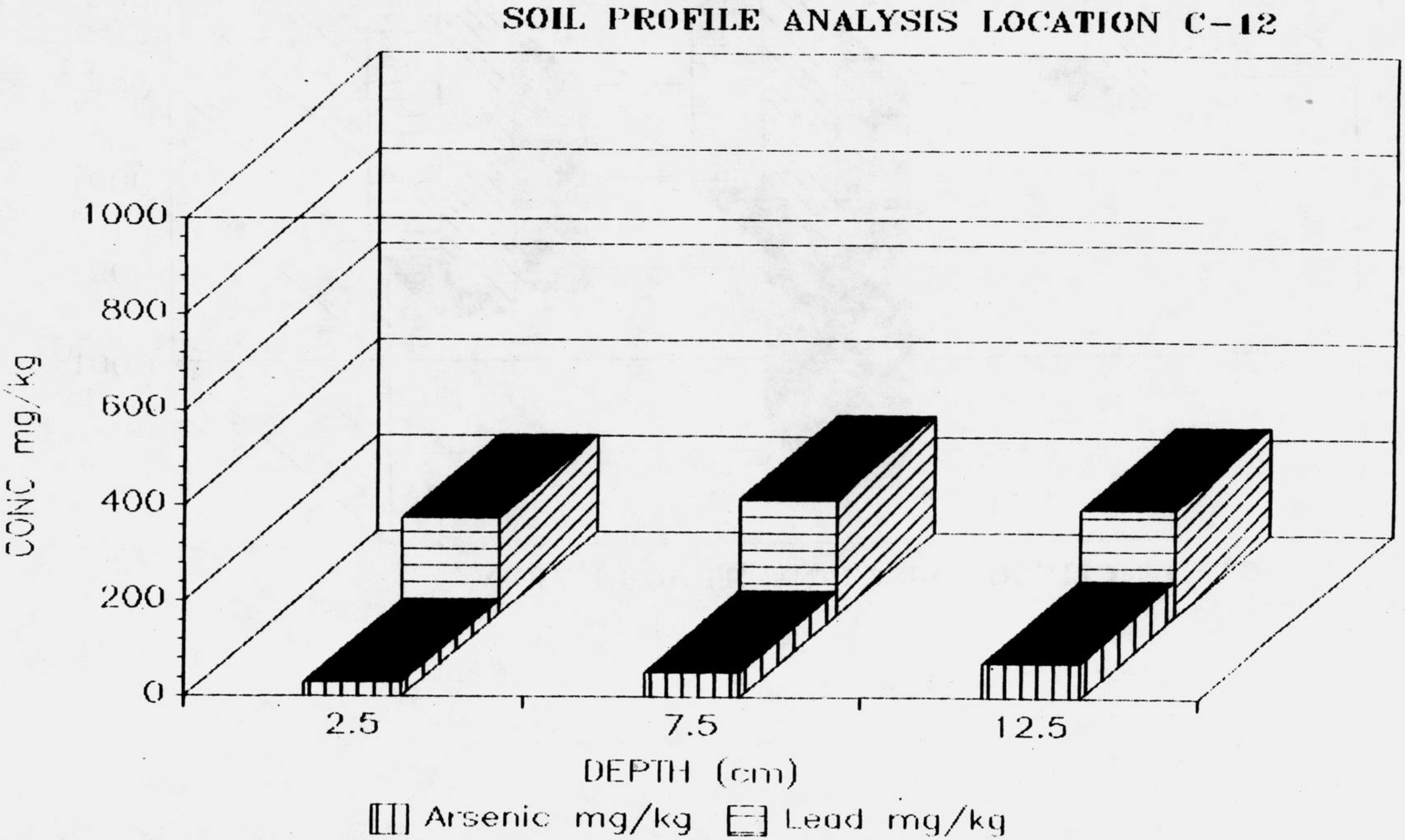


Figure 15. Vertical Distribution of Metals in Core C-12.

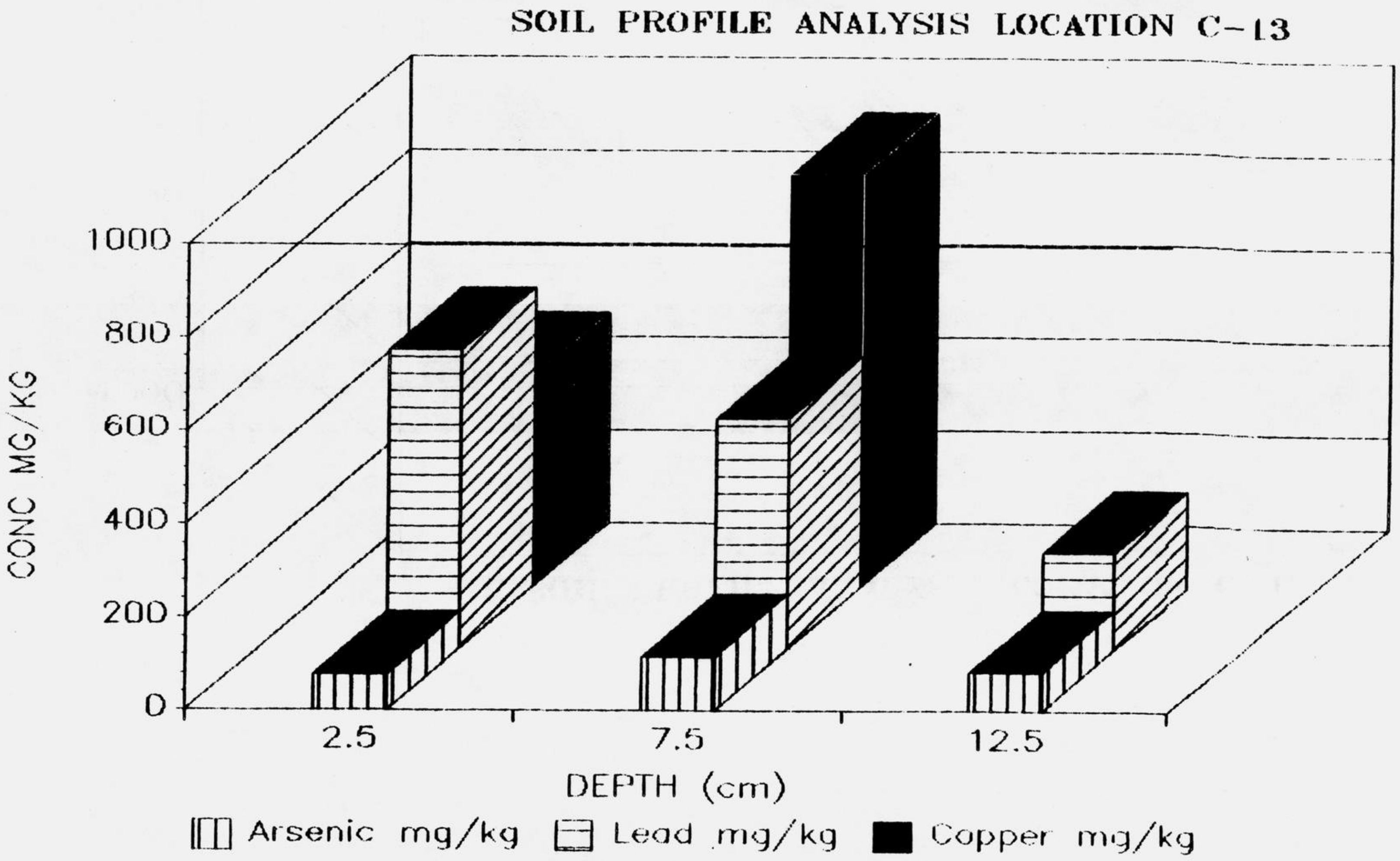


Figure 16. Vertical Distribution of Metals in Core C-13.

The maximum concentration of lead found in any of the core sections was 5000 mg/kg , the maximum concentration of arsenic found was 963 mg/kg. Both maximum values were from the same section of core C-6. Cores C-3, C-6, and C-13 display the trend observed in the pits; the concentration of metal contaminants decreases as on proceeds deeper into the soil column. Cores C-10 and C-12 are nearly identical. Also the levels of arsenic and lead are nearly identical in all six sections of these two cores. Core C-10 was collected from a tilled field therefore one would expect to find a nearly uniform distribution of metals in the soils. Core C-12 was outside of the general plume area but in a heavily vegetated area. It is possible that at one time the soils at this location were also tilled or disturbed even though at present they are untilled.

The vertical distribution of metals in the three pit samples and the cores indicates that the metal contamination is restricted to the upper soil layers. Considering the fact that these materials have been out in the open environment for at least two to three decades, relatively little downward migration of lead and arsenic has occurred. Veneman, 1983, and Hess and Blancar, 1977, both have made similar observations in their studies of contaminated orchard soils.

Removal of the upper 20 to 25 cm of soil would result in fairly safe levels of lead and arsenic in the soils left behind. Burial of contaminated soils at a single location between layers of clay should effectively contain these materials. A single burial location would greatly reduce the effort required to monitor the environment for future problems around the burial site. When removing contaminated soil, care must be taken not to disturb the soils overlying creviced areas. Such disturbances could result in a more direct route for contaminants to enter the groundwater system.

Relationship of Soil Particle Size and Lead Content

A study of the levels of lead associated with various soil particle sizes was also completed. Four soil samples collected from two pits sampling locations were selected for analysis. Three samples were from the top three 5 cm sections of pit location P-4 which was located in the narrow strip of open soil between the "Old Foundation" and the asphalt pad (See Figure 3 for location). The fourth sample came from the 5-10 cm level of pit P-1. The samples were dry sieved, acid digested as previously described, and the level of lead in each size fraction determined. The results of the analysis are presented in Table 3.

Table 3. Concentration of Lead (mg/kg) in Soil Size Fractions

Sample/Mesh Size	<230	>230	>40	>10
P-4 0-5 cm	1410	1660	3240	255
P-4 5-10 cm	52	35	31	20
P-4 10-15 cm	124	46	195	21
P-1 5-10 cm	2910	2160	1040	368

Only two of the four samples selected for analysis had significant levels of lead. The two samples with elevated lead levels showed opposite trends; sample P-4 0-5 cm showed increasing levels of lead as the size increased except for the largest fraction (mesh size >10). Sample P-1 5-10 cm, showed a decrease in lead concentration as the size of the soil particles increased. Smaller sized particles composed most of the soil sample. The conclusion to be drawn from this limited study is that since a significant amount of contaminant is associated with the fine grained soil particles, efforts should be made to prevent erosion from contaminated sites because fine grained materials are the most easily eroded and can be transported greater distances by moving water or wind.

Desorption/Sorption Studies

Experiments were conducted to determine the relative mobility of lead. The first experiments assessed the ability of lead to move from the solid (soil) phase to an aqueous phase. Six different soil samples with lead content varying from 313 mg/kg to 19,000 mg/kg were used to indicate the ability of lead to enter the aqueous phase.

The procedure used was to mix approximately 20 grams of soil with 400 ml of ultra pure distilled water. The slurry was mixed on a Phipps Bird stirring apparatus for 24 hours at room temperature. After 24 hours the samples were filtered with glass fiber filter and the filtrate acidified with ultra-pure nitric acid. The filtrates were then analyzed for their lead content. The pH of the slurry was also measured through the course of the experiment. The results of the soil lead extraction studies are presented in Table 4.

Table 4. Desorption of Lead Contaminated Soils into Distilled Water.

Sample	Wt (g)	Soil Pb ug/kg	Aqueous Pb ug/l	pH-0.5hr	pH-2hr	pH-24hr
P-3 0-5 cm	19.95	313	23	6.3	7.2	7.7
P-2 15-20 cm	21.99	1030	500	6.1	7.1	7.9
P-2 5-10 cm	20.88	2960	1100	5.9	7.5	7.6
Grid 45,59	20.45	10950	1200	8.1	8.0	8.1
P-2 (10)*	19.00	18900	2500	7.5	7.7	7.9
P-2 (RND)*	20.79	19600	4500	7.0	8.0	8.0

*These two samples were selected parts of samples with especially elevated levels of lead.

The results in Table 4 indicate that lead can move from the soil medium to the aqueous medium with relative ease under conditions of vigorous stirring. The data also indicate that the concentration of lead in the extract medium (distilled water) depends on the amount of lead in the soil. The range of concentrations in the aqueous extract medium ranged from 23 to 4500 ug/kg Pb. All but one of the aqueous sample extracts contained lead concentrations above the 50 ug/l drinking water standard.

RMT 1987, also studied the leachability of contaminated soils collected from other Door County pesticide mixing sites. They developed two predictive equations that relate the concentration of lead in the aqueous phase to the concentration of lead in the soil matrix. Their first equation is based on the extraction of lead from soils into distilled water. The predictive equation found was:

$$\text{Log Aqueous Pb (ug/l)} = 1.47\text{Log Pb Matrix Conc (mg/kg)} - 1.89$$

When the data was combined with Extraction Procedure (EP Toxicity Test) data, the equation changed only slightly to:

$$\text{Log Aqueous Pb (ug/l)} = 1.44\text{Log Pb Matrix Conc (mg/kg)} - 1.72$$

Subjecting the data in Table 4 to the same type of analysis, the predictive equation soluble lead concentration for the data in Table 4 is:

$$\text{Log Aqueous Pb (ug/l)} = 1.01\text{Log Pb Matrix Conc (mg/kg)} - 0.76$$

The slope of the line in this equation for the data in Table 4 is 2.5 times less than the slope reported in the RMT study. There are several possible reasons for the difference. First, soil samples used for extraction studies were different. A difference in the amount of clay could easily account for such a change in ease of extraction. Second, the extraction conditions used for studies in this report were not as vigorous as those used in the RMT report. Third, the final ionic strength and or the pH of the extraction solutions were significantly different because of the nature of the soil sample. The pH of RMT data was either 5 or unreported. They do state that pH values between 5 to 8 had little effect on the final concentration of lead in the aqueous phase. The affect of pH on extractability of lead deserves more study as the number of samples actually studied is too limited. In either case, both studies indicate that lead is leachable from contaminated soils and thus water moving from sites of contamination and thus could find its way into groundwater.

The final pH of the aqueous extracts of the six soils were all alkaline and ranged from pH 7.6 to 8.1. Three of the initial (0.5 hour) pH values were in the acidic range; however, after 2 hours the pH of these samples was either neutral or in the alkaline range. All in all, the pH values determined for these soil extracts would indicate that these soils are quite alkaline. Most soils have a pH between 4 to 8. The alkaline nature of these soils should decrease the mobility of lead from soils compared to soils that are more acidic. Thus, as a management strategy, it is important to take measures which would prevent the soils from becoming more acidic. Soils in the acidic range could be made more alkaline through the addition of lime to reduce the rate of lead migration.

The sorptive capacity of the dolomitic aquifer materials for lead was also investigated. Because well water at some locations in Door County has been found to have elevated levels of lead (Stoll 1988), the capacity of aquifer materials to remove lead from solution was investigated. Six contaminated soils were extracted with distilled water for 24 hours to produce an aqueous extract with elevated levels of lead. After the 24 hour extraction period, the soil extracts were filtered through glass fiber mats. The lead levels in the extracts were determined. Approximately 150 ml of the filtrate was mixed with dolomite cuttings from the 190 to 260 foot levels of monitoring Well 2 drilled on the site. (Details concerning the construction of this well are found in Appendix II.) Only cuttings greater than 200 mesh were included in the sorption experiment. The extraction mixture was held at room temperature and sampled after 1 day and 2 days. The pH was also measured over the course of the equilibration experiment. The results for the analysis of lead in the original soils, extracts and the supernatant in contact with the dolomite cuttings are found in Table 5.

Table 5. Sorption of Lead onto Dolomite Cuttings from Aqueous Solution.

Sample	Soil Conc ug/kg Pb	Extract Conc ug/l Pb	Supernate (Day 1) ug/l Pb	Supernate (Day 2) ug/l Pb	pH (Day 2) units
P-3 0-5 cm	313	23	5	BLD	8.1
P-2 15-20 cm	1030	500	32	BLD	7.8
P-2 5-10 cm	2960	1100	9	3	8.1
Grid 45,59	10950	1200	6	BLD	8.0
P-2 (10)*	18900	2500	12	5	8.2
P-2 (RND)*	19600	4500	20	7	8.2

*These two samples were selected parts of samples with especially elevated levels of lead.
BLD = Below Detection Limit of 3 ug/l Pb.

The results of the sorption experiment show that fresh dolomite surfaces are capable of reducing lead levels in contaminated water relatively quickly and to levels below 10 ug/l

Pb even when the initial concentration was as high as 4500 ug/l Pb. The importance of this result is that for well contamination by lead to occur, a direct route for the contaminated water to the point of water removal must exist. As contact time increases, the levels of lead would be expected to decrease significantly. The contact area/volume ratio for water moving through both the zone of aeration and the saturated zone is also important. Small volumes of contaminated water moving through small pores or crevices would have much more contact with the dolomite than would large volumes of water moving through large openings. Finally, in actuality dolomite aquifer materials are frequently coated with iron (III) hydroxides. The surface of iron hydroxides are also know to be good sites for the absorption of metal ions such as lead (II) and thus they should provide an additional mechanism for lead removal. Clays in crevices or bedding planes should also aid in removal of lead. In karstic regions such as Door County, the route traveled by contaminated water may be by conduit flow, especially during periods of rapid recharge. If contaminated water flows frequently through a conduit, it may become saturated with metal ions. In this case, the surfaces of the conduit would loose their capacity to remove the lead from contaminated water flowing through such conduits.

V. Groundwater Monitoring Studies

Well Construction

Because a region with high levels of lead and arsenic was known to be present on the study site, the potential for groundwater contamination in the immediate vicinity of the site was thought to be a possibility. To determine if the groundwater was being contaminated, three monitoring wells were proposed for the site. The specific location of the monitoring wells were decided upon consultation with the landowner, Larry Sahs, President of Door County Fruit Growers, Inc., and Dr. Kenneth Bradbury of the Wisconsin Geological Natural History and Survey. The locations of the three groundwater monitoring wells are given in Figure 17. Wells 1 and 2 were intended to be monitoring wells located down the hydraulic gradient, whereas, Well 3 was designed to be an upgradient monitoring well.

The three monitoring wells were constructed under a subcontract to a licensed well driller, Bill Van De Yacht of Green Bay. Descriptions of the three well installations are given in Appendix II.

The cuttings from well 2 were examined and described in detail. The detailed description of the materials removed from well 2 are also found in Appendix II.

Well Monitoring--Lead Levels

All three monitoring wells were sampled over the course of approximately one year. The sampling frequency varied during the year. An intensive well-water monitoring effort was made during

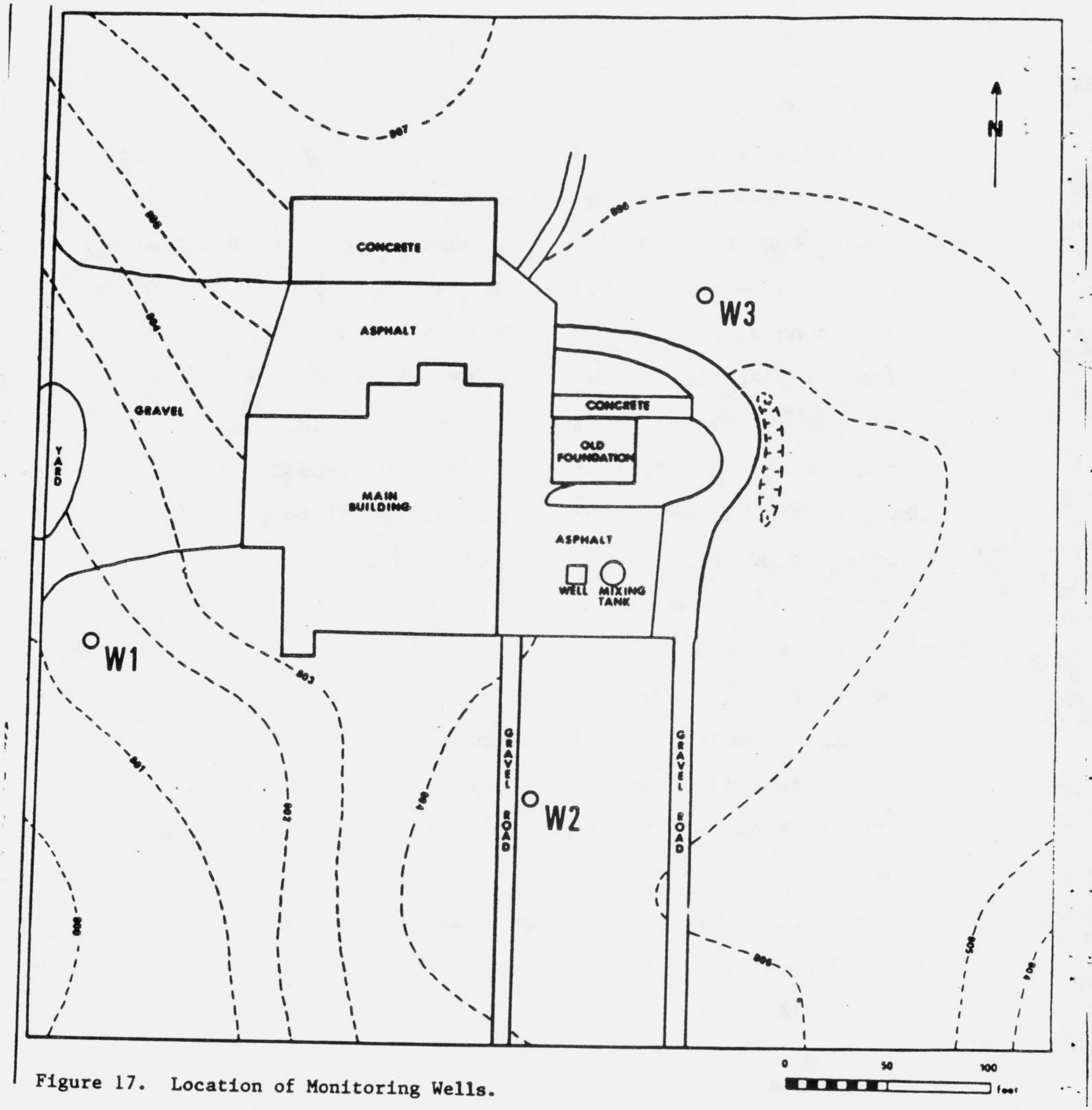


Figure 17. Location of Monitoring Wells.

the early to mid-spring of 1988. This is normally the time of maximum infiltration and thus would be the period mostly likely for lead contamination to occur if it was going to occur. Stoll 1988, in his investigations of lead contamination in well samples from Door County had found the highest levels and rates of contamination during the spring months.

The monitoring wells were sampled on 21 different dates. The sampling dates concentrated on the "wetter" times of the year, namely, the spring and fall. Sampling was discontinued during the winter months when the ground was frozen.

Lead concentrations were determined in addition to the measurement of some basic water chemistry measurements on the monitoring well water samples. Analysis included: pH, specific conductance, chloride, and nitrate. Lead, nitrate and chloride were determined in the laboratory while pH and specific conductance were determined immediately in the field. Depth to water table measurements were also made during most of the sampling collection trips.

All samples were collected with a plastic bailer. The bailer was rinsed with distilled water three times in the field prior to being lowered into the well. Stainless steel cable on a hand-operated winch assembly was used to lower the sampler into the well. In every case, the first sample collected from a given well in a bailer was discarded.

The second sample removed from an individual well was first used to rinse a new 30 ml plastic sample bottle before filling it for subsequent lead analysis. Initially, the samples for lead analysis were split into two separate samples. One water sample for lead analysis was first filtered through glass fiber mats and then acidified with ultra-pure concentrated nitric acid. The filtrate was then analyzed for lead levels at a later date. A second water sample for lead analysis was simply acidified with concentrated ultra-pure nitric acid and stored until lead analysis was completed. The amount of nitric acid used was sufficient to bring the sample below pH 2. Since lead levels were below the detection limit for most samples in the early stages of the investigation, samples collected later in the investigation for lead analysis were simply acidified without filtering. Only the results of unfiltered samples are reported in this report.

When sampling each well a 500 ml plastic bottle was also filled with well water and used as a source of sample for field measurement of pH and specific conductance. The unused portion of this sample was transported to the laboratory, stored at 4 degrees Celsius and latter analyzed for chloride and nitrate. After sampling a well, the bailer was rinsed three times with distilled water just prior to being lowered the next well.

Lead analysis on the acidified, unfiltered water samples were performed at Robert E. Lee Labs, Green Bay, WI. This laboratory is certified by the State of Wisconsin. Standards were prepared at Robert E. Lee Labs using commercially available standards. Calibration curves were run prior to sample analysis and at the end of an analytical run. In addition, every tenth sample was a lead standard. The detection limit for the procedure was calculated to be 2.0 ug Pb/l.

The results of the lead analysis in the monitoring wells are presented in Table 6. Of the 63 samples analyzed for lead, six samples were found to contain lead at the detection limit or above the detection limit. The six samples that had measurable levels of lead were in Well 1 and Well 2. Each well had three samples with measurable lead levels. Well 3 had no samples with detectable lead levels. The levels of lead measurable were significantly below the drinking water standard of 50 ug Pb/l. No pattern for detection of lead was discernible over time. In every case if Well 1 had a detectable level of lead, levels of lead in Well 2 were below the detection limit and vice versa.

Table 6. Results of Lead Analysis from Monitoring Well Samples

(All values reported in ug Pb/l)

Sample Date	Well 1	Well 2	Well 3
8-21-87	BLD	BLD	BLD
9-2-87	BLD	BLD	BLD
9-10-87	BLD	BLD	BLD
9-14-87	2.0	BLD	BLD
9-17-87	BLD	BLD	BLD
9-22-87	BLD	BLD	BLD
9-25-87	BLD	BLD	BLD
9-28-87	BLD	BLD	BLD
10-1-87	N S	BLD	BLD
10-7-87	2.2	BLD	BLD
3-25-88	2.0	BLD	BLD
3-30-88	BLD	6.5	BLD
4-1-88	BLD	BLD	BLD
4-5-88	BLD	BLD	BLD
4-13-88	BLD	3.2	BLD
4-17-88	BLD	BLD	BLD
4-19-88	BLD	BLD	BLD
4-24-88	BLD	BLD	BLD
4-28-88	BLD	BLD	BLD
5-3-88	BLD	2.0	BLD

BLD = Below Detection Limit of 2.0 ug/l
N S = No Sample

Well Monitoring--Water Levels

The distance from the top of the casing of each monitoring well to the water table was measured during each sampling trip. For Well 1 it often was difficult to make a measurement because water was flowing into the well from just below the lower end of the casing. The noise created by the cascading water was sufficient to make it impossible to hear when the end of a plumb line touched the water table surface. Because of these complications, a wood weight which would float, was used at the terminal end of the plumb line to determine the distance to the water table. During some trips it was possible to estimate the relative position of the water table for Well 1 using this device. Measurement of the distance from the top of the well casing to water table surface presented no special problems for Wells 2 and 3. Figures 18, 19 and 20 give the measured distances to the water table for Wells 1, 2, and 3 respectively. Well 3 was only drilled to 61 feet but still contained water throughout the study period.

Measurements of the relative water table position over time indicate that the groundwater is in a continual state of flux. During periods of rain fall or snow melt, rapid infiltration takes place and the elevation of the water table increases significantly. In fact the relative elevations in Well 1 varied by 59.4 ft, Well 2 by 61.4 ft, and Well 3 by 9.1 ft over the study period. The water table reached its lowest level in Wells 1 and 2

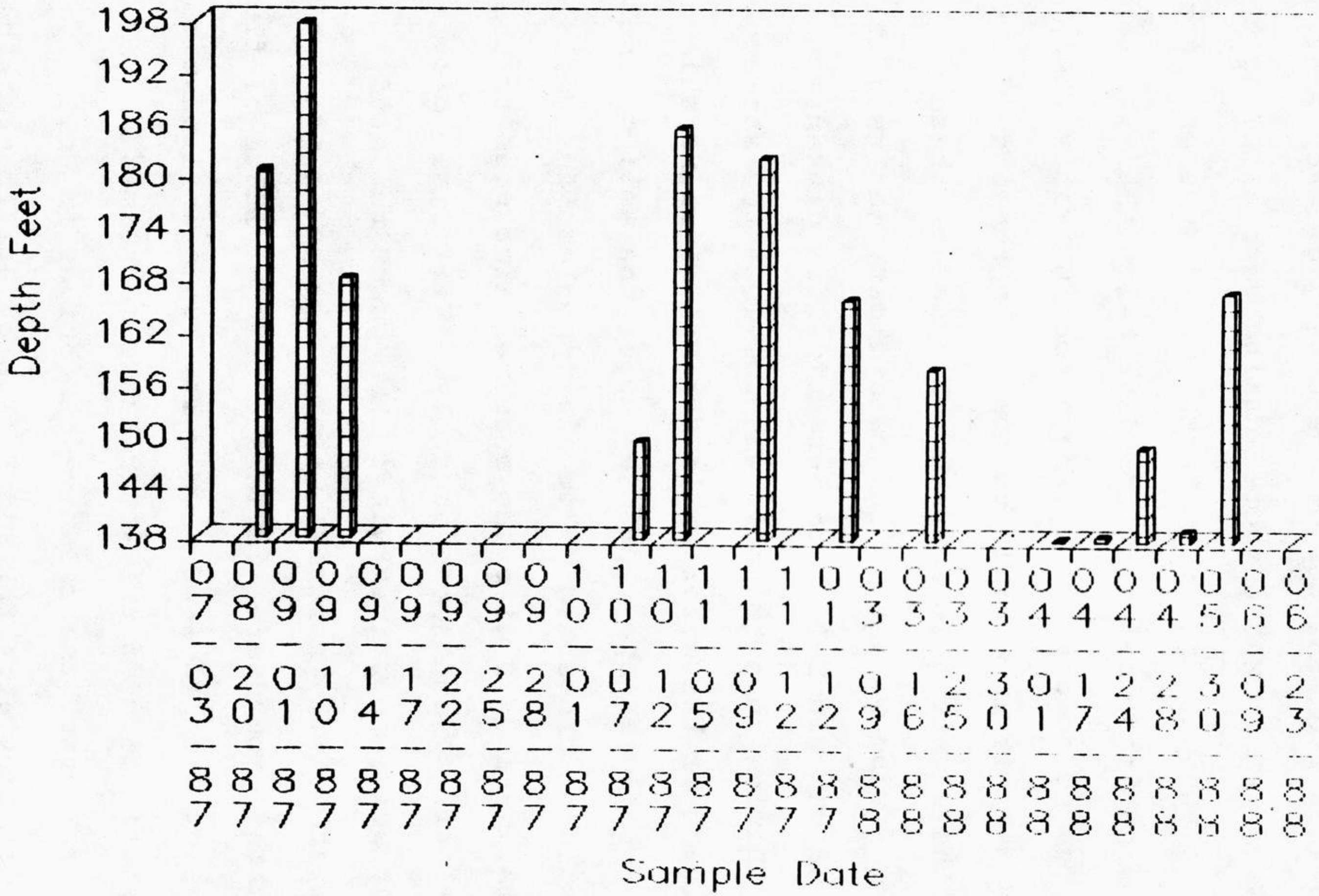


Figure 18. Depth to Water Table for Monitoring Well W1.

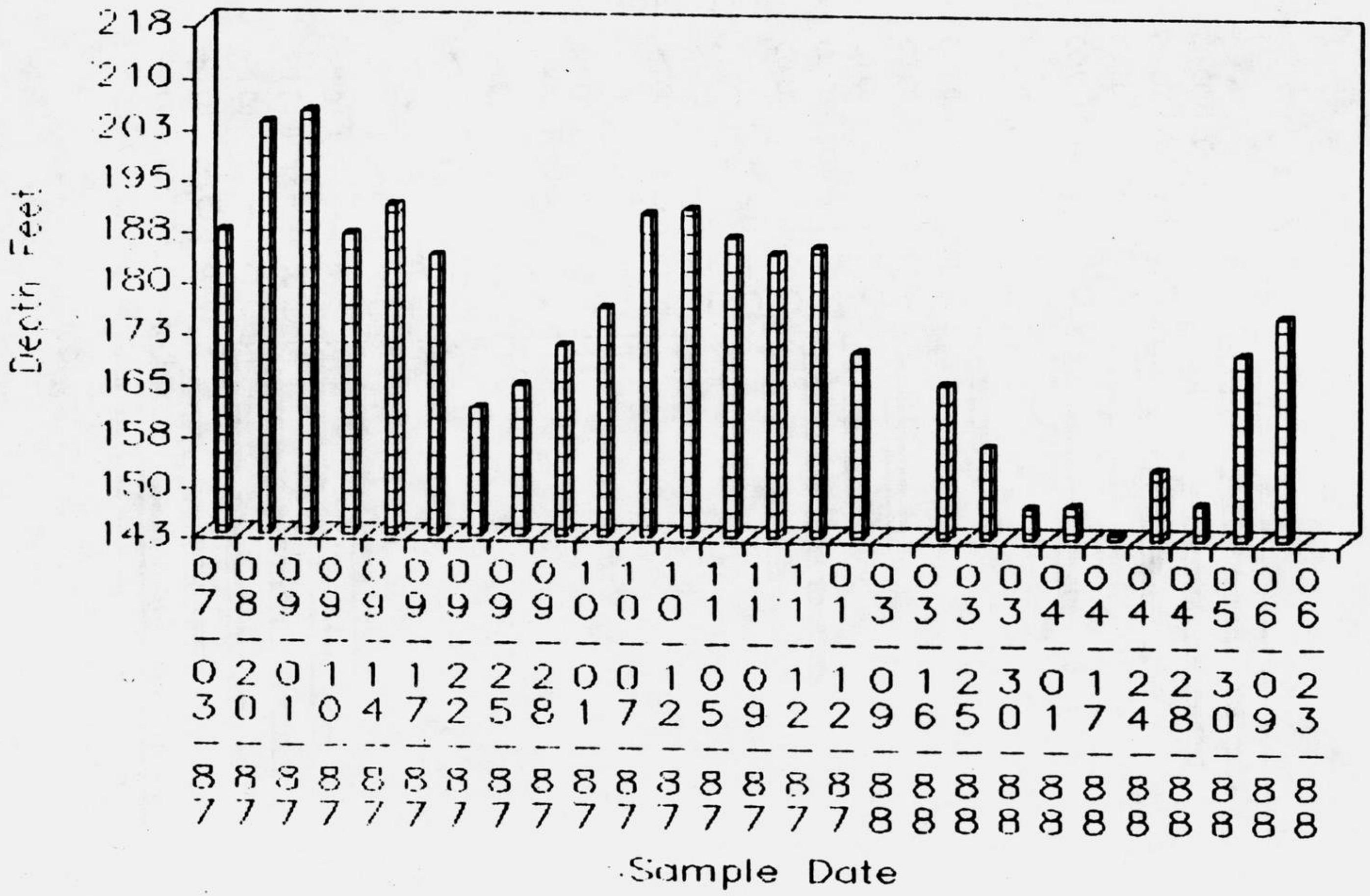


Figure 19. Depth to Water Table for Monitoring Well W2.

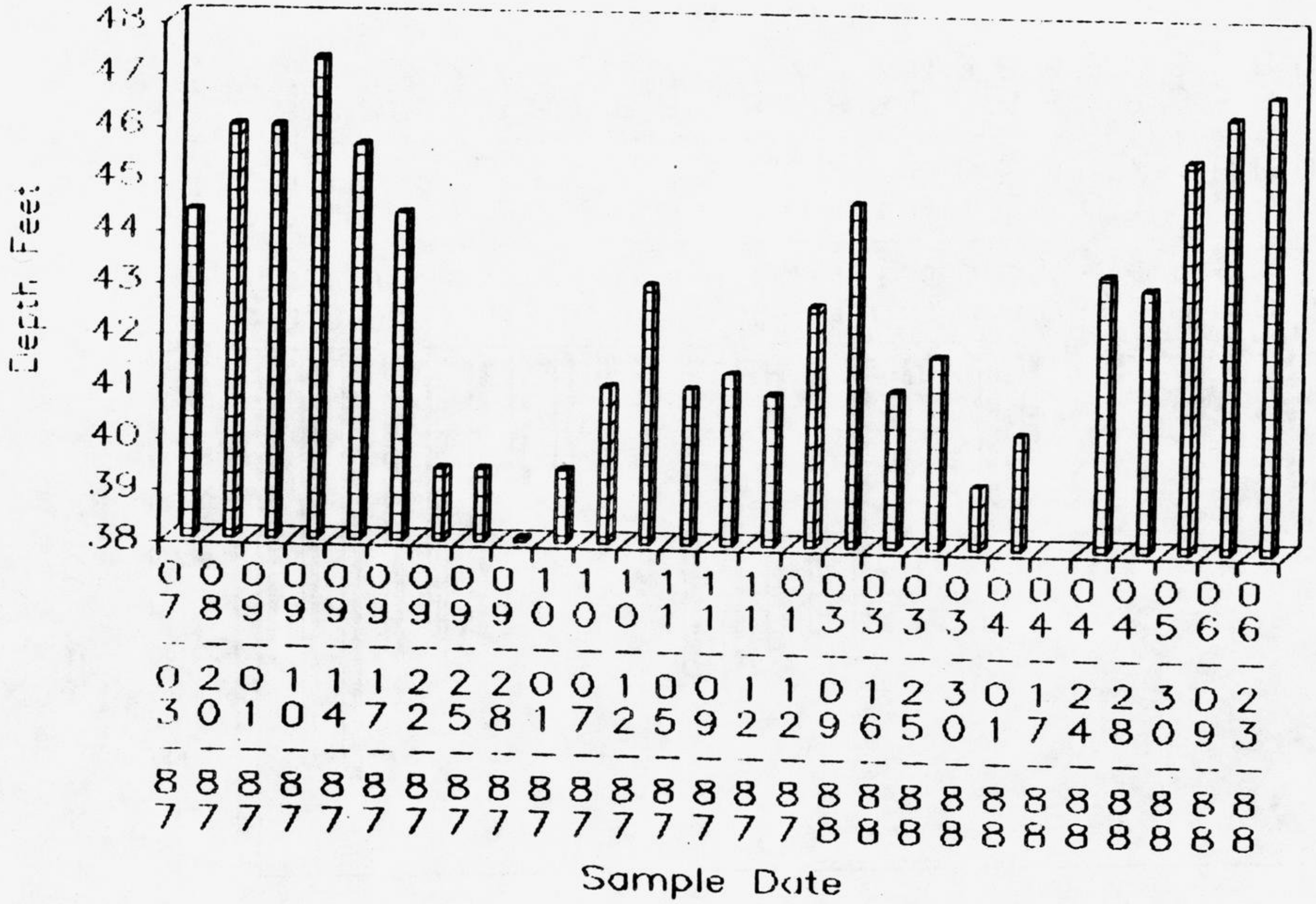


Figure 20. Depth to Water Table for Monitoring Well W3.

on September 1, 1987 and on September 10, 1987 for Well 3. Eighteen days later, September 28, 1987, Well 3 reached the highest elevation recorded. In contrast Wells 1 and 2 reached their highest elevations during the spring snow melt, April 1, 1988 and April 17, 1988 respectively. There is little doubt that water was constantly moving through Wells 1 and 2. As indicated earlier, on most sampling trips water could be heard cascading down the wall of Well 1. On some occasions it was loud enough to prevent measurement of the position of the water surface. During the very dry periods, water ceased to flow from upper levels in Well 1. For Well 2, water could only be heard cascading downward during periods of high infiltration. In no case was the volume of water cascading downward sufficient in volume to create enough noise to prevent making and accurate measurement of the water table position. Water was never heard cascading down the wall of Well 3 probably because this was a much shallower well.

These observations indicate that the water in these wells enters from several distinct levels. Certainly water infiltrating the immediate vicinity but not necessarily the contaminated area, was entering the monitoring wells.

Well Monitoring--Water Chemistry

During each sampling trip the field pH and specific conductance was determined for each monitoring well. The results of pH measurements in the three monitoring wells are given in Table 7. As one would anticipate in a karstic situation, the pH levels in the groundwater varied little during the monitoring period. The range for three wells was 0.6 pH units (6.7-7.3).

Results of the measurement of field specific conductance are given in Table 8. While pH varied little among the three monitoring wells, significant differences in specific conductance values were observed between the wells. The average, standard deviation and difference in specific conductance are also found in Table 8. So that comparisons can be made, the average and standard deviation values were calculated using only dates for which a complete set of data was available.

Well 1 had the lowest value for specific conductance indicating that water from this well had the least dissolved ion content. Well 2, the other deep well averaged nearly 71 umhos/cm higher in specific conductance. Well 3, the shallowest well, was 200 umhos/cm higher than Well 1. These values would indicated that water from Well 3 had much more time to equilibrate with the dolomitic aquifer materials compared to Wells 1 and 2. These data also seem to indicate that water entering Well 1 had less time to equilibrate with the dolomite bedrock. The specific conductance values along with the physical observations referred to above seem to indicate that water moved through Well 1 the most rapidily, and that Well 2 exchanged water more rapidly than did Well 3.

Chloride and nitrate-N concentrations were measured in the three monitoring wells during the fall of 1987. The results of these analysis are found in Tables 9 and 10. The average values for chloride show little difference between wells but, values for chloride varied significantly from well to well on an indivdual sampling date. As observations of other parameter mentioned above have indicated, the chloride levels also give further evidence for separate sources of water for the three wells.

Table 7. pH Level in Monitoring Wells

Date/Well #	Well 1	Well 2	Well 3
11-05-87	7.2	6.9	7.2
11-09-87	7.0	7.0	7.1
11-12-87	7.0	7.2	7.3
01-12-88	7.2	7.2	7.1
03-09-88	N S	7.2	7.2
03-16-88	7.0	7.0	7.0
03-25-88	7.1	7.0	7.1
03-30-88	7.2	7.0	7.2
04-01-88	6.8	6.7	6.8
04-13-88	6.8	6.9	7.0
04-17-88	6.8	6.9	6.9
04-24-88	6.9	6.9	7.0
04-28-88	6.9	7.0	7.1

Table 8. Specific Conductance Field Readings in Monitoring Wells
Values in umhos/cm @ 25 degrees Celsius

Date/Well	Well 1	Well 2	Well 3	Sp Cond Diff (W 1 - W 2)	Sp Cond Diff (W 1 - W 3)
11-05-87	677	N S	N S		
11-09-87	687	N S	N S		
11-12-87	681	N S	N S		
01-12-88	671	N S	N S		
03-09-88	447	564	668	-117	-221
03-16-88	509	574	691	-65	-182
03-25-88	427	557	684	-130	-257
03-30-88	475	551	696	-76	-221
04-01-88	474	556	702	-82	-228
04-13-88	513	562	704	-49	-191
04-17-88	530	563	692	-33	-162
04-24-88	538	565	695	-27	-157
04-28-88	504	560	688	-56	-184
Average =	490.8	561.3	691.1	-70.6	-200.3
Std Dev =	37.6	6.5	10.7		

N S = No Sample

Nitrate-N values were very low except at the beginning of the monitoring period in Well 1. This well was located near a drain field. The tapping of a well in its vicinity may have provided a route for near surface water to enter the monitoring well. After a period of time, the water stored in this region was removed and nitrate-N levels returned to near normal background values. The nitrate-N level observations support the earlier mentioned observation regarding the rapid exchange of water thought to be occurring in Well 1.

Table 9. Chloride Levels in Monitoring Wells (mg/l).

Date/Well #	Well 1	Well 2	Well 3
09-10-87	11.3	4.6	7.8
09-14-78	14.1	11.4	7.7
09-17-87	14.0	12.5	8.1
09-22-87	8.4	5.6	17.3
09-25-87	14.2	6.1	9.4
09-28-87	11.2	5.8	10.1
10-01-87	N S	5.6	9.4
10-07-87	8.1	10.9	8.9
10-12-87	8.2	10.6	8.4
11-05-87	9.1	10.0	8.3
11-09-87	9.0	10.0	8.4
11-12-87	10.0	8.5	8.1

Table 10. Nitrate-N Levels in Monitoring Wells (mg/l)

Date/Well #	Well 1	Well 2	Well 3
09-10-87	17.1	0.0	0.0
09-14-78	6.1	0.0	0.0
09-17-87	2.8	0.3	0.0
09-22-87	0.4	0.1	0.9
09-25-87	1.9	0.0	0.0
09-28-87	1.7	0.2	0.0
10-01-87	N D	0.0	0.0
10-07-87	1.5	0.4	0.0
10-12-87	0.9	0.4	0.0
11-05-87	0.3	0.4	0.0
11-09-87	0.2	0.4	0.0
11-12-87	0.6	0.1	0.0

Monitoring Wells--Temperature Measurements

The temperature of the well water in the monitoring wells was also measures in the field. The results of these measurements are given in Table 11. Well 3, the shallowest well had the highest average temperature followed by Well 1. Well 2 had the lowest average temperature. Because Well 1 and Well 2 are at essentially the same elevation one would expect the average temperature in these two wells to be nearly identical. During the fall Well 1 was significantly warmer than Well 2 but in the spring the trend was reversed. The explanation provided earlier that near surface water was cascading down into Well 1 at a much faster rate than in Well 2 is also supported by the observed temperature differences between these two wells.

Table 11. Temperature Readings in Monitoring Wells

Date/Well #	Well 1	Well 2	Well 3
	(Temperature	Degrees	Celsius)
11-05-87	10.0	8.0	9.3
11-09-87	9.0	8.0	9.9
11-12-87	10.5	9.0	9.2
01-12-88	8.0	8.0	9.6
03-09-88	7.9	7.5	8.3
03-16-88	7.4	7.6	9.0
03-25-88	10.6	9.2	9.1
03-30-88	8.0	7.9	9.2
04-01-88	10.4	10.6	9.3
04-13-88	9.3	8.7	9.3
04-17-88	8.5	8.8	9.3
04-24-88	9.6	10.2	8.3
04-28-88	8.1	8.6	9.2

VI. Well Abandonment

Three monitoring wells were constructed on the site. Well 1 was closed on June 9, 1988. Mr. Harvey Jorns, a Wisconsin licensed well driller, completely filled the well with cement to the surface. Well 3 is presently as it was originally constructed except for the fact that more grout was placed near the surface around the casing. The Wisconsin Geological and Natural History Survey is continuing to monitor this well and has taken over the responsibility for proper abandonment.

Well 2 currently has a three level pieziometer installed in it. Because of the complicated nature of the movement of groundwater in karstic regions, scientists from University of Wisconsin Green Bay, James H. Wiersma and Ronald D. Steiglitz, and the Wisconsin Geological and Natural History Survey decided that Well 2 was located in a region that warranted further study. Funds from this project and additional funds from the WGNHS were used to fund the installation of the pieziometers. The pieziometers were installed by CTW Corporation, Waukesha, WI. The details of the installation of the 3-level pieziometer are found in Appendix III. The Wisconsin Geological and Natural History Survey have also assumed the responsibility for the abandonment of Well 2.

VII. Conclusions

-During snowmelt and rainfall events, most of the water infiltrated directly into the soils with little runoff.

-The area of highest soil contamination was drained in two different directions, north and south.

-Soils on the site are thin, the depth to bedrock ranges from 25 to 45 centimeters.

-Lead concentrations in the soils on the site ranged between 45 to 10,800 mg/kg.

-Arsenic concentrations in the soils on the site ranged between 7 to 2040 mg/kg.

-Copper concentrations in the soils on the site ranged between 35 and 5,600 mg/kg.

-The distribution pattern for the three metal contaminants, lead, arsenic and copper were quite similar. Contamination was essentially confined to an area east of the building complex and in the immediate vicinity of a former mixing site. The contamination pattern was plume shaped with concentrations decreasing as distance from the mixing site increases.

-The same soils that are contaminated with lead and arsenic are contaminated with copper. However, the ratio of the metals is not constant indicating different spray mixtures were used and different parts of the contaminated zone were affected at different times.

-Analysis of samples from soil profiles collected both by hand dug pits and cores, indicates that there has been little downward migration of either lead or arsenic in the soil horizon.

-Removal of the upper 20 to 25 centimeters of soil in the contaminated are would eliminate essentially all of the heavily contaminated soils on the site.

-Soil samples from the highly contaminated zone indicated that high levels of lead were associated with the fine grained materials. Since these are the most easily eroded soils, contaminated sites should be managed to prevent erosion.

-Extracting contaminated soils with distilled water indicated that lead is soluble to levels that would greatly exceed the current drinking water standard.

-Soluble lead concentrations using distilled water as the extraction medium were found to follow the equation:

$$\text{Log Aqueous Pb (ug/l)} = 1.01\text{Log Pb Soil Matrix (mg/kg)} - 0.76$$

-The soils on the site are quite alkaline ranging in pH from 7.6 to 8.1.

-Sorption experiments indicated that fresh dolomite surfaces sorb lead from heavily contaminated soil extracts. Aqueous lead concentrations were reduced to a few ug/l Pb or below the detection limit of 2 ug/l Pb.

-Groundwater samples collected form monitoring wells during periods of high infiltration were found to contain lead at the detection limit for lead or at levels just above the detection limit for lead on six samples of the 40 samples collected.

-Both physical and chemical observations made at the monitoring wells indicated that the groundwater at the site moved rapidly. Groundwater was found to enter deep wells from at least two different levels. Depth to water table, temperature, specific conductance, chloride, nitrate and the sound of cascading water all confirmed the dynamic flow characteristic of groundwater at the site.

-Depth to water table measurements indicated that both the shallow aquifer and the deep aquifer respond quickly to surface infiltration events. The position of the watertable varied by approximately 60 feet in the deep monitoring wells and by 9.1 feet in the shallow up-gradient well during the study period.

VIII. Literature Cited

Burau, R. G., 1982. "Lead", Chapter 21 in Methods of Soil Analysis, 2nd Ed., A. L. Page ed., No. 9 (Part 2) Agronomy Series, American Society of Agronomy, Inc., and Soil Science Society of America, Inc., Madison, WI.

Elliott, H. A., M. R. Liberati, and C. P. Haung, 1986. "Competitive Adsorption of Heavy Metals by Soils." Journal of Environemtal Quality Vol. 15 July-Sept.

Eisler, R., 1988. "Arsenic Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review". Biological Reprt 85(1.12) U. S. Fish and Wildlife Service, U. S. Department of the Interior, 92 p.

Ganje, T. J., and D. W. Rains, 1982. "Arsenic", Chapter 23 in Methods of Soil Analysis, 2nd Ed., A. L. Page ed., No. 9 (Part 2) Agronomy Series, American Society of Agronomy, Inc., and Soil Science Society of America, Inc., Madison, WI.

Hess, R. E., and R. W. Blancar, 1976. "Arsenic Stability in Contaminated Soils. Soil Sci. Soc. Am. J. 40:847-852.
NRCC. 1978. "Effects of Arsenic in the Canadian Environment" Natl. Res. Coun. Canada Publ. No. NRCC 15391. 349 p.

Howard Consultants, Inc., 1982. "Ground Water Resource Development Potential", Report to the city of Sturgeon Bay, WI., 23 p.

Johnson, S. B., and R. D. Stieglitz, 1986. "Inventory and Preliminary Analysis of the Distribution of Karst Features in Northern Door County, WI, Abstract of paper presented at the Meeting of the North Central Section of the Geological Society of America and Associated Societies, Kent, OH.
Residuals Management Technology, 1987. "Door County Lead Arsentate Investigation", Report to the WDNR.

Link, E. G., S. L. Elmer and S. A. Vanderveen, 1978. "Soil Survey of Door County, Wisconsin", U. S. Soil Conservation Service, U. S. Department of Agriculture, 132 p.

Marcus, W. L., 1986. "Lead Health Effects in Drinking Water", Tox. Ind. Health 2:363-407.

Pickering, W. F., 1983. "Extraction of Copper, Lead, Zinc or Cadmium Ions Sorbed on Calcium Carbonate", Water, Air, And Soil Pollution, 20:299-309.

Reyburn, James, 1986. Personal Communication, Wisconsin Department of Natural Reources.
Smith, M. J., 1985. J. Am. Acad. Child Psych. 24:24-32.

Sadiq, M., T. H. Zaidi, and A. A. Mian, 1983. "Environmental Behavior of Arsenic in Soils", Water, Air, and Soil Pollution: 20 369-377.

Schneider, A. F., 1981. "Late Wisconsin Glaciation Of Door County, Wisconsin", Abstracts with porgrams GSA 93rd Annual Meeting, p316.

Sherrill, M. G., 1978. "Geology and Ground Water in Door County, Wisconsin, with Emphasis on Contamination Potential in the Silurian Dolomite", Geological Survey Water Supply Paper 2047, 38 p.
Stoll, Richard C., 1988. Internal Report, Wisconsin Department of Natural Resources.

Thwaites, F. T., and K. Bertarand, 1957. "Pleistocene Biology of the Door Peninsula, Wisconsin", Bull. Geol. Soc. Am. 68:831-880.

Stumm, W., and J. J. Morgan, 1981. <u>Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters</u>, 2nd Ed., Wiley Interscience, New York, NY.

Veneman, P. L. M., J. R. Murray, and J. H. Baker, 1983. "Spatial Distribution of Pesticide Residues in a Former Apple Orchard", J. Environ. Qual. 12: 101-104.,

Woolson, E. A., (ed.), 1975. "Arsenical Pesticides. Am. Chem. Soc. Symp. Ser. 7. 176 p.

APPENDIX I

DESCRIPTION OF SOIL PROFILES

Pit P-1

0-5 cm Sandy organic marl, medium to dark brown, roots.

5-10 cm Sandy with clay, medium to light brown, with organic material

10-15 cm Sandy, clayey, Light reddish brown, roots, pebbles Possibly from surface gravel).

15-20 cm Sandy clayey, light tan-red, slightly sticky, reddish tan mottling.

20-25 cm Light reddish tan, clayey sand, blocky, crumbly clay.

25-30 cm Grayish reddish tan, clay with sand, crumbly, few crystalline dolomite pebbles.

30-35 cm Reddish tan, pebbles, 7-20 mm, coarse sand, sandy clay.

35-40 cm Reddish tan, sandy clay, black mottling, clayey sand, pebbles 3-10 mm.

40-47 cm Reddish tan clay, mottled red, sticky, blocky. (Sample removed from crevice with boring tool.)

Pit P-2

0-5 cm Brown organic sandy layer.

5-10 cm Sandy clayey, light brown to reddish tan with layer of green material at bottom of interval with white mottling.

10-15 cm Reddish tan sand with clay, green veins and lenses.

15-20 cm Sand, light tan with coarse sand and pebbles 8-12 mm.

20-25 cm Light tan sand with blocky, slightly clayey chunks, pebbles 5mm, fine grained sand.

25-27 cm Layer at bed rock interface, sand with a little clay, fine grained sand.

P-3 Soil Description Continued

Pit P-3

0-5 cm   Black organic layer with sand, heavy concentration of roots.

5-10 cm   Brown, dark organic marl, sand, clay, pebbles 5-25 mm.

10-15 cm   Brown sandy clay with pebbles, light gray sand lens, possibly construction material, some organic material.

15-20 cm Reddish brown clayey sand with pebbles, 4-8 mm, roots and organic matter.

20-25 cm Clay with sand, mottled light tan, reddish brown, slightly sticky.

25-30 cm   Reddish brown, mottled with black and tan, clay slightly sticky.

30-35 cm   Reddish tan clay with sand, crumbly, black mottled organic material, roots.

35-40 cm   Dark tan, sandy clay, crumbly.

40-45 cm   Reddish tan clay, crumbly to blocky, organic layer, roots, ribbons.

45-50 cm   Crevice materials--Sandy clayey, light tan, reddish, very wet, crumbly, pebbles, dark brown mottling.

50-55 cm   Crevice materials--Dark brown-reddish tan, mottled, wet clayey sandy, slightly sticky.

55-60 cm   Crevice materials--Reddish brown clay with sand, mottled dark brown, roots.

60-65 cm   Reddish brown clay with sand and coarse sand, wet, dark mottling.

65-70 cm   Dark brow to dark red, sticky, blocky, clay, wet with coarse sand.

70-73 cm   Dark brown with black mottled red, sticky clay, wet.

CORE DESCRIPTIONS

Core 1

0-5 cm Tannish brown, yellow and tan mottles, black organic materials, clayey sand.

5-10 cm Tan brown, black mottles, black organic layer at 10 cm, clayey fine sand.

10-15 cm Dark brown to brown and tan, black organic material at 10 cm, clayey fine sand.

15-20 cm Blackish, dark brown mottles, clayey fine sand.

20-25 cm Medium brown tan, roots, pebbles, dolomite chips, sandy clay.

Core 2

0-5 cm Black to dark brown, humus, pebbles (white), tan yellowish mottles, organic material, fine sand, clay.

5-10 cm Black to dark brown, small pebbles, white mottles, clayey fine sand.

10-15 cm Brown to dark brown, yellowish tan mottles, pebbles, clayey fine sand.

15-20 cm Brown to tan, organic material at 20 cm, clayey fine sand.

20-25 cm Tan, yellow reddish brown mottles, tan white mottles at 25 cm, clayey fine sand to sandy at 25 cm.

Core 3

0-5 cm, Dark brown, surface debris, pebbles, grass roots, organic material, sandy clay.

5-10 cm Dark brown to brown, pebbles, organic material, black vitreous chunk, sandy clay.

10-15 cm Tannish brown, reddish tan mottles, organic material, roots, pebbles, clayey fine sand.

15-20 cm Tan brown, black and yellowish tan mottles, pebbles, clayey fine sand.

20-25 cm Tan brown, black and yellowish tan mottles, pebbles, clayey fine sand.

Core Descriptions Continued

Core 6
0-5 cm Dark brown, tan yellow mottles, pebbles, grass roots, clayey fine sand.

5-10 cm Dark brown, tan yellow mottles, 3-8 mm pebbles, roots, white chunk, clayey fine sand.

10-15 cm Dark to medium brown, tan yellow mottles, dark organic mottles, clayey fine to coarser sand at bottom.

15-20 cm Dark to medium brown, tan yellow and white mottles, pebbles 2-3 mm, coarse sand, clayey sand.

20-25 cm Brown, black mottles, reddish brown sandy section at 25 cm, clayey fine to coarse sand grading to 25 cm.

Core 8
0-5 cm Gray brown, 2-6 mm pebbles, organic material, clayey fine sand.

5-10 cm Brown white mottles, 2-8 mm pebbles, organic material, clayey fine sand.

10-15 cm Dark brown, friable white chunks, 1-10 mm pebbles, fine sandy clay.

15-20 cm Brown gray, white friable chunks, 2-10 mm pebbles, clayey fine sand.

20-25 cm White brown, mostly white friable broken up carbonate rock, clayey fine sand.

25-30 cm Dark brown, pebbles, clayey fine sand.

Core 10
0-5 cm Dark brown, 1-2 mm pebbles, organic material , clayey fine sand.

5-10 cm Dark brown to brown, reddish brown mottles, pebbles, clayey fine sand.

10-15 cm Brown to reddish brown, tan mottles, pebbles, clayey fine sand.

15-20 cm Reddish brown tan, black organic chunks, light tan mottles, pebbles, clayey fine sand.

20-25 cm Tannish brown, black organic material, pebbles, clayey fine sand.

Core 10 Description Continued

25-30 cm Tan, yellowish brown mottles, pebbles, clayey fine sand.

30-35 cm Tan, pebbles, mica flakes, quartz sand, clayey fine sand

35-40 cm Tan, pebbles, mica flakes, clayey sand.

Core 11

0-5 cm Dark brown, tan yellow mottles, grass roots, 2-3 mm pebbles, clayey fine sand.

5-10 cm Dark brown, tan yellow and white mottles, 3-5 mm pebbles, clayey fine sand.

10-15 cm Dark brown to tan, tan yellow mottles, black organic material, clayey fine sand.

15-20 cm Tan, dark brown mottles, 10 mm pebble, clayey fine to coarse sand

20-25 cm Tan, brown mottles, 10 mm pebble, clayey fine sand.

25-29 cm Tan with dark brown layer at 27-29 cm, clayey fine sand, 2-3 mm pebbles.

Core 12

0-5 cm Dark brown, grass roots, organic material, pebbles, clayey fine sand.

5-10 cm Dark brown black organic mottles, pebbles, clayey fine sand.

10-15 cm Brown, tan mottles, pebbles, clayey fine sand.

15-20 cm Brown, black mottles, clayey, fine to coarse sand, pebbles.

20-25 cm Tan, dark brown and black mottles, clayey fine to coarse sand

25-30 cm Tan, dark brown and black mottles, pebbles, clayey fine sand.

30-35 cm Tan, reddish brown mottles, clay and fine sand.

35-40 cm Tan, clay and some fine sand

Core Descriptions Continued

Core 13

0-5 cm Dark brown, humus, grass roots, clayey fine to coarse sand.

5-10 cm Dark brown, white mottles, 3-8 mm pebbles, sandy clay.

10-15 Medium brown, white mottles, clayey fine sand

15-20 cm Brown, tan yellow mottles, 5-7 mm pebbles, clayey, fine to coarse sand.

20-25 cm Brown, tan yellow mottles, black to brown organic material, roots, 2-3 mm pebbles, 10 mm pebbles, clayey fine sand.

25-30 cm Brown, tan yellow and black mottles, pebbles, clayey fine sand.

30-35 cm Brown, tan yellow and black mottles, organic material, clayey fine to coarse sand.

35-40 cm Brown, tan yellow and black mottles, organic material, roots, clayey fine to coarse sand.

40-45 cm Brown, tan yellow and black mottles, roots, organic material, clayey fine to coarse sand.

45-48 cm Brown, tan yellow and black mottles, roots, organic material concentrated at 48 cm, clayey fine sand.

Cores 4, 5, 7, and 9 similar to core 6.

Appendix II. Description for the Installation of Well 1 (260 feet)

Dates:	0-40 ft drilled 16 June, 1987; 40-260 ft drilled 17 June, 1987.
Bore:	Ten inches to 40 ft. Six inches to completion.
Casing:	Eight inch steel to 40 ft. with six inch collar with padlocked lid. Top of casing approximately two ft above grade. Welded seams between 20 ft lengths and collar. Casing grouted from 40 ft. to surface.

Well Log:

Depth (ft)	Description
0-2.5	Soil and overburden
2.5-	dolomite bedrock, small voids encountered throughout drilling
25	large void, approximately 1 ft.
102	water encountered (2-3 gallon per minute estimated yield
100-105	notable color change-cuttings buff color
175	void
215	void
220-225	voids
251-253	water
260	completion (10 gallons per minute estimated yield

Appendix II (Cont.) Description for the Installation of Well 2 (261 feet)

Dates: 0-40 ft drilled 16 June, 1987; 40-261 ft drilled 18 June, 1987.

Bore: Ten inches to 40 ft.
Six inches to completion.

Casing: Eight inch steel to 40 ft. with six inch collar with padlocked lid. Top of casing approximately two ft above grade. Welded seams between 20 ft lengths and collar. Casing grouted from 40 ft. to surface.

Well Log:

Depth (ft)	Description
0-1.5	Soil and overburden
1.5-	dolomite bedrock, small void encountered
15	void, color change buff to gray, larger cuttings from void
30	void
35-40	return to buff colored cuttings
38	void
45	void with water (1 gallon per minute est.)
250	voids
261	completion (5 gallons per minute estimated yield)

Appendix II (Cont.) Description for the Installation of Well 3 (60 feet)

Dates: 0-40 ft drilled 17 June, 1987; 40-60 ft drilled 18 June, 1987.

Bore: Ten inches to 40 ft.
Six inches to completion.

Casing: Eight inch steel to 40 ft. with six inch collar with padlocked lid. Top of casing approximately two ft above grade. Welded seams between 20 ft lengths and collar. Casing grouted from 40 ft. to approximately 2 feet below surface. Fracture encountered at surface; upper two feet regrouted in June 1988

Well Log:

Depth (ft)	Description
0-1	Soil and overburden
1-	dolomite bedrock, small void encountered
5	void
6-	fracture zone, little to no cuttings till 10 ft., large fragments (4-6 inches), blowout of drilling air pressure through soil, fracture intersection centered with drill
10-15	large fragments, rough drilling, buff dolomite
15-20	rough, beginning of dark gray dolomite
20-25	rough, gray with buff cuttings, fragments to several inches in size
25-30	gray, rounded cavings in cuttings, light buff to white
30-35	more uniform drilling, fewer cavings, some chert, gray
35-40	gray, chert
60	completion, probably still in fracture

Comments: Fracture intersection encountered appeared to be a solution feature about 8 ft deep, joint intersection NE-SW 6 inches wide, SE-NW 12 inches wide.

Appendix II. Detailed Description of Well Cuttings

Door County — Fruit Growers #2
Sevastopol Township — Monitoring Well

Depth (feet)	
0-5	Dol., buff to lt. br., microxtln, dense, some rusty and yellow stains, sparry dol., coarsely xtln, appear to be vug or vein fillings.
5-10	Dol. as above, lt. brown, sparry dol. prominent, pores visible
10-15	Dol. as above, rusty appearing surfaces
15-20	Dol. as above 30-35%. Dol, gray to brownish gray, microxtln, brown, amber and black organic fragments on parting surfaces and scattered throughout, some silty appearing thin partings, tr. pyrite, wh. patches and nodules of chert < 1%.
20-25	Dol. as above, sparry dol. filling pores, silty, organic partings, pyrite fine on partings and large xtls in dol., trace. Dol. buff to lt. brown 5-10%.
25-30	Dol. as above, white chert < 1%, sparry dol., pyrite trace, sparry dol. in veins may be rextlzed fossil shells, poorly preserved crinoid columnal in chert and spar, scattered rounded quartz grains in partings.
30-35	Dol. as above, white chert < 1%, scattered rhombs and blobs of pyrite in dol. < 1% some appearing gray and oxidized, amber organic appearing material within dol., rusty patches and stains, clear coarse spar < 1%, brown silty partings, possible fossil debris as ghosts.
35-40	Dol. as above, chert white to lt. gray 5-6%, spar, up to 1 mm

	may be filling vugs or fossils, br. silty partings with organic fragments, scattered pyrite rhombs in dolomite and on partings, trace.
40-45	Dol. as above, brown silty partings, crinoid and other fos frags., spar dol., lt. br. to br., coarse, chert, wh. to lt. gr., 4-5% (sample unusually dirty with fines).
45-50	Dol. lt. br to br fossil frags up to 1.5 mm, brachs, well xtled, brown silty partings, crinoids, chert, scattered wh. to lt. gr.
50-55	Dol. as above lt. brown to buff, some inter xtln porosity. Chert, wh. to lt. gray, some tinged with br., fossils in chert corals, brachs, (ostracods?) filmentous algae, 15-20% spar < 2%. Dol. as above gr. to br. gr. 20-25%.
55-60	Dol. as above, scattered rusty patches, chert, as above 5-8%., spar 2-3%
60-65	Dol. as above lt. br. to buff, scattered amber organic frags, chert as above 10-15%. Dol. as above, gr. to br. gr. 5%, spar < 1%.
65-70	Dol. as above 50-55%. Dol., br. to br. gr, finely xtln scattered pyrite, some brown silty parting 35-40%. Chert as above 3-4%. Spar < 1%.
70-75	Dol as above br. to br. gr., well xtlized, fos. frags. Dol. as above lt. br. to buff 10-12%. Chert as above, with fossil frags, 6-8%. Spar 1%.
75-80	Dol. as above br. to br. gr, chert as above 10-12%, spar 1%.
80-85	Dol. as above, chert as above, some brown 15-20%, spar 1%,

	some inside chert frags.
85-90	Dol. as above, chert as above, coral and crinoid parts recognizable, pyrite, tr. in chert and dolomite.
90-95	No sample
95-100	Dol. lt. br. to buff, med. xtln, fos. frags. up to 1 mm, chert as above, fos. frags. very abundant, needle-shaped (spicules?) crinoids (oolites?), spar, 1%.
100-105	Dol. as above, scattered black organic appearing surfaces, stylolites, large fossil fragments 2.5 mm, pyrite, tr. as stain in vug, spar 1%.
105-110	Dol. as above, well xltized, foss. frags., chert, lt. gray to wh. 1-2%, spar 1%, pyrite, tr. in dol., small cubes.
110-115	Dol. as above, chert as above fossiliferous, < 1%, some as wh. blebs in dol, spar 1%.
115-120	Dol. as above. Dol, br. to gr. br., finely xtln. 10-15%, Pyrite, tr. as cubes in gr. br. dol. Spar 1%.
120-125	Dol. as above, lt. br. to buff, well xltized, good interxtln porosity, granular appearing in part, chert as above < 1%.
125-130	Dol. as above, vugs up to 1.5 mm, larger appear lined with spar, spar veins, chert, wh., blebs in dol., trace.
130-135	Dol. as above, finely xtln, dense, some br. stylolitic seams. Dol. gr. to lt. gr., v. finely xtln dense, bl. organic partings (styolites?), 15-20%. Pyrite scattered cube and blebs primarily in gr. dol., tr. Chert gr., tr.
135-140	Dol. lt. br., med. xtln, interxtln. porosity, laminated in part, pyrite, scattered blebs, tr.

140-145	Dol. as above, gr. br. in part, scattered blebs and small cubes of pyrite, rusty spots and stains.
145-150	Dol. as above, some very dense, some with good porosity, fossil fragment in coarser dol.
150-155	Dol., as above, some vuggy porosity, with spar linings.
155-160	Dol., as above, porous.
160-165	Dol. as above, porous, rusty spots, scattered pyrite cubes.
165-170	Dol. as above. (Green tinge on one frag. seems to be within the pores, may be algae.)
170-175	Dol., as above, porous in part.
175-180	Dol. as above. Dol., lt. gr. br., v. finely xtln, dense, scattered pyrite cubes, 2-3%.
180-185	Dol., as above, lt. gr. br. to lt. gr., v. fine to finely xtln, dense, appears argillaceous in part, scattered cubes and blobs of pyrite. Dol., as above, lt. br., porous, liminated in part, 40-45%.
185-190	Dol. as above, lt. br., med. xtln, porous, some appears more dense and finely xtln., tr. of black organic partings.
190-195	Dol. lt. gr. br. to lt. gr., finely xtln, dense, appears argillaceous in part, small pyrite cubes scattered. Dol., as above, lt. br., porous, 35-40%, chert, wh. blebs tr.
195-200	Dol. as above lt. gr. br. to gr. Dol. as above lt. br., 35-40%.
200-205	Dol. as above, lt. br. Dol. as above lt. gr. br. to lt. gr., 10-15%.
205-210	Dol. as above, lt. br. Dol. as above, lt. gr. br. to lt.

	gr., scattered pyrite cubes, 40-45%.
210-215	Dol. as above lt. br., porous. Dol. as above, lt. gr. br. to lt. gr., 1%.
215-220	Dol. as above lt. br., small pyrite cubes scattered in some chips, some dk. br. silty partings. Dol., lt. gr. br. to lt. gr., some brown, dense, scattered xtls. of spar, 40-45%.
220-225	Dol. as above, lt. gr. br. to lt. gr. Some lt. br., dense. Dol. as above, lt. br., 5-10%
225-230	Dol. as above, lt. gr. to lt. gr. br., scattered pyrite blebs, br. silty partings or stylolite surfaces, efferresces easily in HCl. Dol. as above, lt. br., 1%.
230-235	Dol. as above lt. br., some gr. and med. xtln., br. stylolites and silty surfaces. Dol. as above, lt. gr. to lt. gr. br., pyrite in places, 20-25%.
235-240	Dol. as above, lt. br., some gr. with pyrite. Dol. as above, lt. gr. to lt. gr. br., 20-25%. Chert, gr. br., trace.
240-245	Dol. as above lt. br. to gr. Dol. as above lt. gr. to lt. gr. br. 15-20%. Chert as above, some wh., tr.
245-250	Dol. as above, lt. br., scattered, rusty laminations and surfaces. Dol. lt. br., v. finely xtln. 15-20%. Chert as above, 1% (sample overall lighter color)
250-255	Dol. as above lt. br., some br. to dk. br., br. to blk. stylotes and silty surfaces with scattered pyrite cubes. Dol. as above lt. br. to gr., dense, interlaminated with coarse dol., 15-20%. Chert as above, Tr.
255-260	Dol. as above lt. br. to dk. br., br. to gr. partings or

stylolites, some spar apparently filling vugs or foss. frags. Dol. as above lt. br. to gr., dense, 10-15%. Chert as above, tr.

CW CORPORATION

P. O. Box 994
Waukesha, Wisconsin 53187

Water Wells & Pumps
(414) 542-4040
(414) 646-3935

April 10, 1989

UWGB
Green Bay, Wis 54311-7001

Dear Jim Wiersma:

The following is the report of the contractor's activities for bid #4040 referernce PJN.

Feb 14, 1989 - 210 feet of static water level.
Well depth 259 feet
Proceeded to bail well
In process of running bailer to bottom of well fractured lime stone fell on top of bailer making bailer stuck at bottom of well.

Feb 17, 1989 - Moved in equipment capable of fishing bailer out.
Unsuccessful - returned home for a different style fishing tool.

Feb 20, 1989 - Static water level 209'8"
Able to remove bailer and cleaned out to depth of 264'
264' seemed to be original well depth.
Set in first screen at 260'

March 9, 1989 - Static water level 209'
Sand 252" to 250"
Bentonate 249' to 250'
Graveled from 252' to 264'
1 bag cement from 254' to 249'

March 15, 1989 - Static water level 203'1"
Static water level in screen inside monitoring #1 pipe 209'8"
7 bags of cement 221' to 245'

CW CORPORATION
P. O. Box 994
Waukesha, Wisconsin 53187

Water Wells & Pumps
(414) 542-4040
(414) 646-3935

UWGB - bid #4040 Ref. PJN
page two

March 20, 1989 - Static water level 206'8" in pipe #1
Static level in well 176'9"
6 bags of cement 196' to 221'

March 21, 1989 - Static water in well 169'10"
Water level in monitoring #1 pipe 207'1"
2 1/2 bags cement 180'7" to 196'

March 22, 1989 - Static water level in well 145'
Water level in monitoring #1 pipe 168'10"
Installed 2nd screen to 180'
7 1/2 gallons gravel filled to 172'
2 gallons sand to 171'
1 gallon bentonate to 170'

March 23, 1989 -Static water level in well 135'6"
Water level in monitoring #1 pipe 167'
Water level in monitoring #2 pipe 146' to 165'
6 bags cement

March 27, 1989 - Static water level in well 65'8"
Water level in monitoring #1 pipe 169'8"
Water level in monitoring #2 pipe 171'
8bags cement to 116'

March 28, 1989 - Static water level in well 65'9"
Water level in monitoring #1 pipe 165'3"
Water level in monitoring #2 pipe 172'
6 bags to 78'9"

March 29, 1989 - Static water level in well 41'
Water level in monitoring #1 pipe 165'
Water level in monitoring #2 pipe 173'
4 1/2 bags of cement to 52 1/2'

March 30, 1989 - Static water level in well 25'6"
Put 3rd screen in and set at 50'
Graved from 52' 1/2 feet to 42'
Sand 42' to 40'
Bentonate 40' to 38 1/2'
Added 1 bag cement 30'9" to 38 1/2'

CW CORPORATION

P.O. Box 994
Waukesha, Wisconsin 53187

Water Wells & Pumps

(414) 542-4040
(414) 646-3935

UWGB - Bid #4040 Ref. PJN
page three

March 31, 1989 - Static water level in well 22'7"
Water level in monitoring #1 pipe 167'8"
Water level in monitoring #2 173'
Water level in monitoring #3 38'3"
3 bags of cement filled from 1' to 30'9"

Sincerely,

Bernard A Nooyen

Bernard Nooyen

BAN/ctw

050846- Lead Migration from
Contaminated Sites-- Door
County, WI